Recent Advances in Catalytic Oxidation of Volatile Organic Compounds: A Feature Review Based on Pollutant Sorts and Sources

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Abstract

It is known that urbanization and industrialization contribute to rapidly increasing emissions of volatile organic compounds (VOCs), which are a major contributor to the formation of secondary pollutants (e.g., tropospheric ozone, PAN (peroxyacetyl nitrate) and secondary organic aerosols) and photochemical smog. The emission of these pollutants has led to a large decline in air quality in numerous regions across the world, which has ultimately led to concerns regarding their impact on human health and general wellbeing. Catalytic oxidation is regarded as one of the most promising strategies for the removal of VOCs from industrial waste streams. The review systematically documents the progress and developments made in the understanding and design of heterogeneous catalysts for VOC oxidation over the last two decades. This detailed review addresses how catalytic performance is often drastically affected by the pollutant sources and reaction conditions. It also highlights the primary routes for catalyst deactivation and discusses protocols for their subsequent reactivation. Kinetic models and proposed oxidation mechanisms for representative VOCs are also provided. Typical catalytic reactor and oxidizer for industrial VOC destruction were further reviewed. We believe that this review will act as a great foundation and reference point for future design and development in this field.
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1. Introduction

Volatile organic compounds (VOCs) typically refer to organic compounds which have boiling points below 250 °C under atmospheric pressure (101.325 kPa).¹ Most emitted VOCs can lead to the formation of secondary pollutants such as tropospheric ozone, peroxyacetyl nitrate, and secondary organic aerosols; and their toxicity and carcinogenic human health effects are well documented (Tables S1 and S2).²⁻⁴ Rapid urbanization and industrialization has been linked to the growing VOC emissions.⁵⁻⁶ For example, industrial non-methane VOC emissions in China increased by 11.6 times from 1.15 Tg in 1980 to 13.35 Tg in 2010, which was above the average annual rate of 8.5%.⁷ The emission of VOCs has been linked to a number of anthropogenic sources, which include petroleum refining, petrochemical processing, solvent use, and many other industrial activities.⁸⁻¹² The vast majority of emitted VOCs consist of alkanes, alkenes, alkynes, aromatics, alcohols, aldehydes, ketones, esters, halocarbons and sulfur/nitrogen containing compounds and their environmental impact is typically dependent on the functionality of the given VOC. Aromatics and alkenes are well recognized as highly polluting molecules, which is attributed to their involvement in the formation of photochemical ozone (Tables S1).¹²⁻¹³ Halogenated and chlorinated VOCs require additional attention due to their inherent toxicity and stability.¹⁴ Since 1999, VOC emissions have been heavily regulated by legislation provided by the European Union (EU). The Goteborg protocol provided in 2006 subsequently affirmed that by 2020, all EU countries should half their VOC emissions compared to that observed in the year 2000.¹⁵ Given the environmental impact and toxicity of VOCs and new legislations in place, it is of great importance to develop efficient and applicable methods to reduce global VOC emissions.

There are numerous research initiatives currently under development to meet the challenging environmental regulations. Manifold recovery technologies (e.g. adsorption, absorption, membrane separation and condensation) and oxidative approaches (catalytic oxidation, thermal incineration, biological degradation, photocatalytic decomposition and non-thermal plasma oxidation) have been developed. Each of these technologies however, have practical limitations, which are typically attributed to the large variety of different VOCs and the conditions associated with emission sources.¹⁶ Adsorption-based techniques are only really favorable for the treatment of highly dilute VOC emissions, as they typically rely on condensation approaches, which are
energy intensive and generally limited to the removal of volatile solvents. Absorption is a costly process where the pollutants are scavenged in a liquid for separation and recovery and the disposal of VOCs and spent solvent is the common problem faced by this processes. Membrane separation is another possible alternative for the removal of VOCs owing to the advantages of simple operation to conduct and compact design; however, the membrane separation process is costly and the operation/maintenance of this technology is quite expensive. Low-temperature condensation is energy intensive and limited to treatment of evaporative solvents. Biological degradation is generally selective, concentration and temperature sensitive, and effective only for low weight and highly soluble hydrocarbons and usually requires relatively longer empty bed retention time. Photocatalytic decomposition has a broad-spectrum activity toward various VOCs at ambient temperature; however, the relatively low quantum efficiency and long residence time requirement result in the limited oxidation capability and load adaptability of this technology. A highly reactive environment (active species can react with VOC molecules and decomposed them) can be created in non-thermal plasma without spending high energy on heating the entire gas stream, while the formation of undesired by-products such as O₃, NOₓ and intermediates is uncontrolled due to its non-selectivity and limited capability. Thermal incineration is a convenient and efficient approach, but it typically requires high temperatures (≥ 800 °C) to achieve full oxidation of highly concentrated VOC streams. Due to its high energy demand, this technology is not very economical, although the heat released from incineration can be recovered. Furthermore, incomplete thermal oxidation of VOCs can also produce numerous undesirable by-products such as CO, dioxins and NOₓ. The complete catalytic oxidation of VOCs into CO₂ and water is one of the most effective and economically feasible technologies currently being investigated for the removal of dilute VOC (< 0.5 vol.%) effluent streams. In this approach, the VOCs are oxidized over a suitable catalyst at much lower temperatures (typically; 200-500 °C) than with thermal incineration. In addition, in some cases the product selectivity in catalytic oxidation processes can be controlled, and can be even more energy efficient if the process is coupled with heat exchangers to redistribute the heat effectively.

Due to the obvious merits of this technology, a significant amount of investigations have considered the design and synthesis of catalysts for the oxidation of VOCs. Generally, there are two fundamental types of catalysts used in these processes: noble metal supported catalysts...
(NMSCs) and transition metal oxides (TMOs). Despite being quite costly, noble metal supported catalysts are generally preferred for VOC catalytic oxidation because of their high specific activity and ease of regeneration. The noble metal phases are usually supported by simple and low-cost oxides such as SiO$_2$ and $\gamma$-Al$_2$O$_3$, but also by molecular sieves and TMOs including ZSM-5, Beta, SBA-15, MCM-41, TiO$_2$, and Co$_3$O$_4$ to increase the dispersion of the noble metals and aid adsorption of reactants. Both these can reduce the overall noble metal loading required, which has economic advantages. Platinum (Pt) and palladium (Pd), have been found to be highly active for the total oxidation of C$_2$-C$_8$ paraffins and are the most extensively studied elements of all the noble metals. The catalytic performance of NMSCs is typically dependent on a number of factors, which include: the physicochemical properties of the active metal or support, the interaction between the metal and support, the noble metal precursor used in the preparation, the preparation method used, and the size and morphology of noble metal particles and supports. TMO catalysts are a cheaper alternative to the NMSCs. These typically consist of elements from groups IIIB and IIB in the periodic table and possess high electron mobilities and positive oxidation states. The TMO materials are generally less active than the NMSCs, but they possess other advantages such as their low cost, excellent reducibility and thermal stability, and resistance to poisoning. Efforts have been made to develop efficient TMO catalysts for VOC catalytic oxidation, with the primary aim of enhancing the low-temperature reaction activity, to bridge the activity gap between these systems and NMSCs. The development of different types of catalysts for catalytic oxidation of VOCs has been widely reported in the literature and a number of previous reviews have been published. In 1987, Spivey et al. presented an overview of the catalytic systems used for the oxidation of VOCs. Everaert and Baeyens subsequently published a review in 2004, which linked the catalytic oxidation of VOCs with theoretical oxidation kinetics and highlighted how influential reactor design could be on the catalytic performance observed. Li et al. followed on from this, by publishing a review which in 2009 which predominantly focused on the catalytic oxidation of VOCs over non-noble metal catalysts, whilst Liotta reviewed the development of catalytic oxidation of VOCs over supported noble metals in 2010. Scirè and Liotta followed on from this with a review focusing on the use of Au supported catalysts for the oxidation of VOCs. In 2014, Aranzabal et al. reported on the catalytic oxidation of chlorinated VOCs (CVOCs). Huang and
co-authors\textsuperscript{47} reviewed catalysts which were focused on the low-temperature oxidation of VOCs in 2015 and in 2016, Zhang \textit{et al.}\textsuperscript{7} provided an overview of catalytic VOC oxidation from a technological and applicative perspective. In the same year, Li \textit{et al.}\textsuperscript{50} reviewed the development of synthesis, fabrication, and processing of nanostructured noble metals and metal oxides and their performance in catalytic oxidation of VOCs.

As discussed previously, catalytic oxidation is perhaps one of the most promising approaches for end-of-pipe dilute VOC emission control.\textsuperscript{24,51-54} Despite this, there are still some limitations with the use of this methodology. One fundamental challenge that remains is the development of a definitive criterion for selecting an appropriate catalyst for a given purpose. There are numerous examples of catalysts in the literature which are efficient for the catalytic oxidation of VOCs, which have been documented in the reviews presented previously. While this is a useful means of compiling data, many of the reviews do not account for catalytic performance under realistic practical operational conditions; it is known that industrial flue streams typically consist of undesirable substances such as water vapor, halogen or sulfur-containing organic compounds, sulfur oxides, and ammonia,\textsuperscript{55} which can hinder catalytic performance. It is therefore, often very difficult to identify the best catalysts and catalytic reaction conditions to use for the oxidation of a specific VOC. In addition, the catalytic activity, reaction kinetics, regeneration behavior, and oxidation mechanism may have significant differences in performance for a VOC derived from diverse emission sources.

Previous reviews about catalytic oxidation of VOCs predominantly focused on progresses in catalyst design and only encompassed a small variety of common pollutants. In this review, we provide a systematical summary on the progresses and achievements in VOC catalytic oxidation since 1990 with the primary target of clarifying the fundamental principles which drive the catalytic oxidation of VOCs. We hope to provide reputable representation to the research which has been conducted in this field under practical emission conditions. Emphasis has been placed on reviewing the effect of the emission source and documenting the progresses made for the catalytic oxidation of a wide variety of VOCs, including saturated alkanes, unsaturated alkenes and alkynes, aromatics, and heteroatom-containing hydrocarbons. Following on from this, we clarify the effect of reaction conditions (water vapor, inorganic NO\textsubscript{x}, or ozone, and organic pollutant composition) on catalytic VOC oxidation and highlight the main causes for catalytic deactivation such as
coking, poisoning, and sintering. Subsequently, approaches for catalytic reactivation is also reviewed and discussed. Proposed kinetic models and oxidation mechanisms of representative VOCs are discussed and clarified. Finally, typical catalytic reactors and oxidizers for industrial VOC destruction were further reviewed. We believe that a comprehensive review on this subject will be both informative and instructive in expanding the understanding of the fundamental principles which drive catalytic VOC oxidation reactions. We hope that this review will provide a crucial reference point for future catalyst design of materials for the catalytic oxidation of VOCs under applicative reaction conditions.

2. Major VOC emission sources and sorts

VOCs can be emitted from a wide range of sources including petroleum refining, organic chemical raw material production, synthetic resin, textile dyeing and printing, leather manufacturing, pharmaceutical industry, pesticide manufacturing, coating, printing ink, and adhesive manufacturing, spraying, printing, and the manufacture of electronic equipment.\textsuperscript{24} The nature of industry typically dictates the type of VOC emitted, which can include: alkanes, alkenes, alkynes, aromatics, oxygen-containing hydrocarbons (alcohols, aldehydes, ketones, ethers, and esters), halocarbons, and sulfur/nitrogen containing compounds.\textsuperscript{56-58}

2.1. Petroleum refining

Petroleum refining refers to a number of processes which are involved with the production of fuel, oil, lubricating grease, solvent oil, petroleum coke, paraffin wax, asphalt, refined oil, naphtha, and oil additives from crude oil refining, including the primary processing (crude distillation), secondary processing (cracking, catalytic reforming, coking and refining, etc.), and third processing (refinery gas processing).\textsuperscript{59,60} In these processes, VOCs are predominantly emitted from process waste streams but can also be emitted during the handling of reactants or products and from unexpected leaks. The primary pollutants emitted from these processes are ethane, propane, isobutane, cyclohexane, $n$-hexane, butene, propene, benzene, toluene, xylene, methyl ethyl ketone and 2-propanol.\textsuperscript{46,61,62}

2.2. Organic chemical raw material production

A large variety of VOCs are also emitted from industries which produce large quantities of organic chemicals such as the polymer, fine chemical, and solvents industries. These industries
typically emit a wide variety of VOCs which can include: ethane, cyclohexane, ethylene, propene, benzene, toluene, xylene, ethylbenzene, methanol, formaldehyde, acetaldehyde, chloroethane, dichloroethane, trichloroethylene, vinyl chloride, chlorobenzene and acrylonitrile.46,57,63,64

2.3. Synthetic resin

The synthetic resin industry is also responsible for the emission of a number of VOC pollutants in the processes of producing synthetic resin (e.g., polyethylene, polypropylene, polyvinyl chloride, polystyrene, acrylonitrile-butadiene-styrene copolymer, polyamide, polycarbonate and polymethyl methacrylate) from basic chemical raw materials mainly include pentane, ethylene, propene, toluene, ethylbenzene, styrene, methanol, ethanol, vinyl chloride, dichloromethane, acrylonitrile and hexamethylenediamine.57,65

2.4. Textile dyeing and printing

The textile and dyeing processing industry using cotton, wool, linen, silk, and chemical fiber as raw materials can emit a wide variety of alkanes, aromatic hydrocarbons, alcohols, aldehydes, ketones and esters to the environment,66-68 such as n-hexane, benzene, toluene, xylene, styrene, methanol, ethylene glycol, formaldehyde, acetone, methyl ethyl ketone, ethyl acetate, methyl chloride, trichloroethane and vinyl chloride.

2.5. Leather manufacturing

The leather (or artificial/synthetic leather) manufacturing process requires a large amount of organic solvents, which discharge lots of VOC pollutants including benzene, toluene, xylene, ethylbenzene, 2-butanol, 2-propanol, formaldehyde, cyclohexanone, 2-butane, acetone, butyl acetate, ethyl acetate, vinyl chloride and dimethylamine.24

2.6. Pharmaceutical industry

Pharmaceutical industry includes pharmaceutical raw materials manufacturing, chemical drug manufacturing, and biological drug manufacturing, and all these processes release large numbers of VOCs into atmosphere,46,57,68,69 which primarily includes cyclohexane, benzene, toluene, xylene, methanol, ethanol, 2-propanol, acetone, ethyl acetate, dichloromethane, 1,2-dichloroethane and trichloromethane.

2.7. Pesticide manufacturing
Pesticides can be divided into three major categories of herbicides, insecticides, and sterilizers, which mainly refer to various chemical pesticides, microbial pesticides, and biochemical pesticides. The organic pollutants emitted from the pesticide production processes are epoxypropane, benzene, toluene, xylene, methanol, 2-propanol, butanol, formaldehyde, butanone, acetic acid, methyl chloride, chlorobenzene, pyridine, acrylonitrile and ethylenediamine.\textsuperscript{64,69}

2.8. Coating, printing ink, and adhesive manufacturing

Coating manufacturing refers to the production of covering materials made by adding pigments, solvents and auxiliary materials to natural resins or synthetic resins, and the primary VOCs emitted in these activities are toluene, ethylbenzene, xylene, butanol, ethylene glycol, acetone, butanone, cyclohexanone, butyl acetate, and styrene.\textsuperscript{62,70,71} Printing ink manufacturing refers to the activities for production of colored slurry (obtained by mixing, grinding and modulation of pigments, fillers, and coupling materials (e.g., vegetable oils, mineral oils, and resins)) used in printing and inks for printers and duplicators. N-hexane, cyclohexane, benzene, toluene, xylene, methanol, ethanol, 2-propanol, butanol, ethyl acetate, and butyl acetate are usually existed in the tail gas of ink production.\textsuperscript{61,72,73} Adhesive manufacturing refers to the production of various types of adhesives using synthetic or natural materials, and main organic pollutants in these processes are benzene, toluene, formaldehyde, methanol, styrene, trichloromethane, carbon tetrachloride, 1,2-dichloroethane and ethylenediamine.\textsuperscript{74-76}

2.9. Spraying

Production of various equipment and tools (automobile, motorcycle, bicycle, furniture, ship, container, household appliance, wire, cable, etc.) generally involves the surface coating process, which releases different types of VOCs into atmosphere, such as benzene, toluene, xylene, ethylbenzene, methanol, 2-propanol, n-butanol, ethyl acetate and butyl acetate.\textsuperscript{24,70}

2.10. Printing

The paper, plastic, and offset printing and packaging material manufacturing (e.g., soft packaging material coating) processes emit large amounts of alkanes, aromatic hydrocarbons, alcohols, and esters into the environment,\textsuperscript{68,73} including n-butanol, n-butane, toluene, xylene, methanol, ethanol, n-propanol, 2-propanol, propanediol, n-butyl alcohol, methyl acetate, ethyl acetate and butyl acetate.
2.11. Electronic equipment manufacturing

VOCs are generally emitted from four discharge sections in the electronic equipment production processes,\textsuperscript{57,66,77-79} that is, (1) semiconductor and integrated circuit manufacturing with benzene, toluene, xylene, 2-propanol, acetone, methyl ethyl ketone and butyl acetate as the primary pollutants; (2) flat panel display manufacturing with 2-propanol, propanediol, acetone and dimethyl sulfoxide as the main pollutants; (3) printed circuit board with benzene, toluene, xylene, ethanol, \textit{n}-propanol, 2-propanol, butanol, formaldehyde, butanone, ethyl acetate and butyl acetate as the major emissions; and (4) electronic terminal product manufacturing with benzene, toluene, xylene, ethanol, 2-propanol, cyclohexanone, acetone, butyl acetate, dichloromethane and trichloroethylene as the main pollutants.

3. Oxidation of different sorts of VOCs

3.1. Saturated alkanes

Alkanes are the simplest organic compounds containing hydrogen and carbon, but contribute to a large proportion of the VOC emitted each year. This is primarily because of their widespread application as feedstocks for the industrial synthesis of chemicals. There are numerous examples of alkanes which qualify as VOCs. Those which are commonly emitted including ethane, propane, \textit{n}-hexane, \textit{n}-butane, pentane, cyclopentane, cyclohexane, \textit{n}-heptane, methyl cyclohexane and \textit{n}-octane.\textsuperscript{2,80-82} Many of these compounds have different environmental and toxicological effects. The catalytic oxidation of alkanes has been widely investigated; most of which has predominantly focused toward the oxidation of ethane, propane and \textit{n}-hexane. To date, the work in this area has used a wide variety of different catalysts and includes the use of noble metal (Pt, Pd, Ru, and Au) based catalysts,\textsuperscript{83-89} transitional metal (Co, Ni, V, Mo, Cu, Mn, and Fe) oxides,\textsuperscript{90-96} perovskite- and spinel-type materials\textsuperscript{97-102} and hydrotalcite derivative oxides.\textsuperscript{103}

3.1.1. Ethane

Ethane is an important low weight VOC, which is formed as a major by-product from coal gasification, rock oil outgassing and numerous chemical processes such as petroleum refining and the production of organic chemicals.\textsuperscript{104} There are numerous reports published on the total catalytic oxidation of ethane to CO$_2$ and water over Pd and Au supported on base metal oxides such as NiO, Cr$_2$O$_3$ and Co$_3$O$_4$.\textsuperscript{86,89,105-107}
SnO$_2$ was previously shown to be active for the total oxidation of methane.$^{108}$ For this reason, Tahir and Koh$^{95}$ subsequently prepared a series of M/SnO$_2$ (M = Mn, Co, Cu, Ce, and Ni) catalysts using an impregnation technique and found that the catalytic activity for ethane oxidation varied quite significantly. The order of activity observed for this series of catalysts was as follows: Mn/SnO$_2$ = Co/SnO$_2$ > Cu/SnO$_2$ > Ce/SnO$_2$ = Ni/SnO$_2$. The Mn/SnO$_2$ was determined to exhibit a higher stability than that of Co/SnO$_2$, which was connected with the in situ production of a Co$_3$O$_4$ surface modification during the reaction. Cu/ZSM-5 has been extensively studied as a catalyst in the low-temperature decomposition of organic compounds.$^{109,110}$ Kucherov et al.$^{94}$ reported that isolated Cu$^{2+}$ species located in a square-planar coordination was responsible for the high activity observed over this catalyst. This was related to the interaction between the bivalent cations and oxygen atoms located in the zeolitic framework which are linked to Al$^{3+}$ ions. In the same study, they also reported that the addition of fairly large quantities (5 wt.%) of La or Ce to this material could further enhance catalytic performance, which was attributed to the dopant metals involvement in the stabilization of the square-planar Cu$^{2+}$ cations at high temperatures.$^{94}$

It is well known that perovskite-type oxides with the general formula of ABO$_3$ have a high structural stability, where A sites may be occupied by rare-earth, alkaline-earth, alkali, or other large ions, and the B sites are usually filled with transition-metal cations. Moreover, the perovskite composition can be widely changed by the partial replacement of A and/or B cations with other metals, which can change the physicochemical properties of the material.$^{100}$ In general, changing the oxidation states of the A-site typically affects the oxygen adsorption capacity of the material, whereas B-site replacement influences the nature of adsorbed oxygen.$^{111,112}$ Preparing and testing materials with different A and B site combinations can be a productive method to acquire and understand how the physicochemical properties of a catalyst effect its performance in a given reaction.$^{113}$ Lee et al.$^{98}$ investigated how the partial substitution of La$^{3+}$ with alkali metals in a LaMnO$_3$ perovskite effected catalytic performance in the oxidation of ethane. It was determined that the partial substitution of La with K resulted in a strong reduction in oxygen non-stoichiometry and oxygen desorption of the perovskites material. The incorporation of K however, was found to have a negative effect on the catalytic activity since K facilitating oxygen activation and reduction to O$_2^-$ lattice oxygen, promoting the oxydehydrogenation of ethane to ethylene (Fig. 1i).
Due to their inherent stability, it is exceptionally difficult to oxidize alkanes over TMOs and perovskites. NMSCs such as supported Pd materials however, are well known to be highly efficient catalysts for the oxidation of alkanes. Samorjai and co-workers recently investigated the catalytic oxidation of ethane over Pd foils in temperatures ranging from 573-698 K at 800 Torr (total pressure). Post-reaction characterization of the catalyst by auger electron spectroscopy (AES) showed that a significant proportion of PdOₙ species were present, regardless of the reaction conditions used. They determined that a surface oxygen monolayer coverage of 0.3-0.5 was found to be optimum for ethane oxidation. Kolade et al. used monolith (made of Pd/active carbon) as an adsorptive catalytic reactor for ethane disposal (Fig. Iii). This structure provided a high surface area, low pressure drop, and low resistance to the transport of particulate and can maintain high VOC conversion while preventing thermal loss.

Au has historically been considered as an element catalytically inert, in particular with respect to alkane oxidation. However, Au has been shown to be a metal capable of excellent catalyst activity when present as nanocrystals on a support. Solsona et al. conducted a study which compared the activity of Au supported on MnOₓ and CoOₓ for the oxidation of ethane. It was determined that the total oxidation of ethane could be achieved at temperatures as low as 250 °C (GHSV of 15,000 h⁻¹) over the Au/CoOₓ catalyst synthesized by a co-precipitation method. The presence of Au in the catalyst was determined to enhance the reducibility of the support and a correlation between the redox properties of the catalysts and the catalytic activity was established.

3.1.2. Propane

Propane is an alkane present in both oil and natural gas. The quantity of propane emitted from stationary sources continues to increase and is believed to be directly linked with the continued development of chemical processes and products. Recent developments in catalytic oxidation of propane has primarily involved the use of single or multiple metal oxide systems containing Co, Mn, Fe, Ni and Cu. The most promising metal oxides systems developed to date typically consist of either Co and/or Mn oxides. Co₃O₄ has been consistently found to the more active than other stable Co phases, such as CoO, which has been attributed to the lower oxidation state of Co in Co₃O₄. Similar observation have been made regarding manganese oxides; partially reduced phases such as Mn₂O₃ and Mn₃O₄ have been found to display a higher
catalytic destruction activity.  

It is known that Co$_3$O$_4$ is one of the most efficient catalysts currently available for the total oxidation of propane.  

High surface area cobalt oxide is typically desirable as it is more easily reduced, which is attributed to a reduced Co-O bond strength and higher defect concentration. Ordered Co$_3$O$_4$ oxides with surface areas as high as 173 m$^2$·g$^{-1}$ were successfully obtained through a nanocasting route using a mesostructured KIT-6 silica template. The mesoporous Co$_3$O$_4$ was found to display a higher activity for this reaction when compared to conventional Co$_3$O$_4$, which has been ascribed to the higher surface area of the material and greater proportion of oxygen vacancies. The ordered structure in this material however, did not appear to have an influence on the catalytic performance. A subsequent study by Salek et al. provided a novel method for obtaining high surface area Co$_3$O$_4$ (up to 100 m$^2$·g$^{-1}$), which was achieved by using CoO(OH) as the catalyst precursor. The CoO(OH) was calcined at 250 °C in air and was found to totally convert propane (0.4 vol.%) at just 230 °C (volumetric flow rate of 1.63 cm$^3$·s$^{-1}$). The enhanced activity was attributed to the increased accessibility of reactants to catalyst surface. Alternative approaches have targeted the immobilization of Co$_3$O$_4$ on various support materials, which can have a dramatic influence on the physicochemical properties of the active Co$_3$O$_4$ phase. Zhu et al. determined that the propane oxidation activity of a Co$_3$O$_4$/ZSM-5 synthesized by a hydrothermal method, was higher than that of a bulk Co$_3$O$_4$ material. The excellent catalytic activity exhibited by the Co$_3$O$_4$/ZSM-5 catalyst was attributed to a number of factors, which included; enhanced reducibility of Co$^{3+}$ species, a higher proportion of Co$^{3+}$ species and surface lattice oxygen, and increased lattice oxygen mobility (Fig. 2i and ii). It is also important to note that in some cases, supporting Co$_3$O$_4$ can also have detrimental effects on the catalytic performance observed. Taylor and co-worker determined that highly dispersed Co$_3$O$_4$ exhibited strong interactions with the support material, which ultimately led to a reduction in the observed catalytic activity.

MnO$_x$ is an abundant, low cost alternative catalyst for the oxidation of VOCs. The catalytic oxidation of C$_3$ hydrocarbons over Mn$_3$O$_4$ was studied in detail by Busca and co-workers. Only propene and trace quantities of ethylene were observed at incomplete propane conversions; CO$_2$ was only detected under a highly oxidizing atmosphere. To rationalize this, a propane oxidation mechanism over Mn$_3$O$_4$ was proposed, offering an explanation as to
how the propene was produced. Both Co and Mn oxide catalysts have been prepared by a wet oxidation procedure and utilized organic acids as a reducing agent. A previous study indicated that the organic acids could act as a template in the metal oxide precipitation.\textsuperscript{121} When the Co and Mn oxides were prepared in this way, both materials were found to be highly active for this reaction. The enhancement in performance was owing to an increased proportion of the reduced phase with the Mn oxide. The high activity observed with the Co oxide however was merely attributed to an increase in surface area.

As the catalytic performance in propane oxidation strongly depends on their surface structure and surface active sites, there is often a direct relationship between catalytic activity and the crystal plane figure/crystal facet Miller indices and/or geometric features of the catalyst surface. Xie \textit{et al.}\textsuperscript{122} reported that the crystal phase of MnO\textsubscript{2} catalysts (\(\alpha\)-, \(\beta\)-, \(\gamma\)-, and \(\delta\)-MnO\textsubscript{2}) significantly influenced their catalytic activity in this reaction. Of the materials tested, \(\alpha\)-MnO\textsubscript{2} exhibited the best activity, with 90\% of propane oxidized at 290 °C (GHSV of 30,000 h\textsuperscript{-1}). Unlike the other Mn oxide phases discussed previously, with MnO\textsubscript{2}, the surface area and reducibility of MnO\textsubscript{2} do not appear to be influential factors which drive the catalytic activity. DFT calculations were subsequently conducted, which simulated the adsorption of propane on the different crystal phases of MnO\textsubscript{2}. It was determined that the crystal phases had a dramatic effect on the adsorption energy of the propane on the MnO\textsubscript{2} (Fig. 2iii). The calculated binding energies were found to vary in the following order: \(\alpha(310) > \gamma(120) > \beta(110) > \delta(001)\). This aligned with the activity observed for these materials and so, the activity was directly attributed to the adsorption energy of propane over MnO\textsubscript{2}. Besides, the presence of translational motion in \(\alpha\)-MnO\textsubscript{2} along with its stronger deformation and stretching modes may lead to its better catalytic activity for this reaction.\textsuperscript{122}

Although the Fe oxide is typically less active than both Co and Mn oxides for this reaction, it has a high thermal stability and is therefore less susceptible to sintering deactivation routes. In addition, Fe oxide is environmentally benign and readily available, which ultimately merits economic benefits. Fe oxide has been found to display some promise as a catalyst for the low temperature oxidation of propane and propene.\textsuperscript{137} Mesoporous Fe oxides have been found to be much more active than bulk Fe oxide, which has been attributed to enhancements in the total surface area and reducibility of the material and a superior reactant mass transfer resistance.\textsuperscript{138} Recently, Nieto and co-workers\textsuperscript{96} prepared a series of mesoporous Fe oxide materials by a soft
chemistry method; utilizing oxalic acid as the precipitating agent and a hard template method; KIT-6 silica was used as the hard template. These materials were subsequently characterized and tested for this reaction. The mesoporous Fe oxide prepared using oxalic acid exhibited a higher activity for this reaction, which was partly attributed to the formation of nanocrystalline aggregates on the catalysts surface. A direct relationship between the catalysts reducibility and activity was observed.

Mixed metal oxides have significantly different properties (textural, morphological, redox and acid-base) compared to single metal oxides. There are numerous examples of mixed-metal oxide materials displaying better activity for the oxidation of VOCs than their mono-metallic oxide counterparts.\textsuperscript{139-143} The observed enhancement in catalytic performance is often owing to the multiple available energy levels of the metals and their associated oxygen anions in the mixed-metal systems, facilitating increased interactions between the VOC and surface-bound active oxygen anions. This property is also likely to result in a higher mobility of surface oxygen and/or substrate and increase electron transportation through the materials lattice. One such example of this, was provided by Morales et al.\textsuperscript{125} who prepared a series of Cu-Mn mixed metal oxides by a co-precipitation method with varied ageing times. The Cu-Mn mixed oxide catalysts all displayed a higher propane oxidation activity than that observed over Mn$_2$O$_3$ and CuO. Increasing the ageing time during the preparation of the Cu-Mn oxide was also found to further increase the activity and CO$_2$ selectivity.

CeO$_2$ has displayed a lot of potential as a catalyst for the total oxidation of VOCs, which has been attributed to a host of unique properties such as its high oxygen storage capacity and ability to undergo redox shuttling between Ce$^{3+}$ and Ce$^{4+}$\textsuperscript{144,145} Ce is often utilized as structural and electronic promoter, owing to its high oxygen storage capacity\textsuperscript{24,25} Mesoporous Ce$_{1-x}$Mn$_x$O$_2$ catalysts with Ce : Mn of 1.5 exhibited a very high activity for propane oxidation and could totally convert propane to CO$_2$ and water at 300 °C.\textsuperscript{124} Lu and co-workers\textsuperscript{91} have also demonstrated that Mn-Ni oxide materials were highly active for the catalytic oxidation of propane. Of the catalysts tested in this study, a MnNi$_{0.2}$O$_x$ catalyst exhibited the highest catalytic activity; a 90% propane conversion was observed at 240 °C (GHSV of 30,000 h$^{-1}$). The high activity observed was linked to the formation of a Mn-Ni-O material which was found to form when only small quantities of Ni were incorporated in the preparation. The synergistic interaction between
Ni and Mn was related to a number of factors, which included an increased proportion of surface Mn$_{4+}$ species and oxygen vacancies, a higher oxygen mobility and enhanced reducibility of the material (Fig. 3i).

A significant quantity of work has also investigated the use mixed metal oxide spinel structured materials, hydrotalcite-derived oxides and perovskites for the catalytic oxidation of VOCs. Spinel structured oxides typically contain cation sites of a specific structure (tetrahedral and octahedral) and have oxide anions arranged in a cubic close-packed lattice$^{146}$. A series of Co$_x$Mn$_{3-x}$O$_4$ spinel oxides (0≤ x ≤ 3), exhibiting specific surface areas up to 250 m$^2$.g$^{-1}$, were synthesized and tested for the catalytic oxidation of propane.$^{102}$ The spinel oxide materials exhibited an exceptional low-temperature catalytic activity for this reaction (Fig. 3iii and iv). The most efficient catalyst (Co$_{2.3}$Mn$_{0.7}$O$_4$) tested, achieved a propane conversion of approximately 90% at only 220 °C (apparent activation energy ($E_a$) of 60 ± 10 kJ∙mol$^{-1}$), which is notably better than other Co oxide catalysts reported in the literature.$^{102}$

Mixed transition metal oxides can be readily obtained through the calcination of LDH precursors. It is known that metal oxide materials prepared in this way typically exhibit a good dispersion of active components and have large surface areas and a high thermal stability. Jiang et al.$^{103}$ determined that Cu$_x$Mg$_{3-x}$AlO materials derived from Cu$_x$Mg$_{3-x}$Al ternary hydrotalcites were highly active for the catalytic oxidation of propane. The performance of these materials for this reaction was found to be highly dependent on the Cu content. A Cu$_{0.5}$Mg$_{2.5}$AlO material exhibited the highest catalytic activity as the strong interactions between the component oxides (Fig. 3ii).

LaCoO$_3$ perovskite materials have also been found to be active for this reaction, which can be enhanced further by substituting with Sr or Ce ions.$^{147-150}$ Merino et al.$^{100}$ were the first to investigate how the partial replacement of La with Ca effected the materials catalytic performance in this reaction. Experimental results revealed that the substitution of Ca$^{2+}$ for La$^{3+}$ generated oxygen vacancies and preserved charge neutrality throughout the material, which resulted in a “reductive stoichiometry”. This resulted in a notable reduction in the $E_a$ for propane activation and ultimately resulted in an increase in the observed catalytic activity.

Supported noble metal (Pd, Pt, Au, and Ru) catalysts have also been extensively investigated as catalysts for the oxidation of propane. Pd- and Pt-supported catalysts have displayed a lot of potential as catalysts for the total oxidation of short chain alkanes.$^{126,151}$ Various support materials
such as Al$_2$O$_3$, TiO$_2$, zeolites and perovskites have been investigated in an attempt to improve the oxidative performance of the noble metal phases$^{27,112,152-157}$ The behavior of these supported Pd or Pt catalysts is strongly influenced by the nature of the support. TiO$_2$ for example, is known to be more resistant to sulphur poisoning than Al$_2$O$_3$.$^{155}$

The total catalytic oxidation of hydrocarbons over Pd supported catalysts is dependent on the redox cycle of palladium; oxygen incorporation in the products proceeds through a PdO$_x$ intermediate species.$^{158,159}$ The performance of these catalysts is therefore likely to be influenced by the Pd dispersion, which is typically driven by the Pd-support interaction.$^{160}$ For this reason, the morphology and exposed crystal planes of support material can have a significant impact on the performance of these catalysts in total oxidation reactions. Hu et al.$^{161}$ recently prepared a series of nanocrystallites CeO$_2$ materials with different morphologies and crystal planes by a hydrothermal method. It was determined that Pd species on CeO$_2$ rods and cubes predominantly formed Pd$_x$Ce$_{1-x}$O$_2$ phases which contained -Pd$^{2+}$-O$^{2-}$-Ce$^{4+}$- linkages. In contrary, when Pd was supported on CeO$_2$ octahedrons, large quantities of PdO$_x$ nanoparticles were observed. Interestingly, the highest reaction rates and turnover frequencies (TOF) for propane oxidation were observed over the Pd/CeO$_2$-octahedron catalyst. This increase in activity was owing to an increased proportion of (111) facets in the CeO$_2$-octahedron support material (Fig. 4i), inducing strong Ce-O surface bonds which favors the production of PdO species.$^{102}$

Pt supported catalysts have also be found to be highly active for this reaction.$^{162,163}$ Aryafar and Zaera$^{164}$ conducted a kinetic study on the oxidation of lower alkanes (methane, ethane, propane and n-butane) over Ni, Pd and Pt foils, and found that Pt was the most active foil for the oxidation of most of the compounds; methane being the only exception. Previously, we have shown that the acid-base properties of the support could significantly effect the activity of Pd-supported catalysts. Brønsted acid sites (BAS) assisted with the dispersion of Pd species and could dramatically effect the Pd oxidation state.

It is found that the BAS are responsible for the formation of the dispersed Pd species and the acid-base property of support has significant influence on the dispersion and oxidation state of Pd.$^{31,165-168}$ Yazawa et al.$^{169}$ investigated how the acid strength of the support influenced the propane oxidation activity with varying concentrations of O$_2$ in the gas feed. It was determined that partially oxidized Pd species were desirable for this reaction. It was concluded that acidic
supports hinder the oxidation of Pd, while basic supports enhance Pd oxidation. As such, it was proposed that a highly acidic support favors oxidation activity under oxygen-rich conditions, whereas basic supports are expected to be more suitable under oxygen-lean conditions. A similar correlation between catalytic activity and the acid-base properties of the support has been observed with supported Pt catalysts; the effect of support acidity on propane oxidation activity over Pt-based catalysts was investigated by Murakami and co-workers. It was proposed that highly acidic supports were favorable as they inhibited the oxidation of the Pt. Further evidence for this was observed by Yazawa et al., who synthesized a series of Pt catalysts on different supports (Pt/MgO, Pt/La2O3, Pt/ZrO2, Pt/Al2O3, Pt/SiO2, Pt/SiO2-Al2O3 and Pt/SO42−-ZrO2) and tested them for the low temperature oxidation of propane. Once again, it was determined that the more acidic supports displayed a higher catalytic activity (Fig.4ii).

The oxidation of saturated aliphatic hydrocarbons is typically conducted over Au catalysts at higher temperatures than those used with Pd and Pt supported catalysts. As with Pd and Pt, it is generally accepted that the catalytic activity of Au supported catalysts for VOC oxidation is dependent on the nature of the support material. Solsona et al. investigated the use of a Au/Ni-Ce-O catalyst for this reaction, and proposed that the excellent activity observed was attributed to their high total surface area, low Ni-O bond strength and highly reducible Ni sites. One of the most commonly used mixed metal oxide catalysts used for total oxidation reactions is Hopcalite; a mixed copper and manganese oxide originally discovered approximately ninety years ago. More recently, Solsona et al. utilized Hopcalite as a support materials for Au nanoparticles and determined that the performance of Au/Hopcalite catalysts in this reaction were dramatically affected by the calcination temperature. Calcination at 300 °C was found to produce the most active catalyst, which was linked to an improvement in the reducibility of the Hopcalite, induced from the incorporation of a Au phase. Au/Co3O4 has also been found to be highly active for the total oxidation of saturated hydrocarbons. A transient propane oxidation experiment was conducted over an Au/CoOx catalyst and monitored using a temporal analysis of products (TAP) reactor. The enhanced performance observed from the introduction of Au onto the surface of CoOx was attributed to an increase in oxygen mobility between lattice and surface oxygen. More recently, Solsona et al. investigated the performance of Au deposited on a series of mesoporous Co oxide materials for this reaction. Again, Au was found to increase the catalytic
activity when compared to a corresponding Au-free Co$_3$O$_4$ material, which was ascribed to an improved reducibility of the Co oxide in the presence of Au nanoparticles (Fig. 4iv).

The activity of NMSCs can be further modified through the addition of a second active component. Modifiers are generally added to promote activity and enhance catalytic resistance to deactivation. Fe, Mn, W, Re, Ce and La have all been investigated for their promotional effect on NMSCs in propane oxidation. The addition of tungsten to a Pd/TiO$_2$ catalyst was found to significantly enhance the catalytic activity in this reaction (Fig. 4iii). In the standard Pd/TiO$_2$ catalyst, both Pd$^0$ and Pd$^{2+}$ species were observed. Interestingly, after W was added, all the observed Pd presence existed as Pd$^{2+}$. The increased activity observed was attributed to the formation of a WO$_x$-decorated interface between PdO$_x$ and TiO$_2$. Zheng et al. subsequently investigated how the introduction of Ni to a Pt/Ce$_{0.4}$Zr$_{0.6}$O$_2$ catalyst effected its performance in this reaction. The modified material exhibited an enhancement in activity and resistance to sulfur.

It has been proposed that rare earth metals such as Ce can act as both structural and chemical promoters; stabilizing noble metal nanoparticles against sintering and providing an additional source of active oxygen. In addition to this, Gluhoi and Nieuwenhuys investigated how MO$_x$ (M = alkali (earth), transition metal and cerium) promoted the performance of Au/Al$_2$O$_3$ catalysts in this reaction. The addition of MO$_x$ to Au/Al$_2$O$_3$ was found to improve the propane oxidation activity. The observed enhancement was proposed to be ascribed to two factors: (i) stabilization of the supported Au nanoparticles and (ii) increased oxygen activation. As a promoter, La has been shown to improve the thermal stability of alumina. La has also been shown to have additional benefits as a promoter; when doped onto a Pd catalyst, strong interactions between Pd and La can influence the oxidation state of Pd. Li et al. determined that Pd supported onto a La-modified alumina material enhanced the catalytic performance for this reaction, compared to the original Pd/Al$_2$O$_3$ catalyst. As discussed previously, the oxidation state of supported Pd can be affected by the basicity of support material. La can have a similar effect and promote the oxidation of supported Pd, due to its electrophobic nature. For this reason, La can be a useful modifier for catalysts operating at low temperatures or oxygen deficient conditions.

3.1.3. N-hexane

$N$-hexane is a common VOC emitted from oil field gas, petroleum refining, and the textile
dyeing and printing industries. Many catalysts including transition metal (Cu, Co, W, Bi, Ti, and Mn) oxides, noble metal (Pt, Pd, and Au) supported materials, perovskite- and spinel-type oxides have been investigated for the catalytic oxidation of \( n \)-hexane.\(^{84,97,101,184-195}\) Manganese oxide based catalysts are perhaps the most interesting from a commercial perspective, attributable to their low synthesis costs and high activity.\(^{134,196}\) MnO\(_2\) has been reported to be even more active than some NMSCs for this reaction.\(^{197}\) As with some of the other VOCs discussed previously, the high activity of the manganese oxide catalysts for this reaction is attributed to the co-existence of mixed valence states of Mn\(^{2+}/\)Mn\(^{3+}\) or Mn\(^{3+}/\)Mn\(^{4+}\) and lattice oxygen.\(^{198,199}\) Mn-Co mixed metal oxides have also been found to be highly efficient systems for the oxidation of VOCs,\(^{200}\) and are in general, more efficient than their mono-metallic oxide counterparts. Tang et al.\(^{201}\) demonstrated that this was also the case for this reaction.

Zeolites have also gained much attention as catalysts for the oxidation of hydrocarbons, which has been attributed to their pore structures, acidic properties, good thermal stability, and ion exchange properties.\(^{202}\) More specifically, Díaz et al.\(^{188}\) studied the oxidation of \( n \)-hexane over a series of NaX and CaA zeolites, which were modified by Fe exchange with Mn\(^{2+}\), Co\(^{2+}\), and Fe\(^{3+}\). Of the catalysts tested, the Mn-exchanged CaA catalyst exhibited the highest activity for this reaction. The performance of this material was attributed to the Mn instigating changes in the morphological structure, surface acidity, and oxygen affinity of the zeolite.

CeO\(_2\) can act both as an oxygen source or oxygen sink in surface based reactions. In addition, it is known that CeO\(_2\) can enhance the reducibility and dispersion of supported metal particles.\(^{40}\) Ce-Zr oxide materials (Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) and Ce\(_{0.15}\)Zr\(_{0.85}\)O\(_2\)) have been investigated as catalysts for this reaction.\(^{203}\) The insertion of ZrO\(_2\) into cubic CeO\(_2\) lattice distorts the structure of the oxide, which allows for greater lattice oxygen mobility and can improve catalyst activity.\(^{204}\) The introduction of small quantities of Cu into CeO\(_2\) was also been reported to improve its activity in total oxidation reactions.\(^{185}\)

CeO\(_2\) has also attracted attentions as support material for Au nanoparticles and has been applied as a catalyst for the oxidation of various VOCs. Centeno et al.\(^{194}\) studied the catalytic oxidation of \( n \)-hexane over Au/Al\(_2\)O\(_3\) catalysts and found that the addition of CeO\(_2\) to the material, enhanced the metal support interaction and dispersion of Au particles. The enhancement in activity was connected with an increase in the mobility of lattice oxygen and an increased stability.
of the desired Au oxidation state.

TiO$_2$ and MnO$_2$ are commonly used as supports for Au nanoparticles. TiO$_2$ carries a positive charge at low pH, which is less than the value of 6.0 of its isoelectric point, which facilitates strong interactions with anionic Au species (AuCl$_4^-$), enhancing the Au dispersion. Lahousse et al. reported that γ-MnO$_2$ is more active than some of the conventional NMSCs used in VOC oxidation reactions. Grange and co-workers investigated the effect of the Au particle size in Au/TiO$_2$ and Au/γ-MnO$_2$ catalysts by comparing samples prepared by deposition-precipitation (DP) with samples prepared by anion adsorption method. It was concluded that the differences in the Au particle size for the two methods originated from the mobility of Au surface species during the thermal treatment. The Au/γ-MnO$_2$ catalyst prepared by DP displayed the highest Au dispersion but did not exhibit the highest propane oxidation activity, due to a loss in the specific surface area of the material.

In general, supported Pt catalysts are more active than Au supported catalysts for the oxidation of VOCs. Pt nanoparticles supported on high surface area γ-Al$_2$O$_3$, either as a powder or immobilized on a wash-coated monolith is the most commonly used catalyst for VOC abatement industrially. The total oxidation of $n$-hexane has been studied over Pt/Al$_2$O$_3$ catalysts with small and large Pt crystallites. To this catalyst, Mn was subsequently introduced by the DP method and the effect of the precipitating agent was compared. When ammonia was used, predominantly spherical Mn oxide particles were observed on the surface. In contrary, when dimethylamine was invoked as the precipitating agent, fibrous needle-like structures of MnO$_x$ were observed, which were characteristic of a cryptomelane phase. Both the Mn doped Pt/Al$_2$O$_3$ catalysts were more active than the corresponding Pt/Al$_2$O$_3$ catalyst. Of these, the material containing Mn precipitated by dimethylamine exhibited the highest activity, which was attributed to an increase in oxygen mobility and increased proportion of active oxygen species from Pt-O-Mn sites, associated with cryptomelane phase.

### 3.1.4. Other saturated C$_4$-C$_6$ alkanes

The catalytic oxidation of numerous other saturated alkanes such as $n$-butane, iso-butane, $n$-pentane, cyclopentane, iso-pentane, and cyclohexane has also been reported in the literature. A large proportion of the work specifically investigating the catalytic oxidation of $n$-butane and/or
iso-butane has involved the use of supported precious metal (Pt, Ru, and Au) catalysts. Haneda et al.\textsuperscript{209} studied the oxidation of \textit{n}-butane over Pt supported on ZrO\textsubscript{2} and Y-stabilized ZrO\textsubscript{2} and established that the TOF increased as the Pt dispersion decreased. This relationship between the oxidative activity of Pt catalysts and dispersion has also been observed with reactions conducted over Pt/SiO\textsubscript{2} and Pt/TiO\textsubscript{2}.\textsuperscript{210} The addition of Y\textsubscript{2}O\textsubscript{3} to supported Pt catalysts has been shown to improve the thermal stability of the catalyst, which is associated with an enhanced metal-support interaction but does not appear to effect the catalytic activity.\textsuperscript{209} The catalytic oxidation of \textit{n}-butane and iso-butane has also been studied by Okal and Zawadzki\textsuperscript{87} over Ru/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts. In this study, the catalysts pre-treatment conditions; calcination-reduction or direct reduction with H\textsubscript{2}, were found to have a significant influence on ruthenium dispersion and catalytic activity. The presence of chlorine in the catalyst was found to notably reduce the Ru dispersion in the catalyst which was only exposed to reduction in H\textsubscript{2}, which had a detrimental effect on the oxidation activity. The introduction of a calcination step prior to reduction in H\textsubscript{2}, was found to reduce the quantity of chlorine on the catalysts’ surface and ultimately led to increased Ru dispersion and oxidation activity. The activity of the Ru/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts was ultimately owing to the availability of oxygen from the surface Ru\textsubscript{x}O\textsubscript{y} species.

Supported Pt catalysts have also been reported as efficient catalysts for \textit{n}-pentane oxidation.\textsuperscript{211,212} Once again, it is widely accepted that oxidative activity of these catalysts is typically related to Pt dispersion and the acid strength of the supporting material.\textsuperscript{83} The reaction kinetics and \textit{in situ} activation of cyclopentane was also investigated over Pt/Al\textsubscript{2}O\textsubscript{3} catalysts. It was determined that the reaction was first order with respect to both oxygen and cyclopentane, but the reaction order and \(E_a\) did not appear to change when the Pt dispersion was varied. Cyclopentane oxidation is proposed to proceed \textit{via} a surface redox mechanism, with the dissociative adsorption of oxygen considered to be the rate-determining step.\textsuperscript{213} The catalytic activity and adsorption properties of copper-containing pentasilts with Si : Al mole ratios of 20 and 40 have also been investigated for the oxidation of \textit{iso}-pentane.\textsuperscript{214} The catalysts were prepared \textit{via} ion exchange, mechanical mixing, and impregnation methods and were all found to exhibit a high catalytic activity. The activity of these materials was attributed to reducible Cu\textsuperscript{2+} cations, located in square planar co-ordinations in zeolite.

The catalytic oxidation of cyclohexane has also been reported over a number of different
catalysts such as CeO$_2$, Co$_3$O$_4$, MnO$_x$, and Pd supported catalysts.\textsuperscript{215-218} With the Pd supported catalysts, the observed TOF was once again determined to be dependent on the dispersion of the supported Pd nanoparticles.\textsuperscript{217}

3.2. Unsaturated alkenes and alkynes

In addition to alkanes, alkenes make up a large proportion of the VOCs emitted industrially each year. Many of the commonly emitted alkenes have detrimental effects on both the environment and human health. Propene in particular, is recognized as highly polluting compound because of its high photochemical ozone creativity potential (POCP).\textsuperscript{12,219} Given that both ethylene and propene make up such a large proportion of the alkene VOCs emitted each year, the catalytic oxidation of these compounds has been extensively studied over the last decade.\textsuperscript{220-240}

3.2.1. Ethylene

Ethylene is extensively used as a solvent in the production of varnishes, synthetic resins, adhesives, and printing ink due to its low toxicity, good solubility and volatility.\textsuperscript{241} There are numerous examples of mixed metal oxide catalysts used for the total oxidation of ethylene in the literature. Chen \textit{et al.}\textsuperscript{242} pointed out that a mesoporous Cu-Mn oxide catalyst could catalyze the oxidation of ethylene at temperatures as low as 200 °C. Following on from this, Njagi \textit{et al.}\textsuperscript{225} synthesized a mesoporous Cu-Mn oxide catalyst by a redox methodology, which was determined to be highly active for this reaction; complete ethylene oxidation (1.0 vol.\%) was achieved at 200 °C (weight hourly space velocity (WHSV) of 35,000 mL·g$^{-1}$·h$^{-1}$). The incorporation of Cu into this oxide material was found to further enhance the catalytic activity, which was ascribed to increased reducibility of the material and enhanced lattice oxygen mobility. Additional work conducted by Piumetti \textit{et al.}\textsuperscript{243} compared the performance of three mesoporous Mn oxide catalysts (Mn$_2$O$_3$, Mn$_3$O$_4$, and Mn$_x$O$_y$) for this reaction, which were prepared by a solution combustion method. Of the catalysts tested, the Mn$_3$O$_4$ catalyst displayed the highest catalytic activity; ethylene was completely oxidized to CO$_2$ and water at 260 °C (GHSV of 29,100 h$^{-1}$).

In recent times, mesoporous carbon materials have amassed a lot of interest in heterogenous catalysis due to their high surface area, large pore volume, controllable surface properties, and good chemical stability.\textsuperscript{244,245} In a recent report by Li \textit{et al.},\textsuperscript{222} a series of Co catalysts supported on mesoporous carbon spheres, with varied Co weight loadings, were synthesized by an isometric
impregnation method and tested for this reaction. The most active catalyst contained a cobalt loading of 30 wt.% and fully converted 1000 ppm of C2H4 at temperatures as low as 185 °C with a total flow rate of 100 cm³·min⁻¹ (E_a = 79.2 kJ·mol⁻¹).

There are also numerous reports on the use of NMSCs for this reaction. Isaifan and Baranova investigated how the nature of the support (Y₂O₃-ZrO₂, Sm₂O₃-CeO₂, carbon, and γ-Al₂O₃) influenced the activity of supported Pt nanoparticles in this reaction (Fig. 5i). Of the catalysts tested in this study, the Pt/Carbon catalyst was determined to be the most active. A subsequent study was conducted by the same group, which investigated how the Pt particle size influenced the catalytic activity of the Pt/Carbon catalyst under fuel-lean conditions. It was determined that the performance of the Pt/Carbon catalyst is strongly dependent on the Pt nanoparticle size. Smaller Pt nanoparticles were determined to provide the most active catalysts and a Pt/C catalyst with a mean particle size distribution of 1.5 nm (+/- 0.5 nm) exhibited full ethylene conversion at approximately 100 °C (WHSV of 12,000 mL·g⁻¹·h⁻¹) (Fig 5ii and iii).

The emission of ethylene from fruit and vegetables can lead to a reduced shelf lifetimes as it enhances the rate of ripening. This causes huge economic issues in the agricultural industry as the emission of ethylene in this way has been estimated to cause substantial postharvest food losses (as high as 10-80%) and as such, has provided addition motives for the development of processes to alleviate this impact. Given that these food products are typically stored at temperatures between 0-25 °C, it is important that processes are developed which can efficiently remove ethylene at these mild conditions. This is an exceptionally challenging venture, as the high energy C-C σ bond in ethylene is difficult to activate and break at low temperatures (≤ 25 °C). Previous works have indicated that well dispersed Au nanoparticles supported on metal oxides are highly active for a range of different total oxidation reactions. The efficiency of supported Au nanoparticles for low-temperature oxidation reactions is reported to be dependent on a variety of factors including the Au particle size, the properties of support, and their preparation and heat treatment conditions.

Li et al. investigated the effect of different supports (Fe₂O₃, Co₃O₄, TiO₂, and ZnO) for Au nanoparticles on this reaction at low temperatures. Of the catalysts tested, the Au/Co₃O₄ catalyst exhibited the highest activity; an ethylene conversion of 7.4% was observed at 25 °C and full conversion was observed at 160 °C with a gas flow rate of 33.4 mL·min⁻¹ (Fig. 5iv).
study investigated how the Co$_3$O$_4$ morphology affected the catalytic activity of Au/Co$_3$O$_4$ catalysts. Au supported on mesoporous Co$_3$O$_4$ was determined to be highly active and ethylene conversions of up to 76% were observed at 0 °C with a gas flow rate of 60 mL·min$^{-1}$. HRTEM indicated that the excellent low temperature activity of this catalyst was attributed to a high proportion of exposed {110} facets present in the mesoporous Co$_3$O$_4$ material (Fig. 5v). A subsequent study further probed the relationship between the activity and morphology of Au/Co$_3$O$_4$ catalysts. Co$_3$O$_4$ nanorods, polyhedral, and cubes were synthesized and immobilized with Au. The resulting catalysts exhibited ethylene conversions of 94%, 86%, and 27% respectively, at 0 °C (WHSV of 9000 mL·g$^{-1}$·h$^{-1}$). HRTEM images indicated that the Co$_3$O$_4$ polyhedra and cubes predominantly consisted of exposed {011} and {001} planes respectively, whereas the Co$_3$O$_4$ rods predominantly consisted of exposed {110} facets.

Supported Pt and Ag catalysts have also displayed potential for this reaction. Jiang et al. reported that Pt nanoparticles supported on mesoporous silica (MCM-41) can fully oxidize ethylene at 0 °C. A series of Ag catalysts supported on microporous zeolites (ZSM-5, Beta, Y, and Mordenite) were prepared by Yang et al. and tested for the oxidation of 100 ppm of ethylene at 25 °C. The nature of the zeolitic framework and water content of the gas feed were proposed to have a substantial influence on the stability of the catalysts. The catalysts tested displayed excellent activities and exhibited full oxidation to CO$_2$ and water under these conditions. The stability of the catalysts was proposed to be proportional to the quantity of available Brønsted acid sites. Some deactivation was observed with the Ag/zeolite catalysts, which was attributed to the disappearance of BAS during the reaction. A subsequent study compared a series of noble metal catalysts (Au, Ag, Pt, and Pd) supported on ZSM-5 for low temperature ethylene oxidation at 25 °C. Of the catalysts tested, the Pt/ZSM-5 catalyst was determined to be the most active. It was determined that fluorination of the ZSM-5 material prior to immobilization with Pt led to a further enhancement in the catalytic performance due to an increase in the Brønsted acidity of the support, which enhanced the adsorption and activation of the ethylene compounds. The fluorination step was also credited with enhancing the lifetime of the catalyst which was attributed to increasing the inhibition of the BAS to water.

### 3.2.2. Propene
The catalytic oxidation of propene has been investigated in detail in recent years. This is predominantly due to its abundant production or application in numerous industries. Propene has high POCP and is a primary contributor to photochemical smog, and therefore has substantial environmental impacts. Some examples of catalytic systems reported in the literature are displayed in Table 1.

Table 1 List of some representative catalysts for propene oxidation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant composition</th>
<th>Space velocity /Flow rate</th>
<th>$T_{90}$ (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%Co/ZrO$_2$</td>
<td>0.6% C$_3$H$_6$, Air balance</td>
<td>100 mL·min$^{-1}$</td>
<td>&lt; 210</td>
<td>129</td>
</tr>
<tr>
<td>30%CoO$_4$-70%CeO$_2$</td>
<td>1000 ppm C$_3$H$_6$, 9% O$_2$, He balance</td>
<td>36,000 mL·g$^{-1}$·h$^{-1}$</td>
<td>225</td>
<td>223</td>
</tr>
<tr>
<td>2%Pt/BaO/Al$_2$O$_3$</td>
<td>800 ppm C$_3$H$_6$, 2% O$_2$, N$_2$ balance</td>
<td>1000 mL·min$^{-1}$</td>
<td>225</td>
<td>228</td>
</tr>
<tr>
<td>1%Pt/Al$_2$O$_3$</td>
<td>600 ppm C$_3$H$_6$, 1% O$_2$, He balance</td>
<td>50,000 h$^{-1}$</td>
<td>&lt; 180</td>
<td>227</td>
</tr>
<tr>
<td>1%Pt/Al-PILC$^b$</td>
<td>0.5% C$_3$H$_6$, 10% O$_2$, He balance</td>
<td>2000 h$^{-1}$</td>
<td>250</td>
<td>271</td>
</tr>
<tr>
<td>0.5%Pd/CsFAU</td>
<td>6000 ppm C$_3$H$_6$, Air balance</td>
<td>100 mL·min$^{-1}$</td>
<td>199</td>
<td>32</td>
</tr>
<tr>
<td>0.8%Pd/TiO$_2$</td>
<td>1000 ppm C$_3$H$_6$, 9% O$_2$, Air balance</td>
<td>35,000 h$^{-1}$</td>
<td>162</td>
<td>266</td>
</tr>
<tr>
<td>3.07%Au/Ce$<em>{0.3}$Ti$</em>{0.7}$O$_2$</td>
<td>6000 ppm C$_3$H$_6$, Air balance</td>
<td>100 mL·min$^{-1}$</td>
<td>260</td>
<td>231</td>
</tr>
<tr>
<td>1%Au/ CeO$_2$</td>
<td>1200 ppm C$_3$H$_6$, 9% O$_2$, He balance</td>
<td>150 mL·min$^{-1}$</td>
<td>&lt; 200</td>
<td>232</td>
</tr>
<tr>
<td>4%Au/ Ce$<em>{0.3}$Ti$</em>{0.7}$O$_2$</td>
<td>6000 ppm C$_3$H$_6$, Air balance</td>
<td>150 mL·min$^{-1}$</td>
<td>270</td>
<td>233</td>
</tr>
<tr>
<td>5%Au/ CeO$_x$-Al$_2$O$_3$</td>
<td>0.4% C$_3$H$_6$, 3.6% O$_2$, He balance</td>
<td>30 mL·min$^{-1}$</td>
<td>220</td>
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</tr>
<tr>
<td>1%Au/TiO$_2$</td>
<td>1000 ppm C$_3$H$_6$, 9% O$_2$, He balance</td>
<td>35,000 h$^{-1}$</td>
<td>&lt; 275</td>
<td>277</td>
</tr>
<tr>
<td>3.7%Au/ CeO$_2$</td>
<td>6000 ppm C$_3$H$_6$, Air balance</td>
<td>100 mL·min$^{-1}$</td>
<td>&lt; 200</td>
<td>280</td>
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<tr>
<td>0.5%Pd-1%Au/TiO$_2$</td>
<td>1000 ppm C$_3$H$_6$, Air balance</td>
<td>100 mL·min$^{-1}$</td>
<td>&lt; 225</td>
<td>239</td>
</tr>
<tr>
<td>3%Au-3%Ir/TiO$_2$</td>
<td>1200 ppm C$_3$H$_6$, 9% O$_2$, He balance</td>
<td>7800 h$^{-1}$</td>
<td>&lt; 200</td>
<td>240</td>
</tr>
</tbody>
</table>

*a Catalyst with Pt dispersion of 0.81; $^b$ Al-PILC: Al-pillared montmorillonite; $^c$ Ce$_{0.3}$Ti$_{0.7}$O$_2$ support was calcined at 400 °C. $^d$ Catalyst was firstly activated in a H$_2$ stream; $^e$ Urea as the precipitant agent; $^f$ Prepared by the deposition-precipitation method.

As with many of the other VOC discussed previously, numerous studies have investigated the use of TMOs as a mean of catalytically oxidizing propylene. Among these, Co-based catalysts are widely acknowledged as being the more active. It is known that doping TMO with CeO$_2$ leads to
modifications of materials the redox properties, which can enhance the oxygen mobility and consequently, improve the catalytic activity.\textsuperscript{256} For this reason, Liotta \textit{et al.}\textsuperscript{223} prepared a series of Co$_3$O$_4$-CeO$_2$ catalysts \textit{via} a co-precipitation method, with differing ratios of Co$_3$O$_4$ and CeO$_2$ and tested them for this reaction. Of the catalysts tested, a Co$_3$O$_4$ (30%)-CeO$_2$ (70%) catalyst displayed the highest activity, exhibiting a full propene conversion at 250 °C (WHSV of 36,000 mL·g$^{-1}$·h$^{-1}$). The high performance of this catalyst was ascribed to the well-dispersed Co$_3$O$_4$ particles on the surface of CeO$_2$. Previous work has indicated that the dispersion of a metal phase over an oxide support can be controlled by the introduction of chelating ligand, such as ethylenediamine.\textsuperscript{259} Mixed metal oxides containing Co oxide and ZrO$_2$ or Al$_2$O$_3$ have also been prepared and tested for the oxidation of propene. Of these two catalytic systems, the Co-Al oxide catalyst exhibited the highest activity which was attributed to the enhanced reducibility of the Co species when combined with Al$_2$O$_3$.\textsuperscript{260} The poor activity of the Co-Zr oxide system was on account of weak interactions between the two composite materials, leading to poorer Co oxide dispersion on the surface of ZrO$_2$. Wyrwalski \textit{et al.}\textsuperscript{129} determined that the interaction between Co oxide and ZrO$_2$ could be enhanced by introducing ethylenediamine into the Co(NO$_3$)$_2$ solution during the catalyst synthesis. This was found to increase the dispersion of Co oxide and ultimately, increased the performance of the catalyst in the oxidation reaction. Despite this, Deloume and co-workers\textsuperscript{261} believed that the partial substitution of Zr into the Mn sites of a La-Mn perovskite had a detrimental effect on the catalytic performance for this reaction since ZrO$_2$ increasing the quantity of chemisorbed oxygen species on perovskite surface. Single-phase cobalt-manganese spinel oxides (CMO) have also been investigated as catalysts for this reaction. Of the perovskite materials tested, a Co$_{2.35}$Mn$_{0.65}$O$_4$ perovskite displayed the highest activity, but only displayed similar activity to that observed with pure Co$_3$O$_4$ (Fig. 6i).\textsuperscript{262}

Noble metal (Pd, Pt, and Au in particular) supported catalysts have also been extensively studied for this reaction. As discussed previously, it is well-known that the nanoparticle support plays an important role in the activity and stability of supported noble metal nanoparticles in these types of reactions. The performance of Pd supported catalysts in catalytic oxidation is strongly dependent on the acid-base property of the support and the metal-support interaction.\textsuperscript{263-265} The catalytic performance of Pd/Al$_2$O$_3$, Pd/CeO$_2$, and Pd/TiO$_2$ in this reaction were investigated by Giroir-Fendler and co-workers.\textsuperscript{266} Of the catalysts tested, Pd/TiO$_2$ exhibited the highest activity,
while Pd/CeO$_2$ displayed the poorest activity. The poor performance of the Pd/CeO$_2$ catalyst was related to the CeO$_2$ stabilizing PdO species. The promotional effect of CeO$_2$ on a series of Pd catalysts supported on Al$_2$O$_3$ was however demonstrated in a separate study.\textsuperscript{267}

Zeolites are often been adopted as supports for Pd nanoparticles in the oxidation of VOCS.\textsuperscript{32,268} In one such study, a series of BEA and FAU zeolites were exchanged with different alkali metal cations (Na$^+$ and Cs$^+$), immobilized with Pd and tested for this reaction. The incorporation of different cations in the zeolitic framework led to a decrease in the surface area and micropore volume of Pd/BEA and Pd/FAU materials. The observed activity in this reaction was determined to be heavily dependent on the type of zeolite used and on the nature of the alkali metal cation exchanged. The activity of the Pd catalysts immobilized on FAU zeolite exhibited the following trend; Pd/CsFAU > Pd/ NaFAU > Pd/HFAU. Interestingly, the opposite trend was observed with the BEA supported catalysts. These trends in activity were linked to the influence of the electronegativity of the cation on the Pd dispersion, PdO reducibility, and adsorption energy of propene.\textsuperscript{32}

As discussed previously, in noble metal supported systems, the activity of catalysts are significantly affected by the dispersion of the active metal component. The effect of Pt dispersion on Al$_2$O$_3$-supported catalysts for this reaction has been reported.\textsuperscript{269,270} Haneda \textit{et al.}\textsuperscript{227} reported that the TOF for this reaction over Pt/Al$_2$O$_3$ catalysts increased proportionally with Pt dispersion (Fig. 6ii). Similar results were also observed by Korili and co-workers,\textsuperscript{271} who synthesized a series of Pt and Pd catalysts supported on pillared-clay materials. Interestingly, the activity of Pt supported catalysts in the total oxidation of hydrocarbons is reported to also be affected their surface acidity or basicity.\textsuperscript{272-274} The acidity/basicity of the catalyst was also determined to have an effect on this reaction, as Wan \textit{et al.}\textsuperscript{228} determined that an enhancement in activity was observed upon the doping of BaO onto Pt/Al$_2$O$_3$. Interestingly however, sulfation of a Pt/Al$_2$O$_3$ catalyst was determined to result in the deactivation of Pt/Al$_2$O$_3$, which is contradictory to the results obtained by Burch \textit{et al.}\textsuperscript{275} and Skoglundh \textit{et al.}\textsuperscript{276} in this reaction over sulfonated Pt/Al$_2$O$_3$. Wan \textit{et al.}\textsuperscript{228} proposed that the enhanced activity exhibited by the Pt/BaO/Al$_2$O$_3$ catalyst in this reaction was ascribed to weakened propene adsorption, the formation of a reactive enolic intermediate species and a reduced barrier for the oxidation of intermediate CO species. This is evidenced by the fact that the strong adsorption of propene and CO poisoning are
established to be principle deactivation pathways for the deactivation of Pt/\(\text{SO}_4^2-/\text{Al}_2\text{O}_3\) catalysts in total oxidation reactions.

Au supported catalysts have been widely investigated for application in propene oxidation reactions.\(^{277-279}\) Of these, Au/CeO\(_2\) is considered to be one of the most active catalysts for this reaction and can provide a full conversion to CO\(_2\) at temperatures below 200 °C (GHSV of 35,000 h\(^{-1}\)).\(^{279}\) This is however, heavily dependent on the Au loadings and pretreatment conditions used. The catalytic activity of Au/CeO\(_2\), Au/TiO\(_2\), Au/Al\(_2\)O\(_3\) and Au/CeO\(_2\)-Al\(_2\)O\(_3\) was investigated for this reaction by Giroir-Fendler and co-workers.\(^{279}\) It was proposed that the point of zero charge (PZC) of the support has a dramatic influence on the quantity Au deposited. For example, an oxide with a lower PZC would typically lead to higher Au loadings. As with the other VOC discussed previously, the activity of Au supported catalysts for this reaction is strongly dependent on the Au-support interaction, which ultimately effects the Au particle size and dispersion.

The influence of the supported noble metal (Au, Ag and Cu) and synthesis method (wet impregnation (IMP) and DP) on CeO\(_2\)-supported catalysts was recently investigated for this reaction.\(^{280}\) Of the catalysts tested, the highest activity was exhibited by a Au/CeO\(_2\) catalyst prepared by DP (temperature for 90% conversion of propene (\(T_{90}\)) at around 180 °C (Fig. 6iii)). The enhanced activity of this catalyst was related to the existence of a higher proportion of oxidized Au species. Independently, Lamallem et al.\(^{233}\) also determined that an Au/Ce-Ti-O catalyst prepared by DP was far more active than the corresponding catalyst prepared by IMP. The pre-treatment of Au supported catalysts and incorporation of alkali and transition metal additives can also have significant effect on the activity of Au supported catalysts in this reaction.\(^{231,232,234,235,238}\) Lakshmanan et al.\(^{232}\) reported that calcined Au/CeO\(_2\), Au/Al\(_2\)O\(_3\) and Au/xCeO\(_2\)-Al\(_2\)O\(_3\) samples were less active than corresponding materials which instead, underwent a reductive pre-treatment step. This was once again owing to a particle size effect; the reduced catalysts were found to consist of a larger proportion of small Au nanoparticles. Gluhoi et al.\(^{234}\) investigated the effect of doping different oxides onto a Au/Al\(_2\)O\(_3\) catalyst on propene oxidation activity. A promotional effect was observed from doping the catalyst with different alkali metal oxides (MO\(_x\), M = Li, Rb, Mg and Ba), which was in relation to a decrease in the size of active Au\(^0\) particles and an increase in their relative stability (Fig. 6iv). Despite this, an interfacial effect resulting from the doping of TMO is considered to be more influential than the Au particle size.
The doping of TMO (M = Ce, Mn, Co and Fe) can act as both structural and chemical promoters, stabilizing Au particles against sintering and providing an increase in available active oxygen. A significant enhancement in the catalytic activity of a Au/TiO$_2$ catalyst for this reaction was also observed by the addition of Ir. In this case, the increased activity was on account of a synergistic effect resulting from the formation of Ir-Au bimetallic alloy. The presence of Au was found to hinder the re-oxidation of iridium in the bimetallic nanoparticles upon exposure to air and under typical reaction conditions used for this reaction. This ultimately induced a preservation of the catalytic activity upon subsequent catalytic cycles.

3.2.3. Butene and acetylene

There are only a few reports focusing on the catalytic oxidation of butene and acetylene in the literature. Przekop and Kirszensztejn investigated the use of Pt/B$_2$O$_3$/Al$_2$O$_3$ catalysts for the oxidation of 1-butene. Different ratios of the metal oxide components were assessed and a catalyst with B : Al of 0.3 exhibited the highest activity, which was considerably higher than the activity exhibited by the corresponding Pt/Al$_2$O$_3$ catalyst. The enhanced activity was ascribed to the increased acidic character of the support, which was promoted by the presence of boron oxide. The catalytic oxidation of acetylene was investigated over Co$_3$O$_4$-coated natural clay/commercial cordierite honeycomb monoliths. The complete oxidation of acetylene was achieved at temperatures below 360 °C (GHSV of 50,000 h$^{-1}$). The higher catalytic activity of Co$_3$O$_4$ supported on the clay monolith was highly dependent on the synergetic effects induced by the chemical composition of the clay surface.

3.3. Aromatic hydrocarbons

Aromatic hydrocarbons represent another type of VOCs commonly emitted industrially. Aromatic solvents are used in vast quantities in various paints, thinners, gums, adhesives, lacquers and printing inks. Of the aromatic VOCs; benzene, toluene, ethylbenzene, and xylene (BTEX) contribute to the majority of the total industrial emissions. Aromatic compounds are considered to pose considerable environmental hazards and are often toxic and/or carcinogenic. The catalytic oxidation of BTEX has extensively studied over the past two decades and a large quantity of noble metal (Pd, Pt, Au and Ag) supported catalysts, transitional metal (Co, Mn, Cu, Cr, Ni and Ti) oxides catalysts, rare earth oxide catalysts, perovskite- and spinel-
based oxides catalysts and hydrotalcite derived catalysts have been developed and investigated (Tables 2 and 3).

### 3.3.1. Benzene

As with many of the other VOCs discussed, Co$_3$O$_4$ is also a very attractive material for the oxidation of benzene, which is predominantly due to the high oxygen mobility it exhibits. Mu et al. reported that the doping of CeO$_2$ onto a Co/SBA-15 catalyst by a hydrothermal method, could reduce the catalysts activity in this reaction. This reduction in activity was owing to pore blocking and a reduction in the reducibility of Co$_3$O$_4$ to Co$^0$ (Fig. 7i). In contrary, Zuo et al. reported that the addition of CeO$_2$ facilitated the reduction of Co oxide at lower temperatures, which greatly enhanced the catalytic activity of CoCe/SBA-16 in this reaction (Fig. 7ii). Mesoporous Co$_3$O$_4$-CeO$_2$ catalysts with different Co : Ce ratios have been prepared by Hao and co-workers via a nanocasting methodology, invoking the use of two-(2D) and three-dimensional (3D) hard templates; SBA-15 and KIT-6, respectively. It was determined that the 2D Co$_3$O$_4$-CeO$_2$ catalyst exhibited a lower catalytic activity than the corresponding 3D catalyst. An optimum Co : Ce ratio of 16 was subsequently determined with the 3D Co$_3$O$_4$-CeO$_2$ catalyst. In these materials, the activity of these materials for this reaction was linked to the proportion of hydroxyl and oxygenated species; higher surface oxygen species resulted in a better catalytic activity.

A series of CoMnAlO$_x$ oxide catalysts, obtained from the calcinations of LDH precursors were prepared and tested for this reaction. Of these, a CoMn$_2$AlO$_x$ material exhibited the highest activity; a 90% conversion of benzene was observed at about 238 ºC with a space velocity of 60,000 mL·g$^{-1}$·h$^{-1}$ ($E_a = 65.77$ kJ·mol$^{-1}$). The catalytic oxidation of benzene over CoAlO$_x$ and CoCuAlO$_x$ mixed oxides has also been reported in recent studies, but were found to be less active than the above-mentioned CoMnAlO$_x$ catalysts. Ding et al. found that the preparation method (constant pH precipitation, decreasing pH precipitation and urea homogeneous precipitation) could have a significant on the activity exhibited by CoAlO$_x$ mixed oxides. It was determined that the material prepared by the decreasing pH precipitation method exhibited the highest activity because the enhancement in the reducibility of Co$^{3+}$ species in the Co(Co,Al)$_2$O$_4$ spinels. Li et al. found that the addition of Cu to CoAlO$_x$ materials could further
improve the reducibility of Co oxide component of the material, which resulted in an increase in the activity. A number of reports have also investigated the use Co-containing perovskites as catalysts for this reaction, but in general, far higher temperatures are required (> 400 °C) in order to achieve full benzene conversions.

The catalytic oxidation of benzene and toluene has been studied over a series of Mn oxide catalysts (Mn$_3$O$_4$, Mn$_2$O$_3$ and MnO$_2$). Of these catalysts tested, the Mn$_3$O$_4$ material exhibited the highest catalytic activity. The addition of either K, Ca or Mg to the Mn$_3$O$_4$ material further enhanced the catalytic activity. This improvement in performance was attributed to an increase quantity of surface defects and surface bound hydroxyl species. Tang et al. reported that MnO$_x$ derived from the calcination of a Mn oxalate precursor, was also highly active for the oxidation of a number of benzene, toluene, and xylene compounds. The performance of this material was dependent on a number of factors including, its large surface area, small pore sizes, excellent low-temperature reducibility, rich lattice oxygen stores and appropriate distribution of Mn oxidation states. The morphology of MnO$_x$ materials should also be considered, as it can also influence catalytic performance in this reaction. Hou et al. synthesized and tested a series of birnessite-type Mn oxides and determined that nanoflower morphologies exhibited much higher activities than the corresponding nanowire and nanosheet oxides materials (Fig. 7iii). Three types of MnO$_2$ microspheres (i.e., hierarchical hollow β-MnO$_2$ microspheres, hierarchical double-walled hollow β/α-MnO$_2$ microspheres and hierarchical hollow α-MnO$_2$ microspheres) were prepared by Chen and co-workers. The authors stated that hierarchical hollow α-MnO$_2$ microspheres exhibited the highest catalytic ability ($T_{90} = 320$ °C; WHSV of 60,000 mL·g$^{-1}$·h$^{-1}$). Following this, the researchers from the same group developed a more efficient hierarchical sea-urchin-shaped MnO$_2$ microsphere material, which could decompose 90% of benzene at about 218 °C (WHSV of 60,000 mL·g$^{-1}$·h$^{-1}$).

Numerous studies have investigated how the doping of additional elements (e.g., Ti, Cu, Co, Ni and Ce) onto MnO$_x$ affects the catalytic performance in this reaction. Tang et al. investigated the effect of supporting Co$_3$O$_4$ nanoparticles on a series of 1D MnO$_2$ materials (α-MnO$_2$ nanowires, α-MnO$_2$ nanorods and α-MnO$_2$ microrods). Notable increases in performance were observed when Co$_3$O$_4$ was immobilized on each of the MnO$_2$ materials. The
highest performance was exhibited by Co$_3$O$_4$ supported on MnO$_2$ nanowires; a 90% conversion of benzene was observed at 247 °C (WHSV of 120,000 mL·g$^{-1}$·h$^{-1}$). Following this, a series of Co-Mn oxide catalysts with different nanostructures were synthesized by Wang et al. (Fig. 8), who determined that a Co doped nanocubic MnO$_2$ material exhibited the highest catalytic performance for this reaction. An alternative study, investigated the effect of doping Ti onto a δ-MnO$_2$ material and was also determined to be highly active for this reaction. The promotional effect of copper on the catalytic activity of MnO$_x$-CeO$_2$ has also been investigated. The incorporation of copper was found to significantly improve the catalytic activity of the mixed metal oxide and complete conversion of benzene was achieved at 250 °C. The enhancement in performance was related to the presence of Cu significantly increased the generation of surface defect oxygen species, which increased the number of adsorption sites for benzene. Chen and co-workers pointed out that a 90% conversion of benzene at 232 °C with a WHSV of 12,000 mL·g$^{-1}$·h$^{-1}$ ($E_a = 45.2$ kJ·mol$^{-1}$) could be achieved over a hierarchically porous Mn$_2$Ni$_1$ mixed oxide. The low activation barrier was owing to a synergetic effect between Mn and Ni in the mixed oxide spinel, which increased the quantity of surface-adsorbed oxygen species and an enhanced low-temperature reducibility. MnCoO$_x$ and MnCeO$_x$ composites have also been investigated by Hou et al., but higher reaction temperatures were required (> 260 °C) over these materials in order achieve the full oxidation of benzene.

CuO-CeO$_2$ materials have previously been reported to be highly active as catalysts for a range of different oxidation reactions. In some cases, these materials have even shown comparable activity to NMSCs in total oxidation reactions. Zhou et al. reported that the preparation method used for the synthesis of Cu-Ce mixed oxides had a significant influence on their catalytic performance in BTEX oxidation reactions. CuCeO$_x$ catalysts prepared by a hard-templating approach was determined to possess a higher activity than corresponding catalysts prepared by co-precipitation and other complex methods. The higher activity of this material was relied on its higher porosity and surface area, both of which were important catalytic traits in total oxidation reactions. This was further evidenced by Wang and co-workers, who determined that the reducibility of CuO-CeO$_2$ catalysts was strongly influenced by the total surface area of the material; high surface area materials typically displayed better reducibility. Following this, high surface area mesoporous Cu-Mn oxide (ca. 221 m$^2$·g$^{-1}$) were synthesized by a nanocasting
The nanocasted catalyst displayed an excellent benzene oxidation activity; 90% conversion was obtained at 234 °C over a Cu$_{0.6}$MnO$_x$ sample (WHSV of 60,000 mL·g$^{-1}$·h$^{-1}$), which was 131 °C lower than that observed over the corresponding CuMnO$_x$ catalyst prepared by a co-precipitation method. The catalyst pre-treatment conditions are an important factor to consider when using Cu based catalysts. This was clearly demonstrated by Yang et al. who determined that the reduction of a Cu/SBA-15 in H$_2$ prior to its application, dramatically influenced its activity for this reaction.

It is widely acknowledged that Pd supported catalysts are the most efficient catalysts for aromatic hydrocarbon oxidation. Numerous reports have investigated the use of Al$_2$O$_3$, molecular sieves, and pillared clays as supports for Pd nanoparticles in the catalytic oxidation of benzene. The addition of Pd to a Co/Al$_2$O$_3$ catalyst was determined to increase the quantity of active oxygen species on the surface of the catalyst and enhance the dispersion of Co$_3$O$_4$ on the surface of Al$_2$O$_3$. A novel route for the preparation of porous catalysts was explored by Li et al. for application in total oxidation reactions. For this, a porous Co$_3$O$_4$-supported Pd catalyst was synthesized by the pyrolysis of a metal organic framework (MOF). While the catalytic system proposed in this study only exhibited a modest oxidative activity (temperature for 100% conversion of benzene ($T_{100}$) = 350 °C; WHSV = 60,000 mL·g$^{-1}$·h$^{-1}$)), it provided a novel approach for obtaining high surface area porous materials, which would undoubtedly act as a foundation for future investigation.

The use of mesoporous siliceous materials such as SBA-15, MCM-48, MCM-41 and HMS as catalysts for the oxidation of benzene has also attracted a lot of attentions in recent times. These materials are considered to be desirable in the field because of their controllable pore size, high surface area and surface-rich silanol group content. The performance and oxidation mechanism of five Pd containing catalysts supported on a range of molecular sieves (Beta, ZSM-5, SBA-15, MCM-48 and MCM-41) was investigated by Hao and co-workers for the oxidation of benzene, toluene and ethyl acetate. The activity of these catalysts followed the order; Pd/Beta > Pd/ZSM-5 > Pd/SBA-15 > Pd/MCM-48 > Pd/MCM-41 for all of the substrates examined. While the Pd/Beta catalyst exhibited the highest initial activity, it deactivated quickly due to the in situ formation of coke. In contrary, the Pd/ZSM-5 and Pd/SBA-15 catalyst exhibited a much higher a degree of stability; maintaining their initial activities for 72 h. In addition to
this, Li et al. synthesized a series of Pd/SBA-15 catalysts by traditional aqueous impregnation and grafting methods. It was determined that the catalyst prepared via the grafting method was far more active for this reaction, exhibited complete conversion of benzene below 190 °C (GHSV of 100,000 h⁻¹). A subsequent study by Mu et al. determined that the doping of a lanthanide (e.g., La, Ce and Nd) to this material could further enhance the catalytic activity of the Pd/SBA-15 catalyst. More recently, another study also reported that doping Ni onto a Pd/SBA-15 could also increase its catalytic activity for this reaction. Pd nanoparticles have also exhibited a high catalytic activity when supported on an Al-HMS mesoporous sieve; exhibited a full benzene conversion at 200 °C (GHSV of 100,000 h⁻¹). ZSM-5/MCM-48 micro/mesoporous composite materials, which combine the advantages of mesoporous molecular sieves (large surface area and pore diameter) and zeolites (strong intrinsic acidity and high hydrothermal stability) were used as supports for Pd nanoparticles by Xu and co-workers. The Pd/ZSM-5/MCM-48 composite catalysts exhibited a much higher activity for this reaction than that observed over the corresponding Pd/ZSM-5 and Pd/MCM-48 catalysts.

Pillared interlayered clays (PILCs) are typically highly porous materials and have high total surface areas. For this reason, they are of great interest to be used as supports for noble metal nanoparticles in total oxidation reactions. A series of Zr-, Ce- and Al-pillared laponite clays (Al-Lap, Ce-Lap and Zr-Lap) were synthesized and used as supports for Pd nanoparticles. The catalysts were subsequently tested for the total oxidation of benzene. The results indicated that the Pd/PILC catalysts were far more active than a corresponding Pd/Al₂O₃ catalyst. It was determined that the most active of these catalysts; Pd/Zr-Lap, could completely oxidize benzene at 210 °C (GHSV of 20,000 h⁻¹). An additional study investigated the use of Al-PILC as a support for Ce and Pd in this reaction. It was postulated that the optimized structure of the supports strengthen the interaction between CeO₂ and Al-PILC, which in turn, improved the dispersion of Pd on material surface.

A number of studies have also investigated the use of Au nanoparticles for the oxidation of benzene. CeO₂ has been investigated as a support for Au nanoparticles. The activity of this material was predominantly associated with the high surface area of CeO₂ support and the ability of the surface Au species to dissociate O₂. Another study, investigated the performance of supported Au nanoparticles on three different metal oxides (ZnO, Al₂O₃ and MgO) and tested...
each of the catalysts for their performance as catalysts in the oxidation of benzene, toluene and xylene. The Au/ZnO catalyst exhibited the highest activity, which was due to a strong interaction between Au and ZnO, originating from the similar lattice parameters of the Au \{111\} and ZnO \{101\} planes. Andreeva et al. reported on this reaction over Au/V_2O_5 supported on either TiO_2 or ZrO_2 and a synergistic effect between Au and vanadia was observed. Both catalysts displayed promising activities, but the Au/V_2O_5/TiO_2 catalyst was determined to be the most active. It was proposed that oxygen activation occurred on the surface of the Au nanoparticles and benzene activation occurs on the V oxide surface. Subsequent studies by the same group further investigated the role of V and Mo on Au/CeO_2 and Au/CeO_2-Al_2O_3 catalysts and provided further evidence for the role of Au in these systems. Additional Au/V_2O_5 catalysts supported on mesoporous TiO_2 or ZrO_2 was also investigated by Su and co-workers. It was determined that the Au/V_2O_5/meso-ZrO_2 catalyst exhibited a higher activity than the corresponding catalyst supported on TiO_2, which was ascribed to stronger interactions between the Au nanoparticles and the oxide surface. Recently, mono-(Au, Pd) and bimetallic Au-Pd catalysts supported on Fe-modified CeO_2 for this reaction was investigated by Karakirova and co-workers. The bimetallic AuPd catalyst exhibited the highest activity due to its better reducibility (Fig. 7iv).

There are fewer examples of Pt- and Ag- supported systems in the literature. Li et al. reported that the complete oxidation of benzene over Pt-based catalysts could be achieved at 150 °C (WHSV of 60,000 mL·g^{-1}·h^{-1}), which was notably lower than the previous works utilizing Au and Pd systems. They suggested that the GO support had a significant impact on the high activity observed, proposing that this too had a role in the activation of oxygen. In addition to this, characterization by X-ray photoelectron spectroscopy (XPS) and Raman confirmed that electron transfer between the GO and Pt was also responsible for the high catalytic performance of this material. Pt nanoparticles supported on mesoporous CeO_2 (1 wt.% Pt/CeO_2-MM) and CeO_2 nanocubes (1 wt.% Pt/CeO_2-NC) were investigated by Zhao and co-workers. The TOF of the 1 wt.% Pt/CeO_2-MM catalyst at 140 °C was approximately nine times higher than observed over the 1.0 wt.% Pt/CeO_2-NC. Theoretical and experimental investigation revealed that the partial confinement of Pt nanoparticles in the mesoporous of the mesoporous CeO_2 led to a significant enhancement in the activity of the surface lattice oxygen at the interface between Pt nanoparticles and CeO_2 (Fig. 7v).
In general, Ag supported nanoparticles are reported to be much less active than corresponding Pd-, Au- and Pt-based catalysts for this reaction. Heinrichs and co-workers\textsuperscript{373} investigated the catalytic oxidation of benzene over Ag/SiO\textsubscript{2} xerogel, Cu/SiO\textsubscript{2} xerogel and Pd/SiO\textsubscript{2} xerogel and determined that the temperature for 50% conversion of benzene ($T_{50}$) over the Pd/SiO\textsubscript{2} xerogel was 170 °C (Fig. 7vi). The corresponding $T_{50}$ over the Ag/SiO\textsubscript{2} xerogel was much higher; 260 °C. A synergistic effect between Ag and Mn supported on mesoporous zirconia nanofibers was reported recently by Einaga and co-workers.\textsuperscript{293} Despite the enhancement observed from the addition of Ag, full conversion of benzene was only observed at 498 °C with a flow rate of 200 mL·min\textsuperscript{-1}, which is much higher than many other examples discussed.

**Table 2** Summary of reported active catalysts for benzene low-temperature oxidation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant composition</th>
<th>Space velocity /Flow rate</th>
<th>$T_{90}$ (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO\textsubscript{2}</td>
<td>1000 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>60,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}</td>
<td>209</td>
<td>329</td>
</tr>
<tr>
<td>OL\textsubscript{1b}</td>
<td>2000 mg·m\textsuperscript{-3} C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>48,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}</td>
<td>232</td>
<td>332</td>
</tr>
<tr>
<td>Ti/δ-MnO\textsubscript{2}</td>
<td>1000 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>60,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}</td>
<td>250</td>
<td>333</td>
</tr>
<tr>
<td>MnO\textsubscript{2}@Co\textsubscript{3}O\textsubscript{4}</td>
<td>1000 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>120,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}</td>
<td>247</td>
<td>324</td>
</tr>
<tr>
<td>Porous Mn\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{x}</td>
<td>1000 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>120,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}</td>
<td>237</td>
<td>337</td>
</tr>
<tr>
<td>Mn\textsubscript{0.66}Ni\textsubscript{0.33}O\textsubscript{x}</td>
<td>1000 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>120,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}</td>
<td>249</td>
<td>314</td>
</tr>
<tr>
<td>2.54%Cu/MnO\textsubscript{4}-CeO\textsubscript{2}</td>
<td>200 ppm C\textsubscript{6}H\textsubscript{6}, He balance</td>
<td>30,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}</td>
<td>&lt; 240</td>
<td>335</td>
</tr>
<tr>
<td>Meso-CuO-CeO\textsubscript{2}</td>
<td>1000 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>96,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}</td>
<td>250</td>
<td>350</td>
</tr>
<tr>
<td>Meso-Cu\textsubscript{0.6}MnO\textsubscript{x}</td>
<td>1000 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>60,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}</td>
<td>234</td>
<td>351</td>
</tr>
<tr>
<td>Co\textsubscript{4.75}Cu\textsubscript{0.25}Al</td>
<td>516 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>36,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}</td>
<td>246</td>
<td>312</td>
</tr>
<tr>
<td>CoMn\textsubscript{2}AlO\textsubscript{d}</td>
<td>100 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>60,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}</td>
<td>208</td>
<td>325</td>
</tr>
<tr>
<td>Pd/ZSM-5/MCM-48\textsuperscript{e}</td>
<td>1500 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>32,000 h\textsuperscript{-1}</td>
<td>204</td>
<td>165</td>
</tr>
<tr>
<td>0.3%Pd/Beta</td>
<td>1500 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>26,000 h\textsuperscript{-1}</td>
<td>225</td>
<td>168</td>
</tr>
<tr>
<td>9%Pd/SBA-15</td>
<td>1050 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>100,000 h\textsuperscript{-1}</td>
<td>180</td>
<td>289</td>
</tr>
<tr>
<td>0.9%Pd/Nd-SBA-15</td>
<td>1000 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>100,000 h\textsuperscript{-1}</td>
<td>219</td>
<td>358</td>
</tr>
<tr>
<td>0.9%Pd/Al-HMS (Si/Al = 100)</td>
<td>1050 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>100,000 h\textsuperscript{-1}</td>
<td>&lt; 200</td>
<td>360</td>
</tr>
<tr>
<td>1.5%Pd/SiO\textsubscript{2} xerogel</td>
<td>2550 ppm C\textsubscript{6}H\textsubscript{6}, Air balance</td>
<td>100 mL·min\textsuperscript{-1}</td>
<td>180</td>
<td>373</td>
</tr>
</tbody>
</table>
3.3.2. Toluene

Toluene is a commonly used solvent in the chemical industry and is a significant contributor to the formation of photochemical smog. The catalytic oxidation of toluene has been investigated over a wide variety of different catalysts including Mn-, Co-, Cu-, Fe-, Pd-, Pt- and Au-containing materials, perovskite-type oxides, and pure CeO₂. Many examples of the catalysts used for the oxidation of toluene and their corresponding performance is documented in Table 3.

Table 3 Survey of literature data on catalytic oxidation of toluene at low temperature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant composition</th>
<th>Space velocity</th>
<th>$T_{90}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3%Pd/Ti-SBA-15</td>
<td>1500 ppm C₆H₆, Air balance</td>
<td>26,000 h⁻¹</td>
<td>205</td>
<td>287</td>
</tr>
<tr>
<td>0.3%Pd/Zr-pillared laponite</td>
<td>1050 ppm C₆H₆, Air balance</td>
<td>20,000 h⁻¹</td>
<td>195</td>
<td>290</td>
</tr>
<tr>
<td>0.2%Pd/6%Ce/Al-PILC</td>
<td>130-160 ppm C₆H₆, Air balance</td>
<td>20,000 h⁻¹</td>
<td>240</td>
<td>353</td>
</tr>
<tr>
<td>0.2%Pd/10%Co-0.8%Ce/Al₂O₃</td>
<td>1000 ppm C₆H₆, Air balance</td>
<td>20,000 h⁻¹</td>
<td>190</td>
<td>356</td>
</tr>
<tr>
<td>0.53%Pd/CoO₄</td>
<td>100 ppm C₆H₆, Air balance</td>
<td>60,000 mL·g⁻¹·h⁻¹</td>
<td>221</td>
<td>357</td>
</tr>
<tr>
<td>1%Pt-1%rGO/Al₂O₃</td>
<td>100 ppm C₆H₆, Air balance</td>
<td>60,000 mL·g⁻¹·h⁻¹</td>
<td>140</td>
<td>291</td>
</tr>
<tr>
<td>1%Pt/CoO₂-MM</td>
<td>2000 mg·m⁻³ C₆H₆, Air balance</td>
<td>48,000 mL·g⁻¹·h⁻¹</td>
<td>153</td>
<td>372</td>
</tr>
<tr>
<td>1%Au/CoO₂/Hydroxyapatite</td>
<td>120 ppm C₆H₆, Air balance</td>
<td>30,000 h⁻¹</td>
<td>&lt; 230</td>
<td>292</td>
</tr>
<tr>
<td>3%Au₄%MoCe</td>
<td>4200 mg·m⁻³ C₆H₆, Air balance</td>
<td>4000 h⁻¹</td>
<td>&lt; 160</td>
<td>309</td>
</tr>
<tr>
<td>6.5%Au/meso-CoO₄</td>
<td>1000 ppm C₆H₆, Air balance</td>
<td>20,000 mL·g⁻¹·h⁻¹</td>
<td>189</td>
<td>361</td>
</tr>
<tr>
<td>2.3%Au₂%VCeAl(1:1)</td>
<td>3800 mg·m⁻³ C₆H₆, Air balance</td>
<td>4500 h⁻¹</td>
<td>&lt; 200</td>
<td>366</td>
</tr>
<tr>
<td>0.17%Pd-0.3%Pt/FeCe/KL-NY</td>
<td>1000 ppm C₆H₆, Air balance</td>
<td>20,000 h⁻¹</td>
<td>205</td>
<td>354</td>
</tr>
<tr>
<td>1%Pd-3%AuFeCe</td>
<td>4200 mg·m⁻³ C₆H₆, Air balance</td>
<td>4000 h⁻¹</td>
<td>&lt; 150</td>
<td>368</td>
</tr>
</tbody>
</table>

a Synthesized via an oxalate route; b Octahedral layered birnessite-type manganese oxide with nanoflower morphology; c Heated in autoclave at 140 °C; d Catalyst alcined at 550 °C; e Catalyst with Si : Al molar ratio of 40; f Catalyst with Si : Ti molar ratio of 20; g Al-PILC: alumina pillared clays; h CoO₄ with porous polyhedron morphology and calcined at 350 °C; i rGO: reduced graphene oxide; j CeO₂-MM: microsized mesoporous CeO₂; k KL-NY: porous kaolin/NaY composite; l Prepared by the impregnation method.
<table>
<thead>
<tr>
<th>Material</th>
<th>Gas Composition</th>
<th>Reaction Time</th>
<th>Turnover Rate (h&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Reaction Rate (mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14.8%NiO/NCNTs&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>20,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>240</td>
<td>463</td>
</tr>
<tr>
<td>LaNiO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>5000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 10% O&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt; balance</td>
<td>19,200 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>250</td>
<td>397</td>
</tr>
<tr>
<td>MnO&lt;sub&gt;b&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>15,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>230</td>
<td>376</td>
</tr>
<tr>
<td>Mn&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>10000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>30,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>250</td>
<td>400</td>
</tr>
<tr>
<td>Mn&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt; nanorod</td>
<td>10000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>30,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>225</td>
<td>402</td>
</tr>
<tr>
<td>α-MnO&lt;sub&gt;2&lt;/sub&gt; nanowire</td>
<td>4000 mg·m&lt;sup&gt;-3&lt;/sup&gt; C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>10,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>237</td>
<td>406</td>
</tr>
<tr>
<td>γ-MnO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 20% O&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt; balance</td>
<td>120,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>252</td>
<td>407</td>
</tr>
<tr>
<td>Mn&lt;sub&gt;0.85&lt;/sub&gt;Co&lt;sub&gt;0.15&lt;/sub&gt;</td>
<td>10000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>32,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>&lt; 220</td>
<td>412</td>
</tr>
<tr>
<td>Meso-TiMnCeO&lt;sub&gt;5&lt;/sub&gt;&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 6% O&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt; balance</td>
<td>15,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>180</td>
<td>420</td>
</tr>
<tr>
<td>15%LaMnO&lt;sub&gt;3&lt;/sub&gt;/Y&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;-ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 20% O&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt; balance</td>
<td>100 mL·min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>247</td>
<td>311</td>
</tr>
<tr>
<td>sc-LaMnO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;f&lt;/sup&gt;</td>
<td>500 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 10% O&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt; balance</td>
<td>19,200 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>225</td>
<td>468</td>
</tr>
<tr>
<td>LaMnO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;g&lt;/sup&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 20% O&lt;sub&gt;2&lt;/sub&gt;, He balance</td>
<td>15,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>213</td>
<td>474</td>
</tr>
<tr>
<td>Hollow spherical LaCoO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>20,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>237</td>
<td>469</td>
</tr>
<tr>
<td>La&lt;sub&gt;0.6&lt;/sub&gt;Sn&lt;sub&gt;0.4&lt;/sub&gt;CoO&lt;sub&gt;3.6&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>20,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>240</td>
<td>472</td>
</tr>
<tr>
<td>15%La/CoO&lt;sub&gt;2&lt;/sub&gt;-nanopolyhedra</td>
<td>300 mg·m&lt;sup&gt;-3&lt;/sup&gt; C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>12,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>240</td>
<td>482</td>
</tr>
<tr>
<td>8%CuO/Co&lt;sub&gt;0.8&lt;/sub&gt;Zr&lt;sub&gt;0.2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>4400 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>55 mL·min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>225</td>
<td>447</td>
</tr>
<tr>
<td>20%CuMnCe/ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.5% C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>24,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>&lt; 220</td>
<td>453</td>
</tr>
<tr>
<td>15%CoO&lt;sub&gt;2&lt;/sub&gt;/CNTs&lt;sup&gt;b&lt;/sup&gt;</td>
<td>850 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 20% O&lt;sub&gt;2&lt;/sub&gt;, He balance</td>
<td>60 mL·min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>&lt; 240</td>
<td>432</td>
</tr>
<tr>
<td>5%CoO/meso-SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 20% O&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt; balance</td>
<td>20,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>230</td>
<td>435</td>
</tr>
<tr>
<td>8%CoO&lt;sub&gt;2&lt;/sub&gt;/3DOM-La&lt;sub&gt;0.6&lt;/sub&gt;Sn&lt;sub&gt;0.4&lt;/sub&gt;CoO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>20,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>227</td>
<td>436</td>
</tr>
<tr>
<td>Cake-like Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>20,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>240</td>
<td>462</td>
</tr>
<tr>
<td>0.5%Pd/plateletlike SBA-15</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>32,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>192</td>
<td>484</td>
</tr>
<tr>
<td>0.5%Pd/ZSM-5/KIT-6</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>32,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>203</td>
<td>486</td>
</tr>
<tr>
<td>0.5%Pd/Bimodal mesosilica</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>350 mL·min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>228</td>
<td>487</td>
</tr>
<tr>
<td>1%Pd/ZSM-5 (Si/Al = 25)</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>32,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>212</td>
<td>490</td>
</tr>
<tr>
<td>3.35%Pd-CoAlO</td>
<td>2000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>60,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>226</td>
<td>489</td>
</tr>
<tr>
<td>0.5%Pd/macro/meso-TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>13,200 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>&lt; 200</td>
<td>494</td>
</tr>
<tr>
<td>1%Pd/Co&lt;sub&gt;3&lt;/sub&gt;AlO</td>
<td>0.08% C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>30,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>230</td>
<td>495</td>
</tr>
<tr>
<td>3.26%Pd-CoAlO-Al&lt;sub&gt;1&lt;/sub&gt;</td>
<td>2000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>60,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>207</td>
<td>496</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Conditions</td>
<td>Activity</td>
<td>Selectivity</td>
<td></td>
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<td>----------</td>
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<td></td>
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<tr>
<td>0.5%Pt/Meso-NaZSM-5&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>60,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>185 499</td>
<td></td>
</tr>
<tr>
<td>0.97%Pt(1.9 nm)/ZSM-5</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>60,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>&lt; 150 505</td>
<td></td>
</tr>
<tr>
<td>0.94%Pt/MCM-41</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>100 mL·min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>170 500</td>
<td></td>
</tr>
<tr>
<td>2%Pt/MCM-41&lt;sup&gt;1&lt;/sup&gt;</td>
<td>4340 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>15,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>125 394</td>
<td></td>
</tr>
<tr>
<td>1%Pt/Beta-H&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>60,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>190 497</td>
<td></td>
</tr>
<tr>
<td>1.15%Pt/KBeta-SDSm</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>60,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>&lt; 150 509</td>
<td></td>
</tr>
<tr>
<td>0.2%Pt/CeO&lt;sub&gt;2&lt;/sub&gt;-nanorod</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>48,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>150 501</td>
<td></td>
</tr>
<tr>
<td>0.27%Pt/26.9%CeO&lt;sub&gt;2&lt;/sub&gt;-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;n&lt;/sup&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>20,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>198 502</td>
<td></td>
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<tr>
<td>9%Pt/16%CZB/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;o&lt;/sup&gt;</td>
<td>900 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>8000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>&lt; 100 504</td>
<td></td>
</tr>
<tr>
<td>0.2%Pt-0.1Pd%/MCM-41</td>
<td>5000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 10% O&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt; balance</td>
<td>10,000 h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>175 530</td>
<td></td>
</tr>
<tr>
<td>0.25%Pd-0.25%Pt/SiO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;p&lt;/sup&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>60,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>&lt; 155 26</td>
<td></td>
</tr>
<tr>
<td>6.4%Au/3DOM-La&lt;sub&gt;0.1&lt;/sub&gt;Sr&lt;sub&gt;0.4&lt;/sub&gt;MnO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 20% O&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt; balance</td>
<td>20,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>170 518</td>
<td></td>
</tr>
<tr>
<td>0.13%Ag/MnO&lt;sub&gt;2&lt;/sub&gt; nanowires</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 20% O&lt;sub&gt;2&lt;/sub&gt;, Ar balance</td>
<td>20,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>215 513</td>
<td></td>
</tr>
<tr>
<td>1.95%AuPd&lt;sub&gt;2&lt;/sub&gt;/meso-C&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 20% O&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt; balance</td>
<td>20,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>165 525</td>
<td></td>
</tr>
<tr>
<td>0.9%AuPd&lt;sub&gt;2&lt;/sub&gt;/Ce&lt;sub&gt;0.6&lt;/sub&gt;Zr&lt;sub&gt;0.3&lt;/sub&gt;Y&lt;sub&gt;0.1&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 20% O&lt;sub&gt;2&lt;/sub&gt;, N&lt;sub&gt;2&lt;/sub&gt; balance</td>
<td>20,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>218 523</td>
<td></td>
</tr>
<tr>
<td>3.8%AuPd&lt;sub&gt;1&lt;/sub&gt;/3DOM-Mn&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>40,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>162 529</td>
<td></td>
</tr>
<tr>
<td>3%Pt&lt;sub&gt;1&lt;/sub&gt;1%Au&lt;sub&gt;2&lt;/sub&gt;/ZnO/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.8 mol% C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, Air balance</td>
<td>40 mL·min&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>&lt; 200 528</td>
<td></td>
</tr>
<tr>
<td>1%Ru/Co&lt;sub&gt;3&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;-MOF (ZIF-67)</td>
<td>1000 ppm C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;, 20% O&lt;sub&gt;2&lt;/sub&gt;, Ar balance</td>
<td>60,000 mL·g&lt;sup&gt;-1&lt;/sup&gt;·h&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>238 510</td>
<td></td>
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</tbody>
</table>

<sup>a</sup> NCNTs: Nitrogen-doped carbon nanotubes; <sup>b</sup> Catalyst prepared by an alkali-promoted redox precipitation strategy; <sup>c</sup> Acetic acid (HAc) : Mn molar ratio of 3 in precursor solution; <sup>d</sup> Obtained by removing La cations from three-dimensional ordered macroporous LaMnO<sub>3</sub> perovskites; <sup>e</sup> Molar ratios of Mn : Ti and Ce : Ti were 0.4 and 0.05, respectively; <sup>f</sup> Prepared in a supercritical water (sc-H<sub>2</sub>O) reaction environment; <sup>g</sup> Prepared by the citrate sol-gel method; <sup>h</sup> Precursor ultrasonic at 120 °C; <sup>i</sup> Synthesized by the co-precipitation method; <sup>j</sup> In situ growth of 2D CoAl-LDHs on the AlOOH microsphere; <sup>k</sup> Catalyst was reduced in a H<sub>2</sub> stream before use; <sup>l</sup> MCM-41 synthesis in the presence of fluoride anions; <sup>m</sup> Directly synthesized by Beta zeolite seed; <sup>n</sup> CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> support with three-dimensionally ordered macro-/mesoporous (3DOM) structure; <sup>o</sup> CZB: Ce<sub>0.65</sub>Zr<sub>0.15</sub>Bi<sub>0.26</sub>O<sub>1.9</sub>; <sup>p</sup> Oleic acid (OA) was introduced into the aqueous solution of metal salts.

Mn oxide based catalysts are some of the most widely investigated in this area and have displayed a lot of potential. The desirable performance of these materials is attributed to their high...
oxygen storage capacity and redox properties. The size and morphology of these materials often have a dramatic effect on their catalytic performance in total oxidation reactions. The relationship between activity and morphology of Mn oxide catalysts was demonstrated by Li et al. who prepared Mn$_3$O$_4$ nanorods by a DP method. It was determined that the size of the Mn$_3$O$_4$ rods had a dramatic influence on their activity in the oxidation of toluene. Manganese oxide polyhedra with hollow and solid morphologies were synthesized by Ye and co-workers using a convenient hydrothermal route without any surfactants or templates; the hollow polyhedral manganese oxide showed much higher catalytic activity toward toluene oxidation compared with that of the solid one due to the cavity nature, large quantity of active oxygen, and high manganese oxidation state of hollow MnO$_x$. MnO$_2$ has also demonstrated a lot of potential as a catalyst for this reaction, owing to its multivalent nature and nonstoichiometric composition. Cheng et al. also determined that the morphology of this material had a substantial effect on the catalytic activity; 1D $\alpha$-MnO$_2$ nanowires exhibited a notably higher activity for this reaction than a commercial MnO$_2$ material. Si et al. further evidenced this and reported that a $\gamma$-MnO$_2$ material with a 3D macroporous and mesoporous structure had a very high toluene oxidation activity ($T_{90} = 252$ °C; WHSV of 120,000 mL·g$^{-1}$·h$^{-1}$).

The activity of Mn oxides can be further enhanced by the doping of an additional component to form mixed oxides. Ye and co-workers determined that Mn-Ce mixed oxide nanorods, consisting of a high Mn content, displayed an excellent catalytic activity and high stability for this reaction (Fig. 9i). This was associated with the formation of an intimately mixed Mn-Ce oxide phase giving rise to more Mn$^{4+}$ species and oxygen vacancies. Delimaris and Ioannides subsequently determined that MnO$_x$-CeO$_2$ catalysts prepared by a urea oxidation method also displayed promising potential as catalysts for this reaction; complete toluene conversion was achieved at 260 °C (GHSV of 50,000 h$^{-1}$). Li et al. investigated this reaction over a series of Mn-containing mixed oxides, and determined that a Mn-Zr mixed oxide material, prepared by the reverse microemulsion method, exhibited a higher activity than a corresponding material prepared by co-precipitation.

There are some examples of TiO$_2$ and Al$_2$O$_3$ being adopted as a support to increase the dispersion of MnO$_x$. In addition to this, MnO$_x$ was loaded onto a series of different supports ($\alpha$-Al$_2$O$_3$ and $\gamma$-Al$_2$O$_3$ obtained from Boehmite, commercial $\gamma$-Al$_2$O$_3$, SiO$_2$, TiO$_2$ and ZrO$_2$) and
tested for the catalytic oxidation of toluene.\textsuperscript{419} Of the catalysts tested, a 9.5 wt.% MnO$_2$/α-Al$_2$O$_3$ material exhibited the highest activity; toluene conversion up to 90% was achieved at 289 °C (GHSV of 15,000 h$^{-1}$).

Recently, Li and co-workers\textsuperscript{420} proposed that MnO$_2$ supported on a mesostructured LaMnO$_3$ perovskite was an active catalyst for toluene oxidation, over which toluene could be totally oxidized to CO$_2$ and water at 290 °C (WHHSV of 120,000 mL·g$^{-1}$·h$^{-1}$) (Fig. 9ii). Catalytic oxidation of toluene over MnMgAl or MnCoMgAl mixed oxides obtained by calcination of the corresponding LDH precursors was also reported.\textsuperscript{421,422} Dula \textit{et al.}\textsuperscript{415} confirmed that a MgAlMn mixed oxide material derived from Mn(II) incorporating MgAl-LDH was more active than a corresponding material derived from MnO$^4^-$-intercalated MgAl-LDH. The enhanced performance was related to an increase in the quantity of surface Mn$^{4+}$/Mn$^{3+}$ species, which have important redox properties in total oxidation reactions. It was subsequently determined that the substitution of Mg with Mn (or Co) could lead to an even greater catalytic activity.\textsuperscript{422}

The catalytic oxidation of toluene over porous 1D Co$_3$O$_4$ nanowires and nanorods was studied by Au and co-workers.\textsuperscript{424} These materials exhibited a high catalytic performance for this reaction, which was attributed to their large surface area, high surface oxygen content, and excellent low-temperature reducibility. Ordered mesoporous Co$_3$O$_4$ oxides were also synthesized and investigated by the same group. The highly ordered nature of these materials was considered to be pivotal for the high oxidative activity they exhibited.\textsuperscript{425,426} More recently, 3D hierarchical Co$_3$O$_4$ nanocatalysts with different morphologies and various exposed crystal planes (Fig. 10), were synthesized by Ye and co-workers\textsuperscript{427} via a hydrothermal process. Of the catalysts tested, a hierarchical cube-stacked Co$_3$O$_4$ microspherical material exhibited the highest toluene oxidation activity ascribable to its high surface area, highly defective structure, abundance of surface adsorbed oxygen species, and large proportion of high valence Co ions. Co$_3$O$_4$ supported on montmorillonite consisting of an expanded mesoporous system was also determined to possess a high catalytic activity for this reaction.\textsuperscript{428} It has been reported that the doping of Ce or La onto cobalt oxides can enhance the activity of the parent Co$_3$O$_4$ catalyst.\textsuperscript{429} This enhancement was proposed to be a result of strong interactions between Ce (or La) and Co, leading to an increased dispersion of the active oxide phases.

There are numerous other examples of different support materials been investigated in an
attempt to enhance the activity of CoO\textsubscript{x} phases in the oxidation of toluene. Carbon nanotubes (CNTs) are considered as one of the promising supports ascribed to their good electrical conductivity, mechanical strength, thermal stability and high quantity of surface defects.\textsuperscript{430,431} Jiang and Song\textsuperscript{432} suggested that the surface defect structures in CNTs could not only enhance the ability of Co\textsubscript{3}O\textsubscript{4} to develop reduction/oxidation cycles, but also increased the proportion of the adsorbed oxygen species to the surface lattice oxygen. Interestingly, the CO\textsubscript{2} selectivity was observed to increase proportionally with the quantity of COOH present on the surface of the CNTs. With the best catalyst, the complete conversion of toluene was achieved at 257 °C with a CO\textsubscript{2} selectivity of 100\% (flow rate of 60 mL·min\textsuperscript{-1}), which is much better than with Co\textsubscript{3}O\textsubscript{4}/Beta, Co\textsubscript{3}O\textsubscript{4}/ZSM-5 and Co\textsubscript{3}O\textsubscript{4}/SBA-15.\textsuperscript{432} Mesoporous silicas are commonly used as supports in catalysis as their high surface area and regular pore structure typically facilitates a good dispersion of active metal or metal oxide particles.\textsuperscript{433,434} Lin and Bai\textsuperscript{435} synthesized a series of CoO\textsubscript{x}/SiO\textsubscript{2} spheres with either a hollow or mesoporous structure (CoO\textsubscript{x}/hSiO\textsubscript{2} and CoO\textsubscript{x}/mSiO\textsubscript{2}) and determined that of the two catalysts, the CoO\textsubscript{x}/SiO\textsubscript{2} exhibited the highest activity for this reaction. This was related to a number of factors, including; an increased proportion of Co present in the active phase (Co\textsubscript{3}O\textsubscript{4}), a higher proportion of surface Co\textsuperscript{3+} content and increased reducibility of Co\textsuperscript{3+} at low temperatures. 3D ordered macroporous (3DOM) La\textsubscript{0.6}Sr\textsubscript{0.4}CoO\textsubscript{3} (LSCO)-supported Co\textsubscript{3}O\textsubscript{4} was prepared using an in situ poly(methyl methacrylate)-templating strategy by Au and co-workers.\textsuperscript{436} It was determined that an 8 wt.% Co\textsubscript{3}O\textsubscript{4}/3DOM LSCO material exhibited the best catalytic performance for toluene oxidation; 90 \% toluene was converted at 227 °C (WHSV of 20,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}). The high activity of this material was associated with the high surface oxygen content of this catalyst, the high surface area of the LSCO, good low-temperature reducibility, and strong interactions between Co\textsubscript{3}O\textsubscript{4} and LSCO.

MgAl-based hydrotalcite is an important precursor for obtaining various mixed oxides, which are active for the oxidation of toluene.\textsuperscript{315,316,437} Gennequin et al.\textsuperscript{437} demonstrated that the doping of Co on Mg-Co-Al hydrotalcite catalysts has a beneficial effect on the observed catalytic activity. The reconstruction of the layered structure enhances the interaction between the cobalt species and the support and improves the performance of the catalyst in this reaction.\textsuperscript{438} More recently, the effect of doping Ce into CoMgAlO\textsubscript{x} mixed oxides was investigated by Moreno and co-workers.\textsuperscript{439} The Ce/CoMgAlO\textsubscript{x} catalyst, which utilized [Ce-EDTA] as the Ce precursor,
provides a better toluene conversion activity than a corresponding catalyst prepared by wet impregnation. The enhancement was in relation to improvements in the catalysts redox properties.

Cu-based binary or ternary mixed oxides (e.g., CuMnO₃, CuCeOₓ, CuAlOₓ, CuMnCeOₓ and CuZnMnOₓ)³¹,⁴⁰-⁴⁴ and supported Cu catalysts (Al₂O₃, ZrO₂, CeZrOₓ or molecular sieves as the support) have also been investigated as catalysts for the total oxidation of toluene.³⁸⁴,⁴⁴⁵-⁴⁴⁸ The potential of CuMnO₃ oxide catalysts is well known industrially for total oxidation reactions. Behar et al.³¹³ reported that cubic spinel Cu₁.₅Mn₁.₅O₄ nanoparticles; approximately 10 nm in size, were highly active catalysts for this reaction; complete oxidation reported at 240 °C (flow rate of 100 mL·min⁻¹). Previously, we have reported on the synthesis of mesoporous CuCeOₓ mixed oxides prepared by a self-precipitation approach.⁴⁴⁹ This method of preparation allowed for a large proportion of Cu²⁺ ions to be doped into the mesoporous CeO₂ lattice, which enhanced the proportion of oxygen vacancies at the CuOₓ and CeO₂ interface. Of the catalysts tested, the highest activity was exhibited by a Cu₀.₃Ce₀.₇Oₓ material; 90% toluene was converted 212 °C (GHSV of 36,000 h⁻¹). This was significantly lower than corresponding catalysts prepared by impregnation and thermal oxidation methods (Fig. 9iii). The enhanced performance of these materials was connected with a higher quantity of surface oxygen species and enhanced low-temperature reducibility.⁴⁴⁹ Bialas et al.⁴⁴³ subsequently reported that a CuAl₂O₄ catalyst was more active than its corresponding Co-Al monometallic oxide counterparts.

A series of different transition metal (Cu, Fe, Mn, Cr, Co, Mo and Ni) catalysts supported on Al₂O₃ were prepared and tested for the oxidation of toluene. Of the catalysts tested, Cu/Al₂O₃ catalyst exhibited the best activity. The activity of the other catalysts tested followed the order: Fe/Al₂O₃ > Cr/Al₂O₃ > Mn/Al₂O₃ > Co/Al₂O₃ > Mo/Al₂O₃ > Ni/Al₂O₃.³⁸⁴ This was also evidenced by Nah and co-workers.⁴⁵⁰ CeO₂ doped with metal ions such as Cu, Mn and Co have exhibited promising activity as catalysts for this reaction. The high activity of these catalysts was owing to their large quantities of lattice defects and ion vacancies, which provided major transfer channels for surface oxygen (O²⁻, O') and lattice oxygen (O²⁻).⁴⁵¹ Developing highly active CeO₂ catalysts which exhibit a high thermal stability is a challenge. Chen and co-workers⁴⁴⁵,⁴⁵² developed a Cu-Mn-Ce/ZrO₂ catalyst which possessed both of these attributes. The high thermal stability of this catalyst was attributed to the interaction of ZrO₂ and Cu-Mn-Ce instigated through the heat treatment of the material. A series of CeₓZr₁-xO₂/CuO catalysts have also been
investigated for this reaction. The doping of Zr into CeO$_2$ was observed to promote the dispersion and reducibility of the active copper species. An 8%CuO/Ce$_{0.8}$Zr$_{0.2}$O$_2$ catalyst calcined at 400 °C exhibited the highest activity; full conversion of toluene was achieved at 275 °C (GHSV of 33,000 h$^{-1}$).

In addition to metal oxides, molecular sieves have demonstrated a lot of potential as catalyst supports for Cu-containing catalysts. Popova et al. determined that immobilizing Cr and Cu species on SBA-15 catalysts could provide active catalysts for the total oxidation of toluene. The study indicated that the optimal metal oxide content for these catalysts was 3 and 7 wt.% for Cr and Cu, respectively. The effect of immobilizing both Cu and Mn on a series of different mesoporous and microporous molecular sieves has also been investigated (Cu-Mn/MCM-41, Cu-Mn/β-zeolite, Cu-Mn/ZSM-5 and Cu-Mn/porous silica) for this reaction. Of the catalysts tested, the Cu-Mn/MCM-41 catalyst exhibited the highest catalytic activity due to highly dispersed Cu-Mn mixed oxides phases in the mesoporous structure.

Other transition metal (e.g., V, Ti, Ni, Cr and Fe) supported catalysts have also been investigated for toluene oxidation. It was reported that a Ti/MCM-41 catalyst, obtained by a direct synthesis route, which consisted of a substantial quantity of Ti exhibited a notably higher activity than that of a corresponding catalyst prepared by the wet impregnation technique on TiO$_2$-anatase. Mesoporous nickel oxides with two different morphologies; nanorods and nanocubes, were prepared using a microemulsion strategy and tested for this reaction. The NiO nanorods were determined to possess a better catalytic activity. Another study reported on the synthesis of a cylindrical Cr$_2$O$_3$ material with a rhombohedral structure and determined that this material displayed a promising activity for this reaction (Fig. 9iv). Jiang et al. reported that a NiO supported nitrogen-doped carbon nanotubes (NiO/NCNTs) catalyst exhibited an excellent toluene oxidation activity, which was proposed to a result of its good low-temperature reducibility and proportion surface oxygen. Popova et al. proposed that the doping of small quantities of iron into mesoporous silica (Fe : Si molar ratio of 0.01) enhanced the catalytic activity for this reaction. The increased activity was associated with the formation of stable Fe$^{3+}$ ions in the silica matrix, promoting an Fe$^{3+}$/Fe$^{2+}$ redox cycle.

As discussed previously, perovskite-type oxides have displayed promising potential as catalysts in the total oxidation of various hydrocarbons. Both the external conditions (e.g., preparation
method) and intrinsic factors (e.g., crystal structure, surface area, type of A/B-site cation and number of surface oxygen defect) is known to affect the catalytic performances of perovskite-type oxides. Hosseini et al. determined that a LaMn$_{0.5}$Co$_{0.5}$O$_3$ catalyst was more active than a LaCr$_{0.5}$Co$_{0.5}$O$_3$ and LaCu$_{0.5}$Co$_{0.5}$O$_3$ catalyst for the oxidation of toluene. Deng et al. suggested that the activity of a single-crystalline La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ catalyst was much better than that observed over a corresponding poly-crystalline material as the distinct oxygen nonstoichiometry and single-crystalline structure of the oxide. Rousseau et al. reported that partial substitution of La$^{3+}$ by Sr$^{2+}$ cations could significantly improve the catalytic activity of LaCoO$_3$. A similar study experiment was conducted where Fe was used to substitute in place of the Co. In this case, very little change in the catalytic activity was observed. Zhang et al. determined that the preparation method used could also have a significant influence on catalytic performance of LaMnO$_3$ catalysts in this reaction. A LaMnO$_3$ catalyst prepared by a citrate sol-gel method exhibited a better activity than corresponding materials prepared by glycine oxidation and co-precipitation methods. The material prepared by the citrate method was found to have a higher total surface area and enhanced low temperature reducibility.

In general, perovskite materials typically exhibit low surface areas, which is attributable to the harsh calcination conditions required during their preparation. Given that the activity of total oxidation catalysts is often highly dependent on the materials surface area, it somewhat limits their application in this field. These issues can be avoided to an extent, by targeting the synthesis of porous perovskite materials or by immobilization of these phases onto high surface area supports. Dai and co-workers prepared a series of perovskite oxides with meso- or macroporous structures and tested them for total oxidation of toluene. The porous perovskite materials exhibited significantly higher surface areas and better low temperature reducibilities. These physicochemical enhancements were reflected in the oxidative performance exhibited by the catalysts. A 3D ordered microporous LaMnO$_3$ catalyst achieved a 90% conversion of toluene at 243 °C (GHSV of 20,000 mL·g$^{-1}$·h$^{-1}$). Following this, an additional 3DOM Eu$_{0.6}$Sr$_{0.4}$FeO$_2$ perovskite material was synthesized and used as a support for Co oxide. The synthesized material exhibited a well-defined 3DOM structure, a surface area of 22-31 m$^2$·g$^{-1}$ and fairly well dispersed cobalt oxide nanoparticles; with mean particles determined to be between 7 and 11 nm in size (Fig. 11). Of the catalysts synthesized and tested in this study, the highest toluene oxidation
activity was exhibited by the CoO\textsubscript{x}/3DOM-ESFO catalysts with 3 and 6 wt.% CoO\textsubscript{x} present.\textsuperscript{478}

There are numerous other reports on the use of metal oxides to support perovskite-type materials.\textsuperscript{479,480} In one such study, LaMnO\textsubscript{3} was supported on a range of different oxide materials (Y\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} and TiO\textsubscript{2}) and tested for the oxidation of toluene. The experiments indicated that there was a clear interaction between the LaMnO\textsubscript{3} perovskite phase and both the TiO\textsubscript{2} and Y\textsubscript{2}O\textsubscript{3}-ZrO\textsubscript{2} materials, which affected their oxygen mobility and increased their catalytic performance.\textsuperscript{311} Ce-based oxides are also regularly used as supports for perovskite. A series of CeO\textsubscript{2} materials with different morphologies (rods, cubes and polyhedrons) were synthesized by Wang \textit{et al.}\textsuperscript{481} and utilized as supports for La\textsubscript{0.8}Ce\textsubscript{0.2}MnO\textsubscript{3}. The morphology of the CeO\textsubscript{2} was determined to have a significant effect on the activity of the La\textsubscript{0.8}Ce\textsubscript{0.2}MnO\textsubscript{3} phase. Of the catalysts tested, the La\textsubscript{0.8}Ce\textsubscript{0.2}MnO\textsubscript{3}/CeO\textsubscript{2}-polyhedra exhibited the highest activity; 100 % toluene was converted at 240 °C (GHSV of 12,000 h\textsuperscript{-1}) and the exceptional activity was as a result of the high surface area, high oxygen vacancies and higher proportion of surface oxygen.

Previous reports have indicated that supported Pd catalysts are typically highly active for the catalytic oxidation of toluene. The high performance of these catalysts has been associated to a dual role of the Pd: metallic Pd sites are active for the decomposition of VOCs and PdO provides an additional source of surface oxygen. In addition to this, Liu \textit{et al.}\textsuperscript{482} demonstrated that supported Pd catalysts are often more stable than supported Pt catalysts for this reaction. Porous silica materials, metal oxides and hydrotalcite-derived oxides are typically utilized as the supports for Pd active phase.\textsuperscript{263,483-488} We have previously reported on the use of porous silicas, including microporous zeolites, mesoporous molecular sieves, and micro-/mesoporous composites as supports for Pd nanoparticles. In our investigations, we determined that the ZSM-5 is a stable and coke-resistant support for Pd supported catalysts in this reaction and that the acidity of the support can influence the Pd dispersion, redox potential and CO\textsubscript{2} desorption of the catalyst.\textsuperscript{168,485} Of the catalyst we tested, a Pd/ZSM-5 catalyst (Si : Al molar ratio of 25) exhibited the highest activity for this reaction; a 100 % toluene conversion was observed at 220 °C (GHSV of 32,000 h\textsuperscript{-1}).\textsuperscript{489} Compared to microporous zeolites, mesoporous materials (such as SBA-15, MCM-48 and KIT-6) possess a narrower pore size distribution, higher specific surface areas, and have considerably lower rates of Pd aggregation compared to other supported materials.\textsuperscript{490,491} We determined that the preparation of these material using a grafting method, leaded to the formation of exceptionally
well dispersed Pd nanoparticles on SBA-15. It was also determined that the solvent used in the preparation (ethanol, water, tetrahydrofuran, dimethyl sulphoxide and N,N-dimethylformamide) had a significant effect on the resultant Pd dispersion; the highest Pd dispersion was observed when N,N-dimethylformamide was used.492 Other synthesis procedures have reported using a “two-solvent” approach, which combines the use of a hydrophobic solvent, such as hexane, with a hydrophilic solvent such as water.483,484 We prepared a Pd/SBA-15 catalyst using this approach and determined that acid sites on the catalyst further assisted with the Pd dispersion. Furthermore, the Pd/SBA-15 catalyst exhibited a high thermal stability and a high tolerance to moisture. The most active catalyst prepared in this way was observed to fully convert toluene at 210 °C (GHSV of 32,000 h⁻¹).33 A silica material consisting of both micro- and mesoporous was also used as a support for Pd nanoparticles and was active for the catalytic oxidation of toluene oxidation; 100 % conversion of toluene was achieved at temperatures around 200 °C (flow rate of 350 mL·min⁻¹), which was notably lower than exhibited by catalysts consisting of a single porous system.167,486

Metal oxides and hydrotalcite-derived mixed oxides have also been probed as supports for Pd nanoparticles in toluene oxidation.493-495 Okumura et al.263 investigated how the acid-base properties of a metal oxide support affected the catalytic performance of Pd nanoparticles. It was determined that the electronic interaction between the Pd nanoparticles and the supports had a significant impact on the activity of the catalyst; the highest activity reported in this study was exhibited by a 0.5 wt.% Pd/ZrO₂ catalyst (Fig. 12i), which was on account of an increased proportion of metallic Pd sites on the catalysts surface.263 A series of high surface area hierarchical macro-mesoporous ZrO₂, TiO₂, and ZrO₂-TiO₂ materials have also been synthesized and utilized as supports for Pd nanoparticles in this reaction. All of the catalysts tested exhibited a high oxidation activity due to the in situ aerobic oxidation of Pd⁰ species to form very active [Pd²⁺O²⁻] species, which upon oxidation of the substrate, revert back to Pd⁰.30,493 Previously, we have synthesized a series of Pd/Co₃AlOₓ catalysts, which were derived from hydrotalcite-type precursors (HTLcs) and tested them for this reaction. The Pd nanoparticles were immobilized using a variety of different techniques, including: impregnation, wet ion exchange and co-precipitation. All of the synthesized catalysts were exhibited higher oxidation activities than the comparative benchmark material; a Pd/Co₃AlOₓ catalyst prepared via a thermal oxidation
protocol (Fig. 12ii). The enhanced activity of these catalysts was predominantly associated with the materials high surface areas, small Co$_3$AlO$_x$ crystallite size and the presence of highly dispersed PdO particles.

In general, supported Pt catalysts can oxidize toluene at lower temperatures than corresponding Pd supported catalysts. As with Pt, there are lots of examples of different Pt-supported systems which have been developed and tested for the oxidation of toluene. These include; zeolites and molecular sieves (ZSM-5, Beta and MCM-41), CeO$_2$ and Al$_2$O$_3$.

Once again, the dispersion of Pt on the surface of the supporting material significantly influences the activity of catalyst. One investigation reported on the preparation of a series of Pt/ZSM-5 catalysts, with different sized Pt nanoparticles ranging from 1.3 to 2.3 nm. Of the catalyst tested, a Pt/ZSM-5 catalyst with a mean particle size of 1.9 nm exhibited the highest activity for this reaction; 98 % conversion of toluene was achieved at 155 °C (GHSV of 60,000 mL·g$^{-1}$·h$^{-1}$). The high activity exhibited was attributed to a trade off between the Pt dispersion and proportion of metallic Pt present on the surface (Fig. 12iii).

More recently, a series of mesoporous zeolitic materials were synthesized, in an attempt to combine the advantageous properties of zeolites and mesoporous materials. Pt was subsequently immobilized onto the surface of these materials and tested for this reaction. Pt nanoparticles supported on a mesoporous Beta zeolite exhibited the highest activity, which was owing to a high Pt dispersion and desirable Pt$^0$/Pt$^{2+}$ ratio. When this catalyst was compared to a corresponding catalyst prepared on a conventional Beta zeolite, it was much more active and exhibited a much higher stability.

Chen et al. reported that doping of alkali metal cations (e.g., Na$^+$, K$^+$ and Cs$^+$) onto mesoporous ZSM-5 could enhance the proportion of Pt$^0$ on the surface of a mesoporous Pt supported ZSM-5 catalyst and improve the catalytic activity for this reaction. A subsequent report from the same group also confirmed that a similar effect could be observed from doping K onto a Beta zeolite supported Pt catalyst.

The properties of support material such as the morphology, composition and acid-base site composition can also significantly affect the activity of NMSC. CeO$_2$ nanorods, nanoparticles and nanocubes, which predominantly consist of {110}, {111}, and {100} facets respectively, were utilized as supports for Pt nanoparticles and tested of the oxidation of toluene. The experiments indicated that catalytic activity was highly influenced by the morphology of the support. The highest activity was exhibited by Pt/CeO$_2$ nanorods, which was connected with this
material exhibiting the highest proportion of surface oxygen vacancies and could be reduced at the lowest temperature.\textsuperscript{500}

A highly efficient catalyst with a formula of 7 wt.% Pt/16 wt.% Ce\textsubscript{0.64}Zr\textsubscript{0.15}Bi\textsubscript{0.21}O\textsubscript{1.895}/\gamma-Al\textsubscript{2}O\textsubscript{3} was developed by Imanaka and co-workers.\textsuperscript{503} Over this catalyst, 100% toluene could be converted at temperatures as low as 120 °C (GHSV of 8000 h\textsuperscript{-1}). Experimental results indicated that the Ce\textsubscript{0.64}Zr\textsubscript{0.15}Bi\textsubscript{0.21}O\textsubscript{1.90}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst could readily provide oxygen from the bulk of the material to the surface at temperatures below 100 °C. The mobility of oxygen from the bulk of the material was determined to increase further upon the addition of Pd.\textsuperscript{503} The use of hydrophobic supports can in some instances be desirable, as they can assist with the expulsion of water vapor from the catalyst surface during oxidation reactions. The presence of water vapor in waste streams is common and has been shown to dramatically hinder the catalytic performance and stability of supported metal catalysts. One example of such a system was reported by Wu and Chang,\textsuperscript{513} who synthesized a Pt/styrene divinylbenzene copolymer (SDB) catalyst, which completely oxidized toluene at only 150 °C (GHSV of 21,000 h\textsuperscript{-1}).

Compared with Pt and Pd, Au is much less expensive. Many factors including; the nature of the support, Au particle size and electronic state, the method of immobilizing Au and pretreatment condition can affect the activity of Au supported catalysts in oxidation reactions.\textsuperscript{514,515} In one study, the effect of the support material on the activity of Au nanoparticles for the oxidation of toluene was investigated. For this, Au was immobilized onto a series of different oxides (La\textsubscript{2}O\textsubscript{3}, MgO, NiO and Fe\textsubscript{2}O\textsubscript{3}) and tested, which revealed that the Au particle size and reducibility are primary factors influencing the catalytic activity. Interestingly, the Au oxidation state was determined to have very little effect on the catalytic performance.\textsuperscript{516} Au supported on materials with 3DOM structures have been extensively investigated by Dai and co-workers\textsuperscript{517-520} for this reaction. They determined that 3DOM perovskite oxides materials such as LaSrMnO\textsubscript{x} and LaSrCoO\textsubscript{x} are good supports for Au nanoparticles in this reaction due to their higher surface area and 3D porestructure.\textsuperscript{518} A series of Au/3DOM-Mn\textsubscript{2}O\textsubscript{3} catalysts with varied Au loadings of between 1.9 and 7.5 wt.% were also investigated by the same group. Of the catalysts tested, a 5.8 wt.% Au/3DOM-Mn\textsubscript{2}O\textsubscript{3} catalyst exhibited the highest activity; a toluene conversion of 90% was achieved at 244 °C (WHSV of 40,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}).\textsuperscript{519} Previous studies have confirmed that the addition of TMO to NMSC can considerably improve the materials catalytic activity in the
oxidation of VOCs. This was also shown to be the case with the oxidation of toluene, as Yang et al.\textsuperscript{520} reported that a Au/MnO\textsubscript{x}/3DOM-SiO\textsubscript{2} catalyst was significantly more active than corresponding Au/3DOM-SiO\textsubscript{2} and MnO\textsubscript{x}/3DOM-SiO\textsubscript{2} catalysts.

The incorporation of a secondary metal to produce bimetallic NMSC has been shown to be particularly attractive, as it can significantly enhance the reaction activity, selectivity and stability.\textsuperscript{521-526} This was shown to be the case in the oxidation of toluene by Hosseini et al.,\textsuperscript{525} who synthesized a series of bimetallic Pd/Au/TiO\textsubscript{2}-ZrO\textsubscript{2} catalysts and tested them for this reaction. A Pd : Au molar ratio of 4 exhibited the highest toluene oxidation activity. In a separate study, a series of Pt-Au/ZnO/Al\textsubscript{2}O\textsubscript{3} bimetallic catalysts were synthesized and tested for this reaction. Changing the molar ratio of Pt : Au in bimetallic catalysts supported on ZnO/Al\textsubscript{2}O\textsubscript{3} was determined to have a significant effect on mean particle size. Increasing the Au content resulted in an increase in the mean particle size observed and as a result, the highest activity was observed with the bimetallic catalyst containing the least Au content.\textsuperscript{527}

A series of 3DOM-Mn\textsubscript{2}O\textsubscript{3} supported AuPd catalysts with varying Au : Pd ratios were prepared by Au and co-workers.\textsuperscript{528} Each of the catalysts were determined to have fairly uniformly dispersed AuPd nanoparticles, which exhibited mean particle sizes of 2-4 nm (Fig. 13). A 3.8 wt.% Au1.92 wt.%Pd/3DOM-Mn\textsubscript{2}O\textsubscript{3} catalyst exhibited the highest activity for the oxidation of toluene. The excellent catalytic activity, thermal stability, and high resistance to water of this material was ascribed to its efficiency to associatively adsorb O\textsubscript{2} and the strong interaction between the nanoparticles and 3DOM-Mn\textsubscript{2}O\textsubscript{3} support.\textsuperscript{528}

Silica materials have also been investigated as a support for bimetallic nanoparticles in total oxidation of toluene.\textsuperscript{529,530} Wang et al.\textsuperscript{26} recently reported that a Pd-Pt/SiO\textsubscript{2} catalyst was highly active for this reaction and reported that this catalyst exhibited very little coking during the reaction. It was determined that the activity of this catalyst could be markedly improved by adding oleic acid into the metal salt solution during the catalyst preparation, which was linked to an increase in the proportion of metallic Pd in the resultant catalyst (Fig. 12iv).

3.3.3. Xylene

Xylene is another VOC, commonly used in number of industrial fields despite the fact that the World Health Organization considers it to be chronically toxic and carcinogenic.\textsuperscript{530,531} For this
reason, the catalytic oxidation of xylene has been widely studied over a number of Mn-, Ce- and Pd-supported catalysts. Examples of Au and Pt supported catalysts for the oxidation of xylene are somewhat limited by comparison.

CeO$_2$ catalysts with different morphologies (nanoparticles, nanocubes and nanorods) were synthesized and tested as catalysts for the oxidation of $o$-xylene. Of the catalysts tested, the CeO$_2$ nanorods exhibited both the highest activity and stability. The high performance of these materials was attributed to the increased proportion of (111) and (100) facets they exhibit. These facets were considered to increase the quantity of oxygen vacancies in the material, which are known to be pivotal in the activation of O$_2$.

As discussed previously, MnO$_x$ materials have also been extensively investigated as catalysts for this reaction. Wu et al. reported that an $\alpha$-MnO$_2$ catalyst has much higher $o$-xylene oxidation activity (temperature for 100% conversion of $o$-xylene = 210 °C; flow rate of 50 mL-min$^{-1}$) than that of mixture of $\alpha$-MnO$_2$ and $\delta$-MnO$_2$. The higher activity was attributed the quasi-quadrangular conformation of the of $\alpha$-MnO$_2$ material. For this reason, an additional study was conducted by the same group, who investigated how the preparation method of MnO$_x$ catalysts effected there activity in this reaction. It was determined that utilization of a redox-precipitation method produced a porous hierarchically structured microcrystalline $\alpha$-MnO$_2$ material, which consisted of almost 100% Mn$^{4+}$ ion on its surface. In contrary, a more conventional precipitation method was determined to produce a mixture of MnO$_2$ and Mn$_3$O$_4$ phases, which exhibited a closely packed spherical morphology and contained only 31% Mn$^{4+}$ ion on its surface. The $\alpha$-MnO$_2$ prepared by the redox-precipitation method exhibited a good low-temperature reducibility and converted 100% $o$-xylene into CO$_2$ at 220 °C (GHSV of 8000 h$^{-1}$). Zhou et al. also demonstrated that the chemical composition and structure of MnO$_x$ catalysts are significantly influenced by the preparation method. A MnO$_x$ catalyst prepared by a hard templating method was determined be more active than a corresponding catalyst prepared by a conventional precipitation method.

Pd supported catalyst have been shown to be highly active for the total oxidation of xylene. A series of $\gamma$-Al$_2$O$_3$ supported noble metal (Pd, Pt, Au, Ag and Rh) catalysts were prepared by He and co-workers via a wet impregnation method and tested for the oxidation of $o$-xylene. Of the catalysts tested, the Pd/$\gamma$-Al$_2$O$_3$ catalyst exhibited the highest activity. Kim and
Shim\textsuperscript{85} proposed that subjecting a Pd/\(\gamma\)-Al\(_2\)O\(_3\) catalyst to a H\(_2\) pre-treatment could further increase its catalytic, which is unsurprising given that the activity of Pd supported catalysts in the oxidation of VOCs is typically dependent on the particle size and oxidation state of the Pd nanoparticles. This was further evidenced by Dégé \textit{et al.},\textsuperscript{547} who also reported that activity is dependent on the proportion of Pd\(^0\) present in the catalyst. The \(T_{100}\) for xylene of a Pd/HFAU catalyst reduced from 280 to 240 °C (GHSV of 18,000 h\(^{-1}\)) after a reductive pre-treatment at 300 °C for 1 h. Following this, Wang \textit{et al.},\textsuperscript{548} reported that a series of Pd/Co\(_3\)O\(_4\) materials were also exceptionally active for this reaction. It was determined that the activity of the catalysts was heavily influenced by the method of Pd deposition and was directly related to the dispersion of PdO. In a more recent study, Xie \textit{et al.}\textsuperscript{549} determined that the activity of mesoporous CoO-supported Pd (Pd/meso-CoO) was much more active than a corresponding catalyst supported on mesoporous Co\(_3\)O\(_4\). The higher activity over the Pd/meso-CoO was relied on the Pd-CoO interface which was proposed to be pivotal in the activation of O\(_2\) and assist with the stability of Pd\(^0\) species; considered to be the predominant site for the adsorption of o-xylene.

For practical applications, catalysts should be supported on structured supports, such as ceramic and metallic monoliths. Supporting catalysts on these extrudates reduces the pressure drop from the gas feed into the catalyst bed, reduces diffusion distances, and are generally more resistant to vibrational and thermal shock.\textsuperscript{550,551} A series of MO\(_x\) (M = Cu, Ni, and Co) doped MnCeO\(_x\) oxide catalysts were immobilized onto ceramic monoliths using a sol-gel method by Zhang and Wu.\textsuperscript{552} The doping of this catalyst with CuO\(_x\) resulted in a significant enhancement in the catalytic activity. Of the catalysts tested, a MnCeCu\(_{0.4}\)/monolith catalyst exhibited the highest activity for the oxidation of o-xylene; 90 % o-xylene was converted at 277 °C (GHSV of 10,000 h\(^{-1}\)).

Carbon-coated monoliths have also been investigated as catalyst extrudates. Carbon materials are typically very versatile which is desirable from a catalyst design perspective.\textsuperscript{553-556} Moreno-Castilla and co-workers\textsuperscript{557} have reported on the use of carbon-coated monoliths as extrudates to support Pd and Pt nanoparticles and have tested these materials for the oxidation of \(m\)-xylene. The Pt supported materials were more active than the corresponding Pd materials. The activity of the Pd supported catalysts increased as the mean particle size decreased, but interestingly, the opposite trend was observed with Pt supported catalysts due to a structure
3.3.4. Naphthalene

Polycyclic aromatic hydrocarbons (PAHs) represent a large class of VOCs, which are typically released during the oxidation of organic matter, such as diesels, gasoline, biomass, coal and wood. PAHs are considered to be highly carcinogenic and mutagenic. The emission of PAHs to the atmosphere is widespread and takes place on a large scale and as such, are considered to pose serious environmental and health risks. Naphthalene is considered to be one of the least toxic and simplest PAHs which are commonly emitted and so, is an excellent model compound to study the total catalytic oxidation of PAHs.

The catalytic activities of many different metal oxides (CoO\textsubscript{x}, MnO\textsubscript{x}, CuO, ZnO, Fe\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}, TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and CuZnO\textsubscript{x}) have been studied previously for the oxidation of naphthalene. Of the catalysts tested, a CeO\textsubscript{2} catalyst was determined to be the most active which was ascribed to the high surface area of the catalyst and the strength of the bond between naphthalene and the catalyst surface. A series of nanocrystalline CeO\textsubscript{2} catalysts were subsequently prepared by a combustion method, which employed ethylene glycol (EG) as a fuel for the reaction. The EG : Ce ratio used in the preparation of these catalysts had a pronounced effect on the catalytic activity observed. The highest activity and CO\textsubscript{2} selectivity was exhibited by a catalyst prepared with an EG : Ce molar ratio of 0.75 which was related to a higher proportion of oxygen vacancies present in this material. A subsequent study was conducted by the same group over CuCeO\textsubscript{x} catalysts and the same conclusions were drawn. Another study investigated the activity exhibited by a series of mesoporous CeO\textsubscript{2} catalysts, which were prepared by a nanocasting methodology and invoked the use of 2D SBA-15, 3D KIT-6 and 3D MCM-48 as the template. All the catalysts tested were highly active for this reaction, which was predominantly owing to the high surface areas of the materials and accessibility of the substrate to the active sites.

The doping of Zr into CeO\textsubscript{2} has been shown to be beneficial for the catalytic oxidation of naphthalene. Taylor and co-workers determined that the incorporation of small quantities of Zr into the CeO\textsubscript{2} lattice had a notable effect on the performance of the catalyst. Increasing the quantity of Zr in the CeO\textsubscript{2} lattice was determined to have a detrimental impact on the catalytic performance, which was on account of an increased proportion of hydrophilic OH species on the
Several Mn$_2$O$_3$ catalysts have been synthesized and tested for the total oxidation of naphthalene by Solsona and co-workers. The activity of these materials was related to be highly dependent on their corresponding surface areas, reducibility and lattice oxygen mobility. In addition, it was concluded that a crystalline Mn$_2$O$_3$ phase has a higher intrinsic activity than MnO$_2$. Hopcalite have also been investigated for this reaction. The calcination temperatures of these catalysts were determined to have a significant effect on the resultant activity. A precursor calcined at 400 °C exhibited the highest activity and CO$_2$ ascribable to a high surface composition of amorphous CuMn$_2$O$_4$. Increased calcination temperatures reduced the activity of the catalysts, which was owing to the formation of a more crystalline CuMn$_2$O$_4$ phase.

Noble metal (Pd, Pt and Au) supported catalysts have also been investigated for the oxidation of naphthalene. Garcia et al. reported that a Pd/TiO$_2$ catalyst was more active than corresponding Pd/V/TiO$_2$ and V/TiO$_2$ catalysts. Another study also investigated the activity of Pd nanoparticles catalysts on various supports (i.e., BETA and ZSM-5 zeolites, a silicoaluminophosphate molecular sieve (SAPO-5) and γ-Al$_2$O$_3$) for this reaction. Of the catalysts tested, a Pd/BETA material exhibited the highest activity; a 100 % conversion of naphthalene was converted at 165 °C (flow rate of 50 mL·min$^{-1}$). Ndifor et al. reported that doping a Pt/γ-Al$_2$O$_3$ catalyst with V (0.5 wt.%) could significantly improve the activity of the catalyst. The observed enhancement was attributed to the increased reducibility of surface, due to the presence of V. Further increases in the V content however, was determined to have a detrimental effect on the catalytic performance, which was connected with the formation of V$_2$O$_5$. Mochida and co-workers determined that a Pt/SBA-15 catalyst was more active than a corresponding catalyst supported on γ-Al$_2$O$_3$. Further investigation revealed that the Pt/SBA-15 catalyst was also more active than Ru/SBA-15 and Mo/SBA-15 catalysts, which was owing to differences in the chemisorption of naphthalene on these materials as weak chemisorption of naphthalene. The Al species in the SBA-15 material was proposed to operate as a structural promoter, assisting with the dispersion of Pt and inhibiting the agglomeration of the Pt nanoparticles.

3.4. Oxygen-containing VOCs

Oxygen-containing VOCs such as methanol, ethanol, 2-propanol, formaldehyde, acetaldehyde,
propanal, acetone, methyl ethyl ketone, ethyl acetate and butyl acetate are commonly emitted in industrial waste streams. The environmental and toxicological impact of these VOCs is typically dependent on their functionalization. For example, alcohols can participate in secondary reactions, leading to the formation of aldehydes which are considered to be eye and respiratory irritants which upon repeated exposure, can lead to serious respiratory conditions.\textsuperscript{579,580}

### 3.4.1. Methanol

Methanol is extensively used as a solvent in a number of industrial sectors and is also being trialed as a potential non-petroleum based fuel.\textsuperscript{581,582} The partial oxidation of methanol however, leads to the formation a more toxic pollutant; formaldehyde, which has somewhat limited its application as a fuel additive in the transport sector.\textsuperscript{9,583} The low temperature oxidation of methanol is typically a clean and efficient process,\textsuperscript{584,585} which has been investigated over a wide range of different catalysts.\textsuperscript{586-595}

Numerous reports have indicated that Co\textsubscript{3}O\textsubscript{4} is a highly active catalyst for the oxidation of methanol. Xia \textit{et al.}\textsuperscript{596} reported that the cubic Co\textsubscript{3}O\textsubscript{4} with a 3D ordered mesoporous structure could obtain methanol conversions up to 90\% at 139 °C (WHSV of 20,000 mL⋅g\textsuperscript{-1}⋅h\textsuperscript{-1}). The activity of this material was linked to its high specific surface area and good low-temperature reducibility. The reaction mechanism of methanol oxidation on Co\textsubscript{3}O\textsubscript{4} surfaces was studied by density functional theory (DFT) with a GCA+U framework. The results from these experiments indicated that methanol more favorably adorbs onto Co\textsuperscript{3+} ((110)-B surface) sites as opposed to Co\textsuperscript{2+} ((111)-B surface) sites. Over the (110)-B surface, methanol could readily be oxidized to CO\textsubscript{2} and water. Over the (111)-B surface however, it was determined that methanol could only be oxidized to CH\textsubscript{2}O.\textsuperscript{597} As such, it was concluded that the total oxidation of methanol occurred at Co\textsuperscript{3+} sites.

The acid/base properties of different supports have been reported to influence the dispersion and oxidation state of Pd nanoparticles. A study by Jabłońska \textit{et al.}\textsuperscript{598} investigated the performance of a variety of Pd catalysts (Pd/HY, Pd/NaY and Pd/Al\textsubscript{2}O\textsubscript{3}) for the oxidation of methanol. Of the catalysts investigated, the Pd/HY catalyst exhibited the highest catalytic activity (\(T\textsubscript{90} = 120\) °C; flow rate of 20 cm\textsuperscript{3}\cdot min\textsuperscript{-1}), which was ascribed to the acidity of the material increasing the Pd dispersion. The presence of Pd\textsuperscript{0} and Pd\textsuperscript{2+} species were observed in the active
catalyst and both were reported to be important for the catalysis taking place. It is known that CeO$_2$-ZrO$_2$ catalysts have good redox and oxygen storage properties and typically exhibit high thermal resistance in oxidation reactions.\textsuperscript{599} A series of mesoporous Pd/CeO$_2$-ZrO$_2$ catalysts were prepared by DP method and tested for this reaction.\textsuperscript{600} The mesoporous Pd/CeO$_2$-ZrO$_2$ catalyst exhibited a higher activity than that observed over corresponding mesoporous Pd/ZrO$_2$ and Pd/CeO$_2$ catalysts. Another study investigated how Ba doping effected the catalytic performance of a Pd/Al$_2$O$_3$-Ce$_0.5$Zr$_{0.7}$O$_2$ for this reaction.\textsuperscript{601} An enhanced activity was observed upon doping of Ba to the catalyst, which was attributed to an enhancement in the formation of the methoxy intermediate species, considered to be the rate determining step in this reaction.

Zhao et al.\textsuperscript{590} investigated the catalytic oxidation of methanol over a series of Pt/TiO$_2$ and Pt/CeO$_2$-TiO$_2$ catalysts. The Pt/TiO$_2$ catalysts, which was calcined at 350 °C, exhibited a methanol conversion of 70 % at room temperature. The corresponding Pt/CeO$_2$-TiO$_2$ catalyst, which had approximately 1-2 mol% of the Ce doped into the TiO$_2$ exhibited a very similar activity to the monometallic Pt/TiO$_2$ catalyst, but was determined to be more stable. More recently, Cimino et al.\textsuperscript{602} reported that cathodic electrodeposition of Pt onto Fecralloy foams had high activity in methanol oxidation.

The low temperature oxidation of methanol and its partial oxidation intermediates was investigated over a series of Au catalysts supported on various reducible oxides by Torres Sanchez and co-workers.\textsuperscript{603} Of the catalysts tested, a Au/α-Fe$_2$O$_3$ catalyst exhibited the highest activity. This was also observed by Scirè et al.\textsuperscript{591} who tested a series of Au, Ag and Cu catalysts supported on Fe$_2$O$_3$. The Au supported catalyst was determined to be the most active, which was associated with a weakening of the Fe-O bond enhancing the mobility of lattice oxygen. Au/CeO$_2$ catalysts have also been investigated as catalysts for the total oxidation some VOCs (2-propanol, methanol and toluene).\textsuperscript{604} The performance of these catalysts was attributed to the Au particle size. Smaller Au nanoparticles were proposed to be more active which was in relation to the weakening of Ce-O bonds at the interface of the Au nanoparticle. Petrov\textsuperscript{605} determined that a Au-Co mixed oxide supported on CeO$_2$/TiO$_2$ can totally oxidize methanol at a temperature of 50 °C, which exhibited a better activity than a corresponding Pt catalyst.

Another study investigated supporting Au- and CeO$_2$ on mesoporous SBA-15, which were subsequently doped with additional metals such as Cu and Zr and tested for the oxidation of
The incorporation of Cu was determined to increase the Au dispersion due to electronic transfers from Cu\(^+\) species to metallic Au, instigating strong interaction between the metals on the surface. The addition of Zr and Cu to the catalysts was determined into favor the formation of dimethyl ether and methyl formate, respectively.

A series of \(\gamma\)-Al\(_2\)O\(_3\)-supported Cu, Mn, Ce, K, Ag, Cu-Mn, Cu-Ce, Cu-Ag and Cu-K catalysts have also been synthesized and tested for the oxidation of methanol. Of the catalysts tested in this study, the Ag containing catalysts were determined to be the most active, of which the Ag-Cu/\(\gamma\)-Al\(_2\)O\(_3\) catalyst was the most active. The high activities observed were owing to the presence of Ag\(^+\) species.

### 3.4.2. Ethanol

Ethanol is also widely used as an industrial solvent and fuel/fuel additives.\(^{608,609}\) Like methanol, the partial oxidation of ethanol can lead to the formation aldehydic species which are notably more toxic.\(^{15}\) For this reason, there are numerous examples of catalysts which have been investigated for the low-temperature oxidation of ethanol. Mn-based oxides and Pt supported catalysts have displayed the most potential to date,\(^{610-613}\) but other transition metal (Cr, Co and Ce)-based catalysts and Au supported catalysts have also displayed some promise.\(^{614-618}\)

There are many examples of highly active MnO\(_x\) based catalysts for the oxidation of ethanol documented in the literature. Bai \textit{et al.}\(^{619}\) determined that the morphology of a MnO\(_2\) catalyst could have a dramatic influence on its catalytic performance in this reaction. A series of 1D, 2D and 3D structured MnO\(_2\) catalysts were investigated for this reaction. Of the catalysts tested, the 3D MnO\(_2\) catalysts exhibited the highest activity which was associated with the better low-temperature reducibility and higher proportion of Mn\(^{4+}\) species present in this material. Over the 3D-MnO\(_2\) catalyst, complete oxidation of ethanol was achieved at 150 °C with a WHSV of 45,000 mL∙g\(^{-1}\)∙h\(^{-1}\) (Fig. 14i). Another study, investigated how a series of octahedral molecular sieve (OMS-2) catalysts synthesized from different precursors could influence the catalytic activity for this reaction.\(^{509}\) It is found that the OMS-2 catalyst derived from a MnSO\(_4\) precursor exhibited the highest activity, which was linked to weakened Mn-O bonds.

Another study by Cadús and co-workers,\(^{620}\) reported that the doping of small quantities of Cu (10 wt.%) into a MnO\(_x\) catalyst could improve the materials catalytic activity for the oxidation of
ethanol. The observed enhancement was attributed to Cu instigating a reduction in the crystallinity of the MnO\textsubscript{x} material and increased the proportion of oxygen vacancies. It was however determined, that increasing the quantity of Cu in the catalyst favored the partial oxidation of ethanol. An additional study reported that the total oxidation of ethanol could be achieved at 200 °C (flow rate of 100 mL·min\textsuperscript{-1}) over a MnO\textsubscript{x}-CeO\textsubscript{2} catalyst, which is a much lower temperature than that required over a 0.3 wt.% Pt/Al\textsubscript{2}O\textsubscript{3} catalyst.\textsuperscript{621} Other studies also confirmed that high ethanol activities could be exhibited over Mn\textsubscript{0.6}Ce\textsubscript{0.4}O\textsubscript{2}\textsuperscript{622} and La-Mn based perovskite-type catalysts.\textsuperscript{623}

Investigations into catalysts prepared by the thermal decomposition of LDH precursors have also been investigated for the low-temperature oxidation of ethanol.\textsuperscript{624,625} The performance of such catalysts in this reaction can be further improved by doping these materials with additional transition metal ions. A series of M\textsuperscript{II}-M\textsuperscript{III} LDH precursors materials with M\textsuperscript{II} : M\textsuperscript{III} molar ratio of 2 (M\textsuperscript{II} = Cu, Co, Ni, Cu-Ni, Cu-Co and Co-Ni; M\textsuperscript{III} = Mn or Al) were prepared by the co-precipitation from solutions of the corresponding metal nitrates.\textsuperscript{626} Of the catalysts synthesized, a CuNiMnO\textsubscript{x} mixed oxide material was determined to be the most active and the ternary mixed oxide materials which contained Mn were determined to be the more active than the binary CuMnO\textsubscript{x}, CoMnO\textsubscript{x}, and NiMnO\textsubscript{x} catalysts (Fig. 14ii). A separate study conducted by Aguilera \textit{et al.},\textsuperscript{444} reported that CoMnMgAlO\textsubscript{x} oxide catalyst exhibited a 90 % ethanol conversion at 252 °C (flow rate of 200 mL·min\textsuperscript{-1}), which provide a higher yield of CO\textsubscript{2} than a corresponding catalyst containing Cu (CuMnMgAlO\textsubscript{x} oxide). Kovanda \textit{et al.}\textsuperscript{627} also investigated the use of ternary CoMnAlO\textsubscript{x} oxides materials for the oxidation of ethanol, over which ethanol conversion of 50 % were observed at approximately 180 °C (flow rate of 41.6 mL·min\textsuperscript{-1}). Further enhancements in the performance were subsequently observed when the same material was doped with KNO\textsubscript{3}. When 3 wt.\% K was doped onto the material, an ethanol conversion of 50 % could be achieved at 140 °C, but did increase the selectivity to partial oxidation products such as acetaldehyde.\textsuperscript{628}

The oxidation of ethanol over different noble metal (Pt, Pd, Ir, Rh, and Au) catalysts supported on TiO\textsubscript{2} was investigated by Figueiredo and co-workers.\textsuperscript{629} Of the catalysts tested, a Pt/TiO\textsubscript{2} catalyst was determined to be the most active and the activity of the catalysts decreased in order; Pt/TiO\textsubscript{2} > Pd/TiO\textsubscript{2} >> Rh/TiO\textsubscript{2} ≈ Ir/TiO\textsubscript{2} >> Au/TiO\textsubscript{2}. This order of activity was observed regardless of the preparation method used. Gaálová \textit{et al.}\textsuperscript{630} compared the activity of Au and Pt
nanoparticles supported on a Ce-Zr-O support. The Pt supported catalyst was determined to have a significantly higher activity than the corresponding Au catalyst and was determined to be more active than the corresponding commercial catalyst, Pt-Pd/Al₂O₃. The Pt/Ce-Z-O catalyst exhibited an ethanol conversion of 50% at 99 °C (WHSV of 20 m³·g⁻¹·h⁻¹).

A series of Pt/Ce/activated carbon catalysts were also synthesized and tested for the oxidation of ethanol. The activity of these catalysts were notably higher than that observed over a corresponding Pt/CeO₂ catalyst. The most promising activity was exhibited by a Pt-10Ce/C which achieved a total conversion of ethanol to CO₂ at 160 °C (flow rate of 100 mL·min⁻¹) and was stable in a test run for 100 h. However, under more humid conditions (RH of 40 and 80%), the activity of Pt-10Ce/C did drop slightly, which was attributed to the hydrophobic character of the activated carbon (AC) support (Fig. 14iii). A subsequent study by the same group investigated how the Pt precursor influenced the performance of the Pt-CeO₂/C catalyst in this reaction. A catalyst synthesized from H₂PtCl₆ exhibited a much higher ethanol conversion and CO₂ selectivity than a corresponding catalyst prepared from Pt(NH₃)₄(NO₃)₂, which was attributed to an increase Pt dispersion and a stronger metal-CeO₂ interaction.

### 3.4.3. 2-propanol

2-propanol (isopropanol) is a typical gaseous VOC pollutant with a high level of toxicity and has therefore attracted vast interest from researchers worldwide. Its prominence comes as a result of its versatility as a solvent and reactant in several industrial processes such as printing, coatings, spraying, semiconductors, precision machinery industries and pharmaceutical applications. Cu-based oxides and Au supported catalysts are two of the most reported systems for the total oxidation of 2-propanol.

Supports such as TiO₂, Fe₂O₃, CeO₂ and Al₂O₃ were adopted for Au sites in the total oxidation of 2-propanol. Centeno et al. claimed that the presence of nitrogen in Au/TiO₂ (Au/TiO₂Nₓ) had a negative influence on the oxidation of 2-propanol to CO₂, while an enhancement was observed in partial oxidation to acetone. It was also suggested that the presence of Au⁵⁺ or Au⁰ species as well as Au particle amount and size determined the overall catalytic activity. Galvagno and co-workers confirmed that the Au oxidation state and/or the particle size played a key role in the catalytic oxidation of VOCs such as 2-propanol. The catalytic oxidation of 2-propanol
over various metal oxide-supported Au catalysts (Au/CeO$_2$, Au/Fe$_2$O$_3$, Au/TiO$_2$ and Au/Al$_2$O$_3$) was studied by Liu and Yang.\textsuperscript{536} Of the catalyst studied, Au/CeO$_2$ was found to be the most active in this range. The oxidation state of Au was an important factor for 2-propanol oxidation over Au/CeO$_2$ catalysts with Au$^{+1}$ species exhibiting higher activity than Au$^0$. Scirè \textit{et al}.\textsuperscript{604} reported that the presence of Au enhanced the activity of CeO$_2$ towards 2-propanol oxidation with the catalytic performance being related to the capacity of Au nanoparticles to weaken the adjacent surface Ce-O bonds, thus enhancing the reactivity of the CeO$_2$ surface. Centeno \textit{et al}.\textsuperscript{194} found that CeO$_2$ enhanced the fixation and dispersion of Au particles in Au/CeO$_2$/Al$_2$O$_3$ catalysts, which improved the activity of Au particles in VOC oxidation.

Fierro and co-workers\textsuperscript{643} reported that the Cu-Co$_2$ spinel catalyst exhibited the highest activity in 2-propanol oxidation out of a range of Cu-(Cr, Mn and Co)$_2$ mixed oxides. The researchers ascribed this high reactivity to the higher reducibility under the reaction conditions and a synergistic effect between Cu-Co$_2$ mixed oxide and CuO particles. Various other materials such as Ni-Mn or Zn-Cr spinels were also reported in 2-propanol oxidation.\textsuperscript{644,645} Nanocrystalline AMn$_2$O$_4$ (A = Co, Ni and Cu) manganite spinels were prepared by Nabavi and co-workers\textsuperscript{644} using a sol-gel auto oxidation method. It was found that NiMn$_2$O$_4$ exhibited the best activity due to the synergetic effect between Mn$^{3+}$ and Ni$^{2+}$ phases in nickel manganite oxide, achieving complete conversion of 2-propanol at 250 °C. Following this work, the correlation between structure and activity of MCr$_2$O$_4$ nanospinels (M = Co, Cu, and Zn) in the oxidation of 2-propanol was also studied by the same group,\textsuperscript{645} and revealed that the ZnCr$_2$O$_4$ exhibited the highest activity and stability. The authors believed that the higher activity of ZnCr$_2$O$_4$ was due to the existence of excess surface oxygen on the catalyst, active Cr$^{3+}$-Cr$^{6+}$ pair sites and a synergistic effect between ZnO and ZnCr$_2$O$_4$. The high stability of ZnCr$_2$O$_4$ was explained by the existence of stable Cr$^{6+}$ species on the surface of catalyst.

### 3.4.4. Formaldehyde

Formaldehyde is an important precursor for the synthesis of many other materials and chemical compounds. As such, millions of tons of formaldehyde are used each year, with contamination and waste streams leading to tremendous harm to humans and the environment.\textsuperscript{646-648} It is well known that long-term exposure to air containing formaldehyde, even at very low ppm level, may
cause serious health problems including nasal tumors, irritation of the mucous membranes of the eyes and respiratory tract, skin irritation, decreased concentration and weakened immunity.\textsuperscript{649,650} Catalytic oxidation of formaldehyde is an efficient and environmentally friendly approach for its abatement.\textsuperscript{651} The majority of works focus on the synthesis and development of Mn-, Co-, Pt-, Au- and Ag-based catalysts for the deep oxidation of formaldehyde at low temperature.\textsuperscript{652-660}

Mn based catalysts have been widely studied for formaldehyde oxidation and appeared to be the most active catalysts among the transition metal oxides. \(\alpha\)-, \(\beta\)-, \(\gamma\)- and \(\delta\)-MnO\(_2\) oxides were prepared by the hydrothermal method, and it was found that the \(\delta\)-MnO\(_2\) exhibited the best performance in the series \(\delta\)-MnO\(_2\) > \(\alpha\)-MnO\(_2\) > \(\gamma\)-MnO\(_2\) > \(\beta\)-MnO\(_2\), achieving nearly complete formaldehyde conversion at 80 °C (WHSV of 600,000 mL\(\cdot\)g\(^{-1}\)\(\cdot\)h\(^{-1}\)).\textsuperscript{661} The tunnel structure and active lattice oxygen species were described as the main factors which contribute to the excellent performance of \(\delta\)-MnO\(_2\). Rong \textit{et al.}\textsuperscript{662} reported that single-crystalline \(\alpha\)-MnO\(_2\) nanowires with exposed \{310\} facets exhibited much better activity and stability for formaldehyde oxidation than those with exposed \{100\} and \{110\} facets. It was suggested that the \{310\} facets with high surface energy could not only facilitate adsorption/activation of O\(_2\) and water but also be beneficial to the generation of oxygen vacancies. Wang \textit{et al.}\textsuperscript{663} also indicated that the abundance of manganese vacancies had a positive effect on the performance of birnessite catalysts in the deep oxidation of formaldehyde. 3DOM MnO\(_2\) with disordered polycrystalline walls and a large number of exposed (110) crystal planes (enriched Mn\(^{4+}\) ions) displayed better formaldehyde oxidation activity than common MnO\(_2\).\textsuperscript{664}

In order to enhance the catalytic activity and extend the operating temperature window for formaldehyde oxidation, the combination of two or more transition metal oxides is often employed.\textsuperscript{125,665} MnCoO\(_x\), MnCeO\(_x\) and MnFeO\(_x\) mixed oxides were generally used in formaldehyde oxidation. Shi \textit{et al.}\textsuperscript{666} proposed that the Mn\(_x\)Co\(_{3-x}\)O\(_4\) solid solution synthesized by a co-precipitation method could completely oxidize formaldehyde at 75 °C (GHSV of 60,000 h\(^{-1}\); relative humidity of 50\%) ascribed to the large amount of surface oxygen available on Mn\(_x\)Co\(_{3-x}\)O\(_4\). In addition, they suggested that the oxidation and decomposition of formate and hydrocarbonate species was the rate-limiting step for the catalytic oxidation of HCHO. Following this, the authors from the same group demonstrated that the 3D ordered cubic mesoporous Co-Mn oxide (fabricated by a KIT-6-templating strategy) had a high activity for this reaction as a result.
of its large surface area and 3D ordered mesoporous structure.\textsuperscript{667} The preparation method and post-treatment process can influence the oxidation performance of MnCeO\textsubscript{x} mixed catalysts.\textsuperscript{668,669} Tang \textit{et al.}\textsuperscript{668} reported that MnO\textsubscript{x}-CeO\textsubscript{2} prepared by a modified co-precipitation method (adopting Mn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and KMnO\textsubscript{4} as Mn precursor) had a much higher catalytic activity for total formaldehyde oxidation than analogous samples obtained by the sol-gel and co-precipitation methods (with Mn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O as Mn precursors). This was explained by the modified co-precipitation method leading to a higher proportion of Mn\textsuperscript{4+} species and richer lattice oxygen on the surface of catalyst. Quiroz \textit{et al.}\textsuperscript{669} revealed that treating the MnO\textsubscript{x}-CeO\textsubscript{2} catalysts with an aqueous H\textsubscript{2}SO\textsubscript{4} solution could promote their catalytic activities when the solubility limit of Mn in CeO\textsubscript{2} was exceeded (\textit{i.e.}, Mn content > 50 wt.%). This was due to the acid treatment oxidizing the Mn species to a higher valence state \textit{via} a Mn dismutation reaction (Fig. 15i). The presence of Mn cations and its ability to improve the activity of spinel ferrites for formaldehyde oxidation was also reported.\textsuperscript{670,671} This Mn substitution increased the lattice oxygen content, which facilitated the reduction of ferrite and enhanced the overall oxidative ability of Fe\textsuperscript{3+} and Mn cations on catalyst surface.

It has been reported that the catalytic performance of various cobalt oxides is influenced by their morphology, cobalt source and preparation conditions.\textsuperscript{655,672-674} Nano-Co\textsubscript{3}O\textsubscript{4}, 2D-Co\textsubscript{3}O\textsubscript{4} and 3D-Co\textsubscript{3}O\textsubscript{4} catalysts were prepared by Li and co-workers\textsuperscript{672} and tested in the oxidation of formaldehyde. They revealed that the Co\textsubscript{3}O\textsubscript{4} catalyst with a 3D mesostructure possessed the highest activity with 100\% of formaldehyde oxidized at 130 °C (WHSV of 30,000 mL·g\textsuperscript{-1}·h\textsuperscript{-1}), which was associated with its three-dimensional porous channel structure, larger specific surface area, abundant active surface oxygen species and active Co\textsuperscript{3+} species on the exposed (220) crystal facet. Bai \textit{et al.}\textsuperscript{673} also found that the use of β-cyclodextrin had a strong impact on the final properties of Co\textsubscript{3}O\textsubscript{4}/ZrO\textsubscript{2} catalysts produced with different cobalt sources (cobalt nitrate, acetate and acetyl acetonate), both in terms of reducibility and dispersion of active species. The best combination was obtained using cobalt nitrate with a β-cyclodextrin : cobalt ratio of 1 : 10. Fan \textit{et al.}\textsuperscript{674} found that the KHCO\textsubscript{3}-precipitated Co\textsubscript{3}O\textsubscript{4} was the most active catalyst which was linked to the presence of K\textsuperscript{+} and CO\textsubscript{3}\textsuperscript{2-}, regenerated hydroxyl groups on the catalyst and favorable Co\textsuperscript{3+}/Co\textsuperscript{2+} ratio (Fig. 15ii). Recently, Huang \textit{et al.}\textsuperscript{675} revealed that addition of aqueous alkali (NaOH/KOH) could greatly promote the catalytic activity of 3D-NiCo\textsubscript{2}O\textsubscript{4} nanosheets (Fig. 16) in
this reaction. This was in related to the abundance of surface OH− which could directly react with formate species to produce CO2 and water. Similar results regarding the promotional effect of alkali on Pd- and Pt-based catalysts in this reaction were also proposed in relating studies.676-678

Pt-, Au-, Ag- and Rh-based catalysts were reported for formaldehyde incineration.679-681 Pt-based catalysts exhibit extraordinarily high activity in this reaction even at room temperature.682,683 However, Ag-based catalysts are less active than that of Pt- or Au-based catalysts, with operating temperatures generally higher than 100 °C.684-687 It was reported that the type and morphology of support, constitution and active phase and dispersion of Pt sites have large effects on the catalytic performance of Pt supported catalysts in this reaction.688-692 The higher catalytic activity of Pt/K-OMS in formaldehyde oxidation than that of Ag/K-OMS was presented by Wang and co-workers.693 Following this, TiO2 supported noble metal (Au, Rh, Pd and Pt) catalysts were prepared and used for this reaction by Zhang and He,658 and they revealed that Pt/TiO2 had the best activity with 100% formaldehyde coverted at room temperature (GHSV of 50,000 h−1). Various silica supports such as fumed SiO2, porous granular SiO2 and SBA-15 were adopted to prepare Pt catalysts. It was found that the fumed SiO2 supported Pt catalyst (Pt/f-SiO2) showed the best formaldehyde oxidation activity, due to the presence of a higher ratio of metallic Pt species.688

Yu et al.689 found that the Pt/nest-like MnO2 had a higher catalytic activity for formaldehyde incineration than that of Pt/cocoon-like MnO2 and Pt/urchin-like MnO2. The incorporation of transitional metals (e.g., Mn, Ni and Fe) into Pt-based catalysts has been found to promote their oxidation activities. Shen and co-workers683 suggested that the Pt/MnOx-CeO2 catalyst with a Mn : (Mn+Ce) molar ratio of 0.5 exhibited the highest catalytic activity. Chen et al.690 revealed that MnO2 had a clear promotional effect on catalytic performance of Pt/TiNT catalysts (TiNT: TiO2 nanotube arrays), with 95% of formaldehyde conversion over 0.2 wt.% Pt/MnO2/TiNT being achieved at 30 °C with a WHSV of 30,000 mL·g−1·h−1 (Fig. 15iii). Recently, the promotional effect of nickel hydroxide on Pt/γ-Al2O3 in this reaction has also been proposed by researchers from the same group.691 The promotional effect of Fe on Pt/γ-Al2O3 catalysts was studied by Jia and co-workers.694 They found that the sample with an Fe : Pt ratio of 1 : 1 possessed the highest activity in the oxidation of formaldehyde ascribable to more accessible Pt-O-Fe active sites.

Various reducible oxides (CeO2 and FeOx) and irreducible oxides (γ-Al2O3, SiO2 and HZSM-5)
were prepared and adopted as the support for Au-based catalysts. The results revealed that the Au/\(\gamma\)-Al\(_2\)O\(_3\) catalyst had the highest formaldehyde oxidation activity and stability.\(^{695}\) CeO\(_2\) and MnO\(_2\) are two types of active supports for noble metal nanoparticles. 3DOM Au/CeO\(_2\) catalysts were synthesized by Zhang et al.,\(^{696}\) with 100% conversion of formaldehyde being observed at 75 °C (WHSV of 66,000 mL·g\(^{-1}\)·h\(^{-1}\)), much lower than the traditional powdered Au/CeO\(_2\). Following on from this work, the 3DOM Au/CeO\(_2\)-Co\(_3\)O\(_4\) catalysts were prepared and used for this reaction. The results revealed that the synergistic effect between CeO\(_2\) and Co\(_3\)O\(_4\) could greatly accelerate the surface oxygen migration and activate the Au species which enabled a 100% conversion of formaldehyde at 39 °C (WHSV of 15,000 mL·g\(^{-1}\)·h\(^{-1}\)).\(^{697}\) The catalytic oxidation of formaldehyde over mesoporous Au/Co\(_3\)O\(_4\) and Au/Co\(_3\)O\(_4\)-CeO\(_2\) was also investigated by Hao and co-workers,\(^{698}\) in which they revealed that the 2D Au/Co\(_3\)O\(_4\) exhibited the best activity with 52.1% of CO\(_2\) yield for formaldehyde oxidation at 25 °C with a GHSV of 55,000 h\(^{-1}\) (Fig. 15iv).

Bimetallic (Au-Pt and Au-Pd) catalysts have also been reported for formaldehyde low-temperature oxidation.\(^{699,700}\) Au-Pt bimetallic supported on nest-like MnO\(_2\) catalysts were synthesized by Yu et al.,\(^{699}\) and they proposed that the Au\(_{0.8}\)Pt\(_{0.5}\)/MnO\(_2\) catalyst exhibited the highest catalytic activity for this reaction due to the synergistic effect between Au-Pt nanoparticles.

### 3.4.5. Acetaldehyde

Acetaldehyde is a common pollutant in paints, adhesives, and exhaust gases. The prominence of acetaldehyde as a pollutant has been linked with an increase in the incidence of oral cavities, esophagus, and pharyngeal cancers as well as the sick building syndrome.\(^{701,702}\) Mn oxides have demonstrated good catalytic activities with high sintering resistance which makes them cheap alternatives to noble metal catalysts for the catalytic oxidation of acetaldehyde.\(^{703}\) The structure of Mn oxide (OMS-2) comprises a peculiar sharing of 2 × 2 [MnO\(_6\)] octahedral chains that form one-dimensional tunnel structures with pore size of 0.46 nm × 0.46 nm. This material possesses excellent hydrophobicity and strong affinity for VOCs.\(^{704}\) Wang and Li\(^{609}\) synthesised OMS-2 catalysts with different precursors and sulfate-acidification. It was found that the acidification resulted in a decrease in activity. An OMS-2 catalyst prepared using MnSO\(_4\) as a precursor
exhibited the best catalytic performance with the Mn-O bond being described as the main determinant of the catalytic activity toward acetaldehyde oxidation.

The adsorption and dissociation of acetaldehyde on oxidized and reduced CeO$_2$(100) thin films was investigated by Mullins and Albrecht, who found that acetaldehyde decomposed on oxidized CeO$_2$(111). The primary products were found to be CO, CO$_2$ and water as well as trace amounts of crotonaldehyde and acetylene. The reaction pathway on reduced CeO$_{2-x}$(100) was similar with that of the oxidized CeO$_2$(111); however, the inability to react with surface O on the reduced surface resulted in H$_2$ rather than water desorption, and carbon being deposited on the surface rather than evolution of CO and CO$_2$.

An efficient Pt/CeO$_2$/ZSM-5 catalyst for acetaldehyde oxidation ($T_{100}$ of 200 °C; GHSV of 1200 h$^{-1}$) was proposed by Yamashita and co-workers. Both the synergistic effect of atomization of Pt nanoparticles by addition of a small amount of CeO$_2$ and the enriched adsorption of organic molecules in ZSM-5 were described as being responsible for its superior activity. Yasuda et al. reported that the addition of polyvinylpyrrolidone (PVP) could enhance the specific surface area and surface Pt$^{2+}$ ratio of Pt/CeO$_2$-ZrO$_2$-Bi$_2$O$_3$ catalysts synthesized by the wet impregnation method, and that the presence of PVP during synthesis procedure significantly promoted the activity in this reaction.

Nikawa et al. revealed that small Au nanoparticles (< 3 nm) modified TiO$_2$ caused the rapid and strong adsorption of gaseous acetaldehyde under humid conditions, while the adsorption of acetaldehyde on unmodified TiO$_2$ was low and weak. The catalytic performances of Pd, Pd-Cu and Pd-Au supported Nb$_2$O$_5$ catalysts were investigated by Bozon-Verduraz and co-workers. The results suggested that the addition of Au or Cu inhibited the catalyst deactivation with the best performance in total oxidation being obtained with Pd-Au/Nb$_2$O$_5$. This was ascribed to Au → Pd electron donation, which prevented the surface oxidation of Pd particles.

Various metal oxide-supported Ru catalysts (Ru/CeO$_2$, Ru/SnO$_2$, Ru/ZrO$_2$ and Ru/$\gamma$-Al$_2$O$_3$) were studied in the total oxidation of acetaldehyde. Ru/CeO$_2$ showed the highest activity (acetaldehyde completely oxidized at around 210 °C; flow rate of 100 mL·min$^{-1}$) among these catalysts due to the high dispersion of Ru sites. The catalytic activities of Ru/ZrO$_2$ and Ru/$\gamma$-Al$_2$O$_3$ were enhanced by a reduction treatment due to the formation of ruthenium in the metallic state; however, the formation of intermetallic core-shell species resulted in the
deterioration of catalytic activity of Ru/SnO₂.  

3.4.6. Acetone

Acetone is a common organic solvent which has been widely used in many industries such as plastics, drugs, semiconductors, printed circuit boards, electronic terminal products, varnishes and adhesives. Acetone can cause environmental hazards and is harmful to human health. For example, inhalation of acetone vapor can irritate the respiratory tract and cause coughing, dizziness, dullness, and headaches. Higher concentrations can lead to depression of the central nervous system operation, narcosis, and unconsciousness. The catalytic oxidation of acetone is therefore an important subject of research, with work generally focusing on transitional metal oxides (e.g., Cu, Mn, V and Ce)-based catalysts.

Martínez-Arias et al. reported that the performance of Ce-based oxides in oxidation reactions was greatly enhanced by incorporation of CuO into the CeO₂ lattice, and that the activity of CeO₂ supported CuO catalysts in oxidation reactions was even comparable to that of the NMSCs. Synergistic effects between Ce and Cu were also found in our previous work. CuₓCe₁₋ₓOₙ mixed metal oxides with different Cu contents were prepared and tested for this reaction. The Cu₀.₁₃Ce₀.₈₇Oₓ catalyst was found to be the most active; however, the long-term stability of Cu₀.₁₃Ce₀.₈₇Oₓ still required improvements due to the formation of bulk CuO. The subsequent work revealed that the calcination temperature had a significant influence on the activity and stability of Cu₀.₁₃Ce₀.₈₇Oₓ catalysts. The sample calcined at 700 °C exhibited the best catalytic activity, over which 100% acetone conversion could be reached at around 200 °C (flow rate of 200 mL·min⁻¹). In addition, the catalysts calcined from 400 to 700 °C possessed good stability for this reaction. Following this, CuCeOₓ nanofiber catalysts were synthesized by Qin et al. using an electrospinning method. The results demonstrated that nanofiber catalysts possessed better acetone oxidation performance than catalysts prepared by the urea-nitrate oxidation and sol-gel methods. A Cu₀.₅₀Ce₀.₅₀Oₓ nanofiber catalyst possessed the highest activity primarily due to Ce ions with unusual oxidized states (Ce³⁺) as well as large specific surface areas and abundant oxygen vacancies in the catalyst. Zheng and co-workers reported that CuO supported on Ce-modified and Zr-pillared montmorillonite catalyst had good activity for acetone incineration, with 100% acetone converted at 230 °C.
The low-temperature catalytic oxidation of acetone over different metal (Cu, Co, Ni, Mn and Fe)-modified CeO$_2$ and supported on Al-containing mesoporous silica particles (Al-MSPs) was studied by Lin and Bai.$^{719}$ The team found that Ce was the main active species for all catalysts in the complete oxidation of acetone, and Mn acted as an appropriate promoter for improving the activity of Ce/Al-MSPs catalysts. Of the catalysts studied, Mn-Ce/Al-MSPs with a Mn : Ce molar ratio of 2 : 1 was found to be the most active catalyst for achieving maximum acetone conversion at temperatures of 100-200 °C (Fig. 17i). This was linked with the synergistic effect in MnCeO$_x$ mixed oxides, resulting in higher amount of Ce$^{3+}$ and Mn$^{4+}$ species, enhanced reducibility of catalyst and improved acetone adsorption ability.$^{719}$ Mn-modified hydrophobic TiO$_2$-SiO$_2$ mixed oxides were also adopted for this reaction. The catalytic activity of these materials was dependant on the surface area, surface oxygen and hydrophobic property of sample.$^{720}$ Gil et al.$^{721}$ reported that the Sm Mn O$_x$ mixed oxide had a higher acetone oxidation activity than that of single Mn oxide. Furthermore, the SmMnO$_x$ catalyst calcined at 800 °C possessed the best catalytic activity.

A series of Mn oxides supported on unpillared and Al- and Zr-pillared forms of two natural clays (montmorillonite and saponite) were prepared and applied in this reaction. It was found that the Mn/pillared montmorillonite had better activity than the Mn/pillared saponite. The stability of the catalysts supported on the unpillared clays was higher than that of those supported on the Al- and Zr-pillared clays.$^{722}$ Fe and Mn mixed oxides pillared clays with varying Mn to Fe ratios were successfully synthesized, and revealed that catalyst with high Mn content (Mn(III) : Fe(III) = 16 : 4) acted as a better catalyst for acetone decomposition.$^{723}$

It is well known that transition metal perovskites such as LaMO$_3$ (M = Mn and Co) are highly efficient oxidation catalysts. Porta and co-workers$^{724}$ suggested that the LaMnO$_3$ form had a higher catalytic activity in deep oxidation of acetone than that of LaCoO$_3$. The LaMnO$_3$ surface also demonstrated a higher adsorption of VOCs. It was also noted that an increase in oxygen partial pressure was beneficial for this reaction. The higher acetone oxidation activity of perovskite-type oxides (SrMnO$_3$, FeMnO$_3$, and La$_{0.6}$Pb$_{0.2}$Ca$_{0.2}$MnO$_3$) compared to spinel-type materials (CuFe$_2$O$_4$, MgFe$_2$O$_4$, and Ni$_{0.5}$Co$_{0.5}$O$_4$) was confirmed by Ignat and co-workers (Fig. 17ii).$^{725}$ Recently, Rezlescu et al.$^{713}$ further proved that the partial substitution (20%) of Mn by Ce ions could significantly improve the catalytic activity of SrMnO$_3$ in this reaction. This effect was ascribed to smaller crystallite sizes, larger specific surface area and the presence of Ce and Mn.
cations with variable valences in the perovskite structure.

$V_2O_5/TiO_2$ catalysts with excellent catalytic performance have been widely studied in oxidative processes such as VOC oxidation and photocatalysis. The redox properties of $V_2O_5/TiO_2$ catalysts can be tuned by modification of the electronic interaction between TiO$_2$ and VO$_x$ species. TiO$_2$ nanofiber supported $V_2O_5$ catalysts with hierarchical structures were fabricated by combining electrospinning and hydrothermal growth methods. The results demonstrated that a 5 wt.% $V_2O_5/TiO_2$ nanofiber catalyst illustrated the highest acetone oxidation activity ($T_{90} = 300$ °C; GHSV of 360,000 mL·g$^{-1}$·h$^{-1}$) (Fig. 17iii).

The catalytic performance of mesoporous silica supported metal oxide catalysts was studied by Wang and Bai in total decomposition of acetone. The studies revealed that a supported Ce catalyst had a higher activity than that of Mn, Cu, Fe, or Al supported ones. Spherical mesoporous silica particles (MSPs) possess various advantages over mesoporous materials manufactured via batch processes such as a higher rate of production, higher packing density and a lower pressure drop during operation. A series of bimetallic Ce/Al catalysts supported on mesoporous silica were investigated by Lin and Bai. The authors proposed that the catalytic oxidation of acetone was mainly governed by the surface redox properties and acidity of the catalyst. A spherical Ce/Al-SiO$_2$ sample prepared with an aerosol-spraying temperature of 300 °C had a high surface acidity and strong reducibility and also appeared to be one of the best catalyst for this reaction.

### 3.4.7. Methyl ethyl ketone

Methyl ethyl ketone (MEK) is a widely used chemical due to its outstanding solvent properties and low cost. It is used as a solvent in synthetic resins, adhesive manufacturing, textile dyeing and printing, and electronic equipment manufacturing. Furthermore, MEK is a dewaxing agent in the refining of lubricant oils and a denaturing agent for alcohols. The emission of MEK to atmosphere can lead to human health concerns and wider environmental problems.

The complete oxidation of MEK over various transition metal (Mn, Co, Cr, Fe and Ni)-doped ZrO$_2$ (cubic) catalysts were reported by Pataskar and co-workers. The results demonstrated that the Cr/ZrO$_2$ catalyst had the highest activity for MEK oxidation, whereas the Ni/ZrO$_2$ exhibited the lowest activity. A series of LaBO$_3$ ($B = Cr, Co, Ni and Mn$) and La$_{0.9}$K$_{0.1}$MnO$_{3-δ}$ perovskites were prepared and tested in this reaction. The catalytic activity is sequenced as: $LaMnO_3$>
LaCoO$_3$ ≈ LaNiO$_3$ > LaCrO$_3$ for 100% MEK conversion. Doping with K promoted the catalytic activity of LnMnO$_3$ perovskite due to the increase in surface area and proportion of Mn$^{4+}$ on the surface as well as the formation of non-stoichiometric oxygen. MEK, when oxidized to CO$_2$, goes through acetaldehyde and small amounts of methyl vinyl ketone and diacetylas intermediate products.$^{735}$ The performance of Mn$_2$O$_3$ and Mn$_3$O$_4$ in this reaction (alkali and acid ions were added to the solids) has been investigated by Gil and co-workers.$^{736}$ The addition of Na and Cs resulted in a considerable improvement of the performance, while sulfate had a negative effect.

Picasso et al.$^{737}$ proposed that flow-through catalytic membranes based on Fe$_2$O$_3$, prepared by the precipitation method, showed a higher efficiency in this reaction than their bulk catalyst counterparts, with total oxidation of MEK at around 255 °C. Similar results were also reported in their previous work regarding the catalytic oxidation of MEK over Pt/Al$_2$O$_3$ membrane catalysts.$^{738}$ Recently, Jian et al.$^{739}$ proposed that the MnO$_x$ nanowires with highly exposed $\{101\}$ facets of Mn$_3$O$_4$ had a higher MEK destruction activity than that of MnO$_x$ nanocubes, nanorods and nanospheres respectively exposing $\{321\}$ facets of Mn$_2$O$_3$, $\{110\}$ facets of MnO$_2$, and $\{101\}$ and $\{112\}$ facets of Mn$_3$O$_4$. The authors argued that high affinity of MEK molecule on MnO$_x$ $\{101\}$ facets greatly promoted the oxidation process (Fig. 18).

Hierarchically micro-mesostructured Pt/K-Al-SiO$_2$ catalysts with regular nanorod (Pt/KA-NRS) and spherical nanoflower-like (Pt/KA-SNFS) morphologies were prepared and adopted in MEK oxidation in our previous work.$^{740}$ We found that Pt/KA-NRS catalysts exhibited exceptional low temperature activity, CO$_2$ selectivity and stability for MEK oxidation. This was related to their regular morphology, high Pt$^0$ content and dispersion, excellent MEK adsorption capacity and superior O$_2$/CO$_2$ desorption capability at flow temperatures. Our subsequent work proved that the incorporation of Mn cations could remarkably promote the activity of Pt/SiO$_2$ catalysts.$^{741}$ The presence of a Pt-O-Mn moiety weakened the Mn-O bonding interactions, which ultimately promoted the mobility of lattice oxygen in Mn$_2$O$_3$. Whilst, the Mn$^{4+}$/Mn$^{3+}$ redox cycle in Mn$_2$O$_3$ allowed for the donation of electrons to the Pt nanoparticles, enhancing the proportion of Pt$^0$/Pt$^{2+}$ and in turn increasing the activity and stability of catalyst.

3.4.8. Ethyl acetate

Ethyl acetate (EA) is one of the most widely used, ascendant, and stable fatty acid esters used
as an organic raw material and solvent for coatings and plastics. EA can cause severe environmental pollution and harm to the health of human beings. Catalytic oxidation can eliminate EA from the air in high efficiency and low energy consumption. Many catalyst systems such as Mn-, Cu-, Cr-, Co-, Pt-, Ru- and Au-based catalysts have been developed to target a more efficient elimination of EA (Table 4).

Table 4 Summary of some active catalysts for ethyl acetate (EA) oxidation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant composition</th>
<th>Space velocity/Flow rate</th>
<th>$T_{90}$ (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACMn1.0$^a$</td>
<td>1000 ppm EA, Air balance</td>
<td>280 mL-min$^{-1}$</td>
<td>218</td>
<td>134</td>
</tr>
<tr>
<td>Mn$<em>{0.5}$Ce$</em>{0.5}$O$_x$</td>
<td>1800 ppm EA, Air balance</td>
<td>50 mL-min$^{-1}$</td>
<td>&lt; 230</td>
<td>413</td>
</tr>
<tr>
<td>Mn/SBA-15$^b$</td>
<td>315 ppm EA, Air balance</td>
<td>500 mL-min$^{-1}$</td>
<td>&lt; 250</td>
<td>744</td>
</tr>
<tr>
<td>8.3%Mn/SBA-15$^c$</td>
<td>560 ppm EA, Air balance</td>
<td>500 mL-min$^{-1}$</td>
<td>265</td>
<td>745</td>
</tr>
<tr>
<td>Hollandite manganese</td>
<td>200 ppm EA, Air balance</td>
<td>200 mL-min$^{-1}$</td>
<td>&lt; 210</td>
<td>746</td>
</tr>
<tr>
<td>Cu$_{10}$/Al$_2$O$_3$-M$^d$</td>
<td>1802 mg-m$^{-3}$ EA, Air balance</td>
<td>5.000 h$^{-1}$</td>
<td>250</td>
<td>748</td>
</tr>
<tr>
<td>CuCe$<em>{0.75}$Zr$</em>{0.25}$/ZSM-5</td>
<td>1000 ppm EA, Air balance</td>
<td>24.000 h$^{-1}$</td>
<td>248</td>
<td>751</td>
</tr>
<tr>
<td>Cu/Co-charcoal</td>
<td>600 ppm EA, Air balance</td>
<td>18.000 mL·g$^{-1}$·h$^{-1}$</td>
<td>&lt; 210</td>
<td>753</td>
</tr>
<tr>
<td>meso-Cr-240$^e$</td>
<td>1000 ppm EA, Air balance</td>
<td>20.000 h$^{-1}$</td>
<td>190</td>
<td>754</td>
</tr>
<tr>
<td>20%Co/activated carbon</td>
<td>0.88% EA, Air balance</td>
<td>66.000 mL·g$^{-1}$·h$^{-1}$</td>
<td>210</td>
<td>757</td>
</tr>
<tr>
<td>15%Co-La/CoO$_2$</td>
<td>1000 ppm EA, Air balance</td>
<td>500 mL-min$^{-1}$</td>
<td>244</td>
<td>758</td>
</tr>
<tr>
<td>La$<em>{0.6}$Sr$</em>{0.4}$CoO$_2$-$\gamma$8</td>
<td>1000 ppm EA, Air balance</td>
<td>20.000 h$^{-1}$</td>
<td>170</td>
<td>743</td>
</tr>
<tr>
<td>Ce$_x$Cu$_y$-EM$^f$</td>
<td>466.7 ppm EA, Air balance</td>
<td>53.050 h$^{-1}$</td>
<td>194</td>
<td>759</td>
</tr>
<tr>
<td>Ce$<em>{0.5}$Co$</em>{0.5}$</td>
<td>1000 ppm EA, 25% O$_2$, N$_2$ balance</td>
<td>60.000 mL·g$^{-1}$·h$^{-1}$</td>
<td>195</td>
<td>760</td>
</tr>
<tr>
<td>1%Ru/CoO$_2$</td>
<td>0.1% EA, Air balance</td>
<td>10.000 mL·g$^{-1}$·h$^{-1}$</td>
<td>&lt; 200</td>
<td>764</td>
</tr>
</tbody>
</table>

$^a$Catalyst synthesized by the auto-combustion (AC) method and with Mn$^{2+}$ : Mg$^{2+}$ ratio of 1.0; $^b$Catalyst with KMnO$_4$ as the Mn precursor (Mn : Si = 0.21); $^c$SBA-15 was impregnated by KMnO$_4$ for three times; $^d$With glass fiber corrugated honeycomb monolith (M) as the support; $^e$Precursor heated at 240 °C; $^f$Prepared by the evaporation method (EM).

The effect of Mn precursors in the synthesis MnO$_x$-SBA-15 catalysts for the deep oxidation of EA was reported by Montes and co-workers. They found that the Mn oxide phase obtained
heavily depended on the precursor used. Nitrate precursors mainly produced pyrolusite whereas acetate produced non-crystalline oxide phase with low oxidation state; permanganate produced a mixture of cryptomelane and birnessite. The activity of the catalysts depended on the crystalline phase, with the most active catalysts being those with $\text{Mn}^{4+}/\text{Mn}^{3+}$ pairs (Fig. 19i). Following this work, the SBA-15-supported Mn catalysts with various metal loadings were prepared by the same group via a multi-step impregnation method. The results revealed that the remaining P123 and the presence of $\text{K}^+$ in Mn precursors were responsible for the reduction of permanganate to a mixture of $\text{Mn}^{4+}$ and $\text{Mn}^{3+}$ and formed cryptomelane-like phases. EA oxidation activity was again found to be directly proportional to the Mn average oxidation state and basic nature of K was shown to promote the catalytic activity.\textsuperscript{745}

Mixed metal oxides have also developed for total oxidation of EA.\textsuperscript{134,341,413} MnO$_x$-CeO$_2$ catalysts prepared by a urea oxidation method were reported by Delimaris and Loannides.\textsuperscript{413} It was stated that the larger surface area of MnO$_x$-CeO$_2$ catalysts offset their lower specific activity allowing complete conversion of the VOC at lower temperatures compared to the single oxides. Recently, Chen et al.\textsuperscript{746} proposed that a hollandite Mn oxide (HMO) catalyst could efficiently control both typical particulate matter (PM) and VOC (EA and ethanol) emissions from biomass combustion. They revealed that typical alkali-rich PMs such as KCl particles were disintegrated and the $\text{K}^+$ ions were trapped in the HMO “single-walled” tunnels. The $\text{K}^+$-trapping HMO increased the electron density of the lattice oxygen (Fig. 19ii) and the redox ability, thus promoting the oxidation of soot, PMs and typical VOCs.

Supported Cu materials are some of the highest activity catalysts for EA oxidation. Silica supported Cu catalysts were extensively reported in the literature.\textsuperscript{747-752} Tsoncheva et al.\textsuperscript{747} proposed that Cu and Ce bi-component supported on 3D-structured KIT-6 provided better catalytic activity than that of SBA-15-supported ones as finely dispersed CuO nanoparticles were prone to form over KIT-6 support. The effects of a mesoporous silica support on this reaction over Cu-Cr/Silica catalysts were also studied in the same group. It was suggested that the CuCrO$_4$ species were predominantly formed over SBA-15, leading to a high selectivity to the partial oxidation of EA. Alternatively, the formation of CuCr$_2$O$_4$ species is typical for SiO$_2$ (Cab-o-sil M5) based materials, which contributes to a higher selectivity to CO$_2$ in EA oxidation.\textsuperscript{750} CuCe$_x$Zr$_{1-x}$O$_y$/ZSM-5 ($x = 0, 0.25, 0.5, 0.75$ and $1.0$) catalysts were recently prepared by Dou and
co-workers. The results suggested that the CuCe$_{0.75}$Zr$_{0.25}$O$_y$/ZSM-5 catalyst had the best performance due to its excellent reducibility, offering complete conversion of EA into CO$_2$ at a temperature of 270 °C with a GHSV of 24,000 h$^{-1}$ (Fig. 20i). More recently, Liao et al. indicated that the Cu-Co/charcoal catalysts possessed very high activity with EA being completely oxidized at just 212 °C (flow rate of 30 mL·min$^{-1}$).

Xia et al. synthesized mesoporous Cr$_2$O$_3$ with ordered 3D hexagonal polycrystalline structures at different temperatures with KIT-6 as the hard template. The results revealed that the catalyst obtained at 240 °C had the best activity, with EA being totally oxidized at around 260 °C at a GHSV of 20,000 h$^{-1}$. Rotter et al. found that the chromia aerogel (α-CrOOH) with a high specific surface area (630 m$^2$·g$^{-1}$) was a powerful catalyst for EA oxidation.

Various supported Co catalysts were developed and studied in the deep oxidation of EA. Cobalt oxide modified SBA-15, KIT-5 and KIT-6 mesoporous silicas were synthesized by Linden and co-workers. It was found that supports with larger mesopores facilitated the formation of spinel-type Co$_3$O$_4$, which was highly active in this reaction. AC has been used as a support to provide favorable conditions for the formation of well-dispersed active species. Xie et al. found that preparation of a Co/AC catalyst in an air atmosphere promoted the formation of reactive oxygen species, leading to a high EA oxidation ability compared with the sample synthesized in nitrogen atmosphere. Gómez et al. and Hernández-Garrido et al. reported that Co/La-CeO$_2$ was very active in the oxidation of EA, even more than the Pt/La-CeO$_2$ catalyst.

CuCeO$_x$, NiCeO$_x$ and CoCeO$_x$ mixed oxides were studied for this reaction by Figueiredo and co-workers. It was found that the CoCeO$_x$ oxide catalyst had the highest oxidation activity with EA being totally oxidized at 225 °C with a GHSV of 53,050 h$^{-1}$. It was suggested that the catalytic activity was related to the surface area, amount of Ce contained in the samples, calcination temperature and reducibility of the catalysts (Fig. 20ii). Recently, a series of CeO$_2$-CoO$_x$ catalysts with various Ce to Co ratios have been investigated for this reaction, in which Ce$_{0.5}$Co$_{0.5}$O$_x$ catalysts could achieve 100% conversion of EA at 200 °C. This was associated with the enriched lattice oxygen.

Catalytic oxidation of EA over noble metal (Pt, Ru and Au) supported catalysts were also reported in several works. In general, supported Ru catalysts show higher activity in this reaction compared with Pt- and Au-based catalysts. Catalytic oxidation of EA over Ru/CeO$_2$,
Pt/CeO$_2$, and Pd/CeO$_2$ was studied by Eguchi and co-workers,\textsuperscript{764} and revealed that the Ru/CeO$_2$ showed the best catalytic activity with 90% of EA converted at 180 °C (flow rate of 100 cm$^3$·min$^{-1}$), followed by Pt/CeO$_2$ and Pd/CeO$_2$ (Fig. 20iii). The low temperature reducibility of precious metal species is most likely the reason for the high activity observed. A series of 1.0 wt.% Au supported catalysts (Au/CuO, Au/Fe$_2$O$_3$, Au/La$_2$O$_3$, Au/MgO, Au/NiO, and Au/Y$_2$O$_3$) were prepared and investigated in EA incineration.\textsuperscript{816} The Au/CuO catalyst was found to have the highest activity ($T_{90} = 272$ °C; flow rate of 500 cm$^3$·min$^{-1}$) and the authors proposed that this activity was related to the reducibility of support and the Au nanoparticle size.

### 3.5. Chlorinated VOCs

Chlorinated VOCs (CVOCs, such as dichloromethane, 1,2-dichloroethane, trichloromethane, tetrachloromethane, tetrachloroethane, vinyl chloride, dichloroethylene, trichloroethylene, tetrachloroethylene, chlorobenzene and dichlorobenzene) are hazardous compounds due to their strong bioaccumulation potential, acute toxicity and resistance to degradation.\textsuperscript{765,766} These highly volatile compounds often have long atmospheric lifetimes and have widespread applications in formulations and processing of paints, adhesives, drugs manufacturing and as solvents in chemical reactions.\textsuperscript{33} Halogenated VOCs have a significant impact in the depletion of the ozone layer and as a source of radicals in the atmosphere which in turn contribute to the greenhouse gas effects. The 100-year global warming potential (GWP) of halogenated VOCs range from 10 to 1800, which is far higher than that of CO$_2$ with a GWP of only one.\textsuperscript{767}

#### 3.5.1. Dichloromethane

Dichloromethane (DCM) is one representative of CVOCs used widely as a solvent which is a vesicant and harmful to the respiratory and central nervous systems of humans.\textsuperscript{768,769} DCM is also the most stable chlorinated-alkane and very difficult to be decomposed naturally in the environment. The environmentally friendly decomposition of DCM at low temperatures is a hot topic and studied by many researcher groups.\textsuperscript{770-776} V-, Cr-, Ce- and Pt-based catalysts as well as various zeolites such as HFAU, HY, HMOR and HZSM-5 were investigated in the deep decomposition of DCM.

V-containing catalysts have commonly been shown to possess good stability in Cl$_2$-HCl atmosphere. V$_x$-SBA-15 materials have been prepared by a direct synthesis approach, and this
method is favored for the incorporation of V into the silica walls with formation of isolated sites. It was found that V was present mainly as isolated sites with tetrahedral coordination, and these isolated V sites were catalytically active towards DCM conversion. V-Ni mixed oxides supported on anatase TiO$_2$ were synthesized by Huang and co-workers. It was revealed that the activity of V-Ni/TiO$_2$ was superior to that of V/TiO$_2$ and Ni/TiO$_2$ in DCM oxidation (Fig. 21i). DCM could be completely converted into CO$_2$, HCl, and a small amount of CO over the V-Ni/TiO$_2$ catalyst at 350 °C (WHSV of 15,000 mL·g$^{-1}$·h$^{-1}$) without the formation of other toxic by-products. The high catalytic activity, selectivity and stability of the V-Ni/TiO$_2$ catalyst could be owing to the oxidative dehydrogenation (ODH) ability, enhanced reducibility of active oxygen species and suitable strength of Lewis acidic sites (LAS) upon introduction of nickel oxide.

Cr-containing oxides are very effective for CVOC oxidation. Kang and Lee found that CrO$_x$ supported on AC was effective in the deep oxidation of DCM due to the presence of highly dispersed Cr$^{6+}$ species on catalyst surface. CrO$_x$/Al$_2$O$_3$ catalysts were also tested in DCM oxidation. The best catalyst (18 wt.% Cr) could completely oxidize DCM at 350 °C (GHSV of 20,000 h$^{-1}$) due to the presence of a large amount of Cr in a high oxidation state. Wu and co-workers reported that the Cr/HZSM-5 catalyst possessed a higher stability than that of Cu/HZSM-5 and Fe/HZSM-5 in this reaction (Fig. 21ii). The mechanism of deactivation for Fe/HZSM-5 was found to be coking due to its lower ability to oxidise intermediate products, while the formation of stable Cu(OH)Cl species was the primary reason for the deactivation of Cu/HZSM-5. Structured metal oxides with active species confined in a robust matrix can overcome the disadvantages of the supported metal catalysts in the oxidation of CVOCs. A series of spinel type CoCr$_2$O$_4$ catalysts calcined at different temperatures were prepared and tested in this reaction. The results demonstrated that the catalyst calcined at 400 °C had the best performance with 90% of DCM oxidized at 257 °C with a GHSV of 15,000 h$^{-1}$ (Fig. 21iii). It was proposed that the high activity of this catalyst was mainly linked with the large surface area which provided more surface acidic sites and active oxygen species.

Ce/TiO$_2$ catalysts were prepared and used for DCM incineration by Wu and co-workers. The authors revealed that pure TiO$_2$ oxide tended to deactivate due to the strong adsorption and accumulation of Cl species over the surface. However, surface Cl could be rapidly removed by
CeO₂, which led to a reduced poisoning effect of Cl on Ce/TiO₂ and an enhanced activity and stability in this reaction. Subsequent work found that the preparation method also had a significant influence on the catalytic performance of Ce/TiO₂, resulting in differences in exposure of TiO₂ and CeO₂ at the catalyst surface and varying interaction between TiO₂ and CeO₂. They proposed that the solid mixing method exhibited the best catalytic activity (T₉₇ = 335 °C; GHSV of 30,000 h⁻¹) and anti-chlorine capability compared with the samples synthesized by impregnation and hydrothermal methods. Recently, a two-stage Ce/TiO₂-Cu/CeO₂ catalyst with separated catalytic functions was designed by Wu and co-workers. The results demonstrated that 97% of DCM could be converted at 330 °C (GHSV of 30,000 h⁻¹) with fewer undesired CO, Cl₂, and CₓHᵧClᵦ by-products. Furthermore, the conversion and CO₂ yield were well maintained even in the presence of water.

Results obtained in Lu’s group indicated that catalytic behavior in the oxidation of DCM could be influenced by surface acidity and redox properties of catalysts. The addition of Pt enhanced the activity of CeO₂-Al₂O₃ due to the promotion of surface acidity (by introduction of chlorine species using H₂PtCl₆ as the precursor) and reducibility of the catalyst most likely via the formation of Ce-Pt-O solid solution (Fig. 21iv). Similar results were also suggested by Keiski and co-workers. Further work in Lu’s group found that the addition of K greatly promoted the activity of Pt/Al₂O₃ in this reaction (Fig. 21v) which was attributed to the presence of Pt-O-Kₓ species. These species could significantly accelerate the decomposition of formate intermediates formed on the Al₂O₃ surface and thus promote the overall reaction. Pitkääho et al. reported that Pt-catalysts showed the best performance in this reaction, followed by PtPd- and Pd-catalysts. Moreover, the incorporation of V₂O₅ can improve the catalytic performance of Pt/Al-catalysts, which has a positive effect on DCM oxidation selectivity to HCl. Magnoux and co-workers suggested that the Pt dispersion over Pt/Al₂O₃ had no apparent effects on DCM oxidation rates. Al₂O₃ was found to be highly active and play an important role in catalytic oxidation by enabling the transformation of DCM into CO, CH₃Cl, and HCl. Catalytic oxidation of DCM over Pt/HFAU catalysts was also studied in the same group, and they revealed that DCM transformation was independent of Pt particle size and Pt content. DCM was firstly hydrolysed into HCl and formaldehyde on the BAS over HFAU, after which formaldehyde was oxidized into CO₂ and water on the Pt sites.
Zeolite molecular sieves were widely used as catalysts and catalyst supports in the catalytic oxidation of CVOCs due to their well defined pore structure, superior thermal stability and ion exchange characteristics. López-Fonseca et al. reported that the dealumination process created strong acid sites over zeolites, leading to a higher catalytic activity for DCM oxidation. Further work revealed that the H-MOR, H-ZSM-5 and H-Y protonic zeolites exhibited excellent activity for this reaction (H-MOR > H-ZSM-5 > H-Y) and promising selectivity towards the formation of HCl. As mentioned earlier, the BAS are believed to be effective for DCM adsorption. Pinard et al. reported that the catalytic oxidation of DCM over Na zeolite involves four successive steps: (1) the reaction of DCM with the ONa groups leading to the formation of chloromethoxy species and liberation of NaCl; (2) the hydrolysis of chloromethoxy species into hydroxymethoxy species with liberation of HCl; (3) the desorption of formaldehyde leading to the formation of hydroxyl groups, and the oxidation of formaldehyde to CO, CO₂, and water; (4) the recovery of the ONa groups by reaction of NaCl, produced in dechlorination step, with the hydroxyl groups. Catalytic oxidation of DCM over NaFAU and HFAU was further studied by Zhang et al. in their recent work where NaFAU was found to be more active than HFAU as it facilitated the adsorption and dechlorination steps. The dechlorination of DCM was predicted to be the rate-determining step.

3.5.2. 1,2-dichloroethane

1,2-dichloroethane (1,2-DCE) is one of the most important chlorinated VOCs emitted in industrial flue gases, since it is used as an intermediate in the production of polyvinyl chloride. Additional uses are as a solvent in metal degreasing and paint removers, a starting material for paint, and a dispersant for plastics and elastomers. NMSC materials were seldom used in the deep oxidation of 1,2-DCE, and most of reported works were focused on Co- and Ce-based catalysts as well as zeolites (Table 5).

Table 5 List of some reported catalysts for 1,2-dichloroethane (DCE) low-temperature oxidation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant composition</th>
<th>Space velocity/Flow rate</th>
<th>T₉₀ (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co₃O₄ nanocube</td>
<td>1000 ppm 1,2-DCE, Air balance</td>
<td>30,000 h⁻¹</td>
<td>340</td>
<td>809</td>
</tr>
<tr>
<td>CeO₂ nanorod</td>
<td>1500 ppm 1,2-DCE, Air balance</td>
<td>15,000 h⁻¹</td>
<td>&lt; 230</td>
<td>821</td>
</tr>
<tr>
<td>10%CeZ/IM-Eᵃ</td>
<td>1000 ppm 1,2-DCE, Air balance</td>
<td>15,000 h⁻¹</td>
<td>245</td>
<td>805</td>
</tr>
</tbody>
</table>
Co$_3$O$_4$ with a spinel structure has been shown to be one of the most efficient catalysts in total oxidation of VOCs.\textsuperscript{806-808} Co oxides with different nanostructures (nanocube, nanosheets and nanorods) were prepared and adopted in the oxidation of 1,2-DCE. It was found that the nanocube-shaped Co$_3$O$_4$ had the best activity, achieving total oxidation of 1,2-DCE towards CO$_2$, HCl, and Cl$_2$ at 400 °C (GHSV of 30,000 h$^{-1}$) without any other by-product formation.\textsuperscript{809}

For the supported Co$_3$O$_4$ catalysts, the activity depends mainly on the nature of the support and the metal oxide-support interactions.\textsuperscript{810} De Rivas \textit{et al.}\textsuperscript{811} synthesized a series of Co$_3$O$_4$ catalysts using various routes, and found that catalyst prepared by the precipitation method, with a particle size of 10 nm, gave the highest activity. This was found to be higher than that of the supported noble-metal catalysts for 1,2-DCE oxidation.\textsuperscript{811} Co/SBA-15 catalysts prepared by the wet impregnation method were recently reported by de Rivas and co-workers.\textsuperscript{812} The results revealed that the incorporation of cobalt leaded to the formation of BAS and LAS, and the pores of SBA-15 prevented the excessive growth of cobalt oxide crystals at high temperatures, thus improving their redox property. The simultaneous participation of the acid and redox sites

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>1,2-DCE ppm</th>
<th>GHSV</th>
<th>TON</th>
<th>TOS</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%VO$_x$/CeO$_2$</td>
<td>450 ppm</td>
<td>15,000 mL·g$^{-1}$·h$^{-1}$</td>
<td>225</td>
<td>823</td>
</tr>
<tr>
<td>4.4%Fe-CeO$_2$-ST$^b$</td>
<td>500 ppm</td>
<td>15,000 mL·g$^{-1}$·h$^{-1}$</td>
<td>237</td>
<td>820</td>
</tr>
<tr>
<td>45%CeO$_2$/HZSM-5</td>
<td>1000 ppm</td>
<td>30,000 mL·g$^{-1}$·h$^{-1}$</td>
<td>&lt; 275</td>
<td>824</td>
</tr>
<tr>
<td>CeO$_2$/USY$^c$</td>
<td>1000 ppm</td>
<td>15,000 h$^{-1}$</td>
<td>&lt; 260</td>
<td>825</td>
</tr>
<tr>
<td>CeO$_2$-USY-IM$^d$</td>
<td>1000 ppm</td>
<td>15,000 h$^{-1}$</td>
<td>245</td>
<td>826</td>
</tr>
<tr>
<td>CeO$_2$-USY$^c$</td>
<td>1000 ppm</td>
<td>75 mL·min$^{-1}$</td>
<td>245</td>
<td>827</td>
</tr>
<tr>
<td>(Ce,Co)$_2$O$_3$/HZSM-5</td>
<td>1000 ppm</td>
<td>9,000 h$^{-1}$</td>
<td>230</td>
<td>837</td>
</tr>
<tr>
<td>CeO$_2$-TiO$_2$</td>
<td>1000 ppm</td>
<td>15,000 h$^{-1}$</td>
<td>275</td>
<td>829</td>
</tr>
<tr>
<td>(Ce,Co)$_2$O$_3$/Nb$_2$O$_5$</td>
<td>1000 ppm</td>
<td>9,000 h$^{-1}$</td>
<td>270</td>
<td>830</td>
</tr>
<tr>
<td>Ce$<em>{0.5}$Zr$</em>{0.5}$O$_x$</td>
<td>1000 ppm</td>
<td>30,000 h$^{-1}$</td>
<td>&lt; 260</td>
<td>833</td>
</tr>
<tr>
<td>CeO$_2$-ZrO$_2$-CrO$_x$</td>
<td>1000 ppm</td>
<td>15,000 h$^{-1}$</td>
<td>262</td>
<td>836</td>
</tr>
<tr>
<td>0.5%Pt/CrOOH</td>
<td>0.5%</td>
<td>46,000 h$^{-1}$</td>
<td>317</td>
<td>802</td>
</tr>
</tbody>
</table>

$^a$ ZSM-5 support impregnated with excess of precursor-ethanol solvent (Z/IM-E); $^b$ Synthesized by solvothermal method; $^c$ Mass ratio of CeO$_2$ : USY was 1 : 8; $^d$ Prepared by the impregnation method; $^e$ Ce : Ti molar ratio of 14.
markedly accelerated the 1,2-DCE oxidation process.

Hydroxyapatite (Ca$_{10}$PO$_4$$_6$(OH)$_2$, HAP) has been intensively investigated as a porous support as the presence of phosphate groups can stabilise the structure of active sites and allow the tuning of acid-base properties by varying the calcium : phosphorus ratio.$^{813-815}$ Moreover, the ability of hydroxyapatite to undergo cation and anion exchanges, due to the presence of two types of zeolite-like channels, allows modifications in its chemical properties without damaging its typical hexagonal structure.$^{816}$ These characteristics offer hydroxyapatite catalysts as a new generation of materials with synergistic metal-support interactions which can improve their catalytic activity.$^{817,818}$ Co supported calcium-deficient hydroxyapatite (Ca : P = 1.5) catalysts were studied in the deep oxidation of 1,2-DCE.$^{819}$ It was indicated that the Co-rich catalysts contained easily reducible Co$^{3+}$ and Co$^{2+}$ and had a high stability and excellent CO$_2$ selectivity, while activity of pure HAP support suffered a significant decay with time due to chlorination (Fig. 22i).

Fe doped CeO$_2$ nanosheets with 2D nano-structure were synthesized by Wang et al.$^{820}$ with three different methods (hydrothermal (HT), cold co-precipitation (CP) and solvothermal (ST)) and used in the deep oxidation of 1,2-DCE. The results demonstrated that the 5 wt.% Fe-CeO$_2$-ST exhibited a better catalytic activity and lower selectivity to polychlorohydrocarbon by-products due to its large concentration of oxygen vacancies and active surface oxygen. The authors proposed that the stability and selectivity of Fe-CeO$_2$-ST could be further improved via the loading of VO$_x$ or RuO$_2$.$^{820}$

Supported CeO$_2$ catalysts and CeO$_2$-based oxides were extensively studied and showed promising results in the oxidation of CVOCs due to their remarkable redox properties, thermal stability, and resistance to Cl-poisoning.$^{821-823}$ Microporous zeolites such as ZSM-5 and USY were usually adopted as the supports for CeO$_2$ in the oxidation of 1,2-DCE. Gutiérrez-Ortiz and co-workers$^{805}$ found that the activity of CeO$_2$/H-ZSM-5 catalysts in this reaction was greatly influenced by the synthesis route, and they proposed that catalytic behaviour of CeO$_2$/H-ZSM-5 could be explained on the basis of the synergistic effects of oxygen mobility and acid sites. The catalyst synthesized via impregnation in ethanol possessed the highest activity due to this procedure leading to a highly dispersed CeO$_2$ with a larger amount of oxygen vacancies. Recently, Dai et al.$^{824}$ synthesized a sandwich-structured CeO$_2$@HZSM-5 core-shell hybrid catalyst, which inhibited the formation of poly-chlorinated hydrocarbon by-products during 1,2-DCE oxidation.
This ability arose due to the presence of CeO$_2$ with a high activity for the Deacon reaction which was not directly exposed to 1,2-DCE or HCl molecules. Various Y zeolite (USY, HY and SSY) supported CeO$_2$ catalysts were studied in this reaction in which the CeO$_2$/USY catalyst exhibited the best activity with 98% conversion at 270 °C (GHSV of 10,000 h$^{-1}$). The high stability of CeO$_2$/USY catalyst was confirmed by Zhou and co-workers. It was also demonstrated that the supported catalyst with a CeO$_2$ : USY ratio of 1 : 8 possessed the best catalytic activity which was ascribed to a high dispersion of CeO$_2$ species and a more favourable combination of acidity and redox properties.

The application of CeO$_2$-based mixed oxides in the catalytic oxidation of 1,2-DCE was also reported in the literature. Ce-Zr mixed oxides appear as attractive candidates in the oxidation of CVOCs due to the favourable combination of acid and redox properties. Furthermore, Ce-Zr mixed oxides are also highly resistant to thermal aging and induced chlorine poisoning. Rivas et al. examined this reaction over Ce-Zr mixed oxides after treating them with H$_2$SO$_4$ or HNO$_3$ (1M). A significant increase in the activity was observed with sulphated oxides ascribed to the increase in total acidity and concentration of active sites with a moderate/strong acid strength. In contrast, no activity variation could be observed for the samples modified with nitric acid. Ce-Cr mixed oxides and CeCr supported catalysts were also reported in the literature in this reaction. Yang et al. proposed that the addition of ZrO$_2$ improved the catalytic activity and stability of CeO$_2$-CrO$_x$. It was revealed that the catalytic performance of Ce-Cr mixed oxides could be further improved by loading CeO$_2$ and CrO$_x$ over suitable supports such as HZSM-5 and Nb$_2$O$_5$. For example, researchers synthesized different Ce-Cr/zeolite (HZSM-5, H-BETA, USY and H-MOR) catalysts and found that the Ce-Cr/HZSM-5 had the highest activity which converted 90% of 1,2-DCE at 230 °C with a flow rate of 75 mL·min$^{-1}$ (Fig. 22ii).

### 3.5.3. Vinyl chloride

Large amounts of vinyl chloride (VC) is released in industrial processes such as raw material production, synthetic resin, textile dyeing and printing, leather manufacturing and reprocessing of polyvinyl chloride. For instance, high concentrations of VC (up to 1-2%) are released from the production process of polyvinyl chloride, which leads to environmental damage and detrimental effects on human health.
Supported Ru catalysts were considered for the total oxidation of VC because of their high resistance to chlorine species (adsorbed Cl can be removed via the Deacon reaction on RuO$_2$) and excellent activity in oxidation and reduction reactions. An example of this is the industrial oxidation of hydrogen chloride to chlorine.\textsuperscript{840,841} Wang \textit{et al.}\textsuperscript{842} reported that Ru-modified Co$_3$O$_4$ had improved catalytic activity and HCl selectivity in VC oxidation compared with bulk Co$_3$O$_4$ and Ru/SiO$_2$. The Ru supported Co$_3$O$_4$ catalyst demonstrated higher activity than that of Ru doped Co$_3$O$_4$ material due to the high reducibility of Co oxides, along with interaction between Ru species on the surface and Co$_3$O$_4$ phase.

The effect of B-site substitution by Co, Ni and Fe on catalytic performances of LaMnO$_3$ oxides was studied by Giroir-Fendler and co-workers.\textsuperscript{843} They revealed that all the substituted samples showed a higher catalytic activity than the pure LaMnO$_3$, with the Ni-substituted sample displaying the best catalytic performance with 90\% of VC converted at 210 °C (GHSV of 15,000 h$^{-1}$). The effect of A-site substitution (by Sr, Mg and Ce) on the catalytic performance of LaMnO$_3$ in VC oxidation was further investigated by the same authors,\textsuperscript{844} who found that the partial substitution of La by cerium and magnesium had positive effects on their catalytic performances, whereas strontium substitution negatively impacted the performance. The Ce-doped perovskite catalyst demonstrated the highest catalytic performance due to the higher specific surface area and its low-temperature reducibility.

3.5.4. Trichloroethylene

Trichloroethylene (TCE) is a common chlorinated VOC which is present in adhesives, paints, and coatings.\textsuperscript{845,846} TCE is a pollutant that has been classified likely carcinogenic to humans by the International Agency for Research on Cancer (IARC).\textsuperscript{847} TCE is also one of the responsible components for the depletion of stratosphere as well as being one of the components of the photochemical smog.\textsuperscript{848,849} In addition, TCE is one of the major contaminants of aquifers, largely due to its high density ($>1.0$ g·m$^{-3}$) that causes the stratification at the bottom of groundwater.\textsuperscript{850} The catalytic deep oxidation of TCE has been comprehensively studied over a plethora of materials, such as transition metal (Mn, Fe, Cr, Ce and Cu) supported catalysts,\textsuperscript{851,771,851-856} perovskite-type oxides,\textsuperscript{857,858} hydrotalcite derivedoxides,\textsuperscript{859} Pt-, Pd, and Ru-based catalysts\textsuperscript{860,861} and zeolites.\textsuperscript{202,795,862,863}
Divakar et al.\textsuperscript{851} stated that the incorporation of Fe could improve TCE oxidation activity of zeolites (HZSM-5 and H-Beta), with the synthesis procedure influencing the activity of the resultant Fe-zeolite catalyst. In their recent work, the influence of preparation method on Fe species and catalytic activity of Fe-ZSM-5 in TCE oxidation were investigated.\textsuperscript{864} It was found that extra framework Fe nanoparticles present in ZSM-5 were primarily responsible for oxidation rather than the acidic sites. The sample prepared by an ion exchange method had higher catalytic activity than samples prepared via an impregnation or solid state ion exchange method. The deactivation of Fe-ZSM-5 catalysts was found to be due to the formation of FeCl$_3$ rather than coke deposition.

Cr oxide and Cr supported catalysts were studied in the deep oxidation of TCE.\textsuperscript{853} Miranda et al.\textsuperscript{865} stated that the activity of bulk Cr oxide was higher than that of Mn/γ-Al$_2$O$_3$. Moreover, the presence of water increased the stability of Cr oxide due to the Deacon equilibrium, whereas the Mn catalyst showed the opposite behavior. Meyer et al.\textsuperscript{796} reported that the Cr exchanged USY zeolite (Cr-Y) had higher activity than samples of Co-Y, Mn-Y and Fe-Y in TCE oxidation which was attributed to the higher acidity of Cr-Y. A strong synergistic effect of Cr$_2$O$_3$-CeO$_2$ and USY was also explored by Zhou and co-workers.\textsuperscript{866} They discovered that the interaction between Cr$_2$O$_3$ and CeO$_2$ species led to an optimum ratio of strong to weak acid sites, and also improved the mobility of oxygen species over Cr$_2$O$_3$-CeO$_2$-USY catalysts. This was found to be beneficial to the dehydrochlorination and deeper oxidation of CVOCs. Lee and Yoon\textsuperscript{867} revealed that the presence of a small amount of Ru could enhance the overall catalytic performance (activity, CO$_2$ selectivity and stability) of CrO$_x$/Al$_2$O$_3$ catalyst as highly dispersed Ru oxides rendered less active Cr$^{3+}$ to more active Cr$^{6+}$.

Dai et al.\textsuperscript{854} found that bulk CeO$_2$ had high activity for TCE oxidation which could be ascribed to its surface basicity, high mobility of oxygen and oxygen-supplying ability. However, the activity of CeO$_2$ quickly diminished due to the strong adsorption of HCl or Cl$_2$ produced from the decomposition of TCE and the blockage of active sites (e.g., basic sites and active oxygen sites). Gutiérrez-Ortiz and co-workers\textsuperscript{822} confirmed that the addition of Zr into the CeO$_2$ lattice improved the catalytic activity and stability of CeO$_2$ in TCE oxidation due to the enhanced Ce$^{4+}$ reducibility, lattice oxygen mobility and acidic property.

Hydrotalcites are two-dimensional layered synthetic materials with alternating positively
charged mixed metal hydroxide sheets and negatively charged interlayer anions.\textsuperscript{868} The calcination of hydrotalcites leads to the formation of mixed oxides with interesting properties for catalytic removal of CVOCs, such as small particle sizes, large specific areas and homogeneous dispersion of the metals.\textsuperscript{869,870} Blanch-Raga \textit{et al.}\textsuperscript{859} synthesized different Mg(Fe/Al), Ni(Fe/Al) and Co(Fe/Al) mixed oxides derived from hydrotalcite-like compounds and tested them in TCE total oxidation. They found that the Co catalysts had the highest activity, followed by Ni and Mg catalysts. The activity of all catalysts improved when iron was substituted by Al as the presence of Al enhanced the acid property of catalysts and generated reactive O\textsuperscript{2−} species that are able to oxidize the TCE.

Mayenite (Ca\textsubscript{12}Al\textsubscript{14}O\textsubscript{33}) is a mesoporous calcium Al\textsubscript{2}O\textsubscript{3} with a characteristic crystalline structure. In contrast to aluminosilicate zeolites, the framework of mayenite is composed of interconnected cages with a positive electric charge per unit cell and two constituent molecules, [Ca\textsubscript{24}Al\textsubscript{28}O\textsubscript{64}]\textsuperscript{4+} and the remaining two oxide ions O\textsuperscript{2−}, which is often labelled “free oxygen”, are trapped in the cages defined by the framework.\textsuperscript{871} The ability of storing O\textsuperscript{2−} ions in the cages is a valuable property of mayenite which is exploited in catalysis. These oxygen ions can migrate between the surface and the bulk at temperatures higher than 400 °C, which results in a unique ionic conductivity.\textsuperscript{872} Very recently, the catalytic oxidation of TCE over mayenite was reported by Rossi and co-workers.\textsuperscript{873} The results demonstrated that mayenite had a high catalytic activity and excellent recyclability and thermal stability for this reaction. TCE was totally converted to CO\textsubscript{2} and the released chlorine was incorporated in the mayenite structure. The high performances of the catalyst was connected with its oxidative properties due to the presence of O\textsuperscript{2−} and O\textsubscript{2}β− anions sites that favoured the total oxidation of TCE and avoided the coke formation.

Solid acid supported Pt and/or Pd catalysts were also used for CVOC oxidation.\textsuperscript{860} Pt/Al\textsubscript{2}O\textsubscript{3} and Pd/Al\textsubscript{2}O\textsubscript{3} catalysts are highly active in this reaction.\textsuperscript{874,875} A synergistic effect was found between noble metal and acid sites of Pd/H-BETA.\textsuperscript{876} However, these catalysts presented a remarkable selectivity to C\textsubscript{2}Cl\textsubscript{4}, especially in those containing LAS. Wang and co-workers\textsuperscript{877} proposed that the phosphoric phases interacted with Pt sites in Pt/P-MCM-41 catalysts, resulting in the change of Pt oxidation state and Brønsted acid strength. The catalytic oxidation of TCE over these catalysts showed that modification with phosphoric acid enhanced the catalytic performance without the formation of tetrachloroethylene by-product.
3.5.5. Chlorobenzene

Chlorobenzene (CB) is another typical chlorinated contaminant resulting from industrial processes.\(^7\)\(^8\)\(^7\) As such it is frequently used as the model pollutant for CVOCs because it is a precursor or intermediate product of polychlorinated wastes. For example, CB is used as the model compound for highly toxic polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) due to the structural similarity to these pollutants.\(^7\)\(^6\),\(^8\)\(^7\) Most of work regarding the deep catalytic oxidation of CB focused on Mn- and V-based materials\(^8\)\(^8\)\(^5\)\(^-\)\(^8\)\(^8\) and Pt,\(^8\)\(^5\)\(^\text{Pd}^8\)\(^1\),\(^3\)\(^-\)\(^8\)\(^6\)\(^7\),\(^8\)\(^8\)\(^6\) and Ru\(^8\)\(^7\),\(^8\)\(^8\) supported catalysts (Table 6). Various other works studied catalysts such as perovskite-type oxides, Cu-, U- and Fe-based mixed oxides.\(^5\)\(^3\),\(^0\)\(^-\)\(^8\)\(^9\)\(^7\)

**Table 6** Summary of some typical catalysts for chlorobenzene (CB) oxidation.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reactant composition</th>
<th>Space velocity (h(^{-1}))</th>
<th>(T_{90}) (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1%V9%Mo/TiO(_2)</td>
<td>200 ppm CB, 20% O(_2), N(_2) balance</td>
<td>6000</td>
<td>240</td>
<td>916</td>
</tr>
<tr>
<td>Mn/KIT-6(^a)</td>
<td>5000 ppm CB, Air balance</td>
<td>20,000</td>
<td>211</td>
<td>898</td>
</tr>
<tr>
<td>MnO(_x)/TiO(_2)(^b)</td>
<td>100 ppm CB, Air balance</td>
<td>36,000</td>
<td>&lt; 120</td>
<td>899</td>
</tr>
<tr>
<td>MnO(_x)/TiO(_2)-carbon nanotube(^c)</td>
<td>3000 ppm CB, Air balance</td>
<td>36,000</td>
<td>&lt; 120</td>
<td>909</td>
</tr>
<tr>
<td>Sn-MnCeLaO(_x)(^d)</td>
<td>2500 ppm CB, 20% O(_2), N(_2) balance</td>
<td>20,000</td>
<td>210</td>
<td>902</td>
</tr>
<tr>
<td>MnCeLaO(_x)(^e)</td>
<td>1000 ppm CB, 10% O(_2), N(_2) balance</td>
<td>15,000</td>
<td>&lt; 250</td>
<td>904</td>
</tr>
<tr>
<td>11%MnO(_x)/CeO(_2) nanoparticles</td>
<td>2500 ppm CB, 20% O(_2), N(_2) balance</td>
<td>20,000</td>
<td>275</td>
<td>906</td>
</tr>
<tr>
<td>Ce(_x)-MnO(_x)/TiO(_2)(^f)</td>
<td>2500 ppm CB, Air balance</td>
<td>10,000</td>
<td>198</td>
<td>908</td>
</tr>
<tr>
<td>Cu(<em>{0.15})Mn(</em>{0.15})Ce(_{0.7})O(_x)(^g)</td>
<td>600 ppm CB, Air balance</td>
<td>30,000</td>
<td>255</td>
<td>892</td>
</tr>
<tr>
<td>La(<em>{0.8})Sn(</em>{0.2})MnO(_3)</td>
<td>1000 ppm CB, 10% O(_2), N(_2) balance</td>
<td>15,000</td>
<td>291</td>
<td>889</td>
</tr>
<tr>
<td>1% Ru/Ti-CeO(_2)(^h)</td>
<td>550 ppm CB, Air balance</td>
<td>15,000</td>
<td>&lt; 225</td>
<td>887</td>
</tr>
<tr>
<td>1%Ru-CeO(_2)</td>
<td>550 ppm CB, Air balance</td>
<td>15,000</td>
<td>250</td>
<td>923</td>
</tr>
</tbody>
</table>

\(^a\) Mn : Si molar ratio of 1 : 3; \(^b\) Mn : Ti molar ratio of 1 : 4; \(^c\) Prepared by the sol-gel method; \(^d\) Sn : (Sn+Mn+Ce+La) = 0.08; \(^e\) Mn : (Mn+Ce+La) = 0.86; \(^f\) Catalyst calcined at 400 °C (Ce : Mn : Ti molar ratio of 1 : 1 : 8); \(^g\) Synthesized by the homogeneous coprecipitation method; \(^h\) Ti-CeO\(_2\) support was synthesized by the co-precipitation method with tetrabutyl titanate as the precursor.

A series of metal (Mn, Cu, Fe, Cr, and Sn) loaded mesoporous silica (KIT-6) catalysts were
studied and found that the Mn/KIT-6 (Mn : Si = 1 : 3) possessed the highest activity in this reaction ($T_{90} = 210.7 \, ^\circ C$; GHSV of 36,000 h$^{-1}$) (Fig. 23i).\textsuperscript{898} Mn catalysts on various supports (TiO$_2$, Al$_2$O$_3$ and SiO$_2$) were also investigated with the MnO$_x$/TiO$_2$ demonstrating the best activity. It was found that the highly dispersed MnO$_x$ could be converted into active oxychlorinated manganese species.\textsuperscript{833} Tian \textit{et al.}\textsuperscript{899} further reported that the MnO$_x$/TiO$_2$ catalyst prepared by the sol-gel route with Mn : Ti of 1 : 4 had the best CB oxidation activity compared with samples prepared by solvothermal and co-precipitation methods. The promotion effect of CNTs on MnO$_x$/Al$_2$O$_3$ and MnO$_x$/TiO$_2$ catalysts for CB oxidation was suggested to be due to the superior aromatic adsorption performance of CNTs ($\pi$-$\pi$ interaction between benzene ring and CNTs).\textsuperscript{900,901} Liu and co-workers\textsuperscript{418} stated that the addition of Sn into MnTiO$_x$ mixed oxides markedly enhanced its stability in this reaction (Fig. 23ii). This was linked to a lower average energy being required to desorb Cl species and the absence of MnO$_x$Cl$_y$ on the active sites during the reaction. The above results were also studied and confirmed with SnMnCeLaO$_x$ composites for CB oxidation.\textsuperscript{902}

MnO$_x$-CeO$_2$ mixed oxides and supported MnO$_x$-CeO$_2$ catalysts have been widely studied in the total oxidation of CB. Wang \textit{et al.}\textsuperscript{903} prepared MnO$_x$-CeO$_2$ mixed oxides with different Mn : (Mn+Ce) ratios, and found that the MnO$_x$(0.86)-CeO$_2$ sample exhibited the best catalytic activity and completely oxidized CB at 254 $^\circ$C with a GHSV of 15,000 h$^{-1}$ (Fig. 23iii). Subsequent work indicated that the addition of La promoted the dispersion of MnCeO$_x$ and MnO$_x$ as well as enhanced the stability of MnCeO$_x$ in CB oxidation.\textsuperscript{904,905} The effect of CeO$_2$ morphology (nanoparticle and nanorod) on the performance of MnO$_x$/CeO$_2$ in CB oxidation was reported by Liu and co-workers,\textsuperscript{906} who found that the MnO$_x$/CeO$_2$ nanoparticles possessed a higher catalytic activity.

Many types of oxides have been used as the support for Mn-Ce mixed oxides such as $\gamma$-Al$_2$O$_3$, TiO$_2$, ZSM-5 and cordierite.\textsuperscript{882,907-909} Li and co-workers\textsuperscript{907} suggested that the Mn$_8$Ce$_2/\gamma$-Al$_2$O$_3$ was the most active catalyst in all Mn$_n$Ce$_y/\gamma$-Al$_2$O$_3$ samples which was attributed to its higher reducibility. Subsequent work by the group revealed that the addition of Mg decreased the interaction of Mn and Ce species supported on $\gamma$-Al$_2$O$_3$. Mg addition also promoted the dispersion of Mn and Ce phases and formation of a Ce-Mn-O solid solution, leading to high activity, good selectivity and promising stability of the Mn-Ce-Mg/$\gamma$-Al$_2$O$_3$ catalyst.\textsuperscript{910} He \textit{et al.}\textsuperscript{908} stated that Ce
and Mn species form a solution of MnCeOₓ with perturbed oxygen environments at calcination temperatures of 400 °C which contributed to the high catalytic activity of CeOₓ-MnOₓ/TiO₂. Chen and co-workers⁸⁸² revealed that the Mn₈Co₁Ce₁/cordierite exhibited high activity (T₉₀ = 325 °C; GHSV of 15,000 h⁻¹) and stability for CB oxidation due to the synergistic effect of Ce, Mn and Co and the formation of more lattice defects, more oxygen vacancies and smaller crystallite sizes.

Supported V oxide constitutes a very important class of catalytic materials which are resistant against CVOCs.⁸⁸⁴,⁹¹¹-⁹¹³ Huang et al.⁸⁸³ proposed that a VOₓ/CeO₂ catalyst with monomeric VOₓ had the highest catalytic activity in the deep oxidation of CB. Here, the VOₓ greatly improved the stability of VOₓ/ CeO₂ catalysts through retarding the exchange of Cl for basic surface lattice oxygen of the CeO₂ (Fig. 23iv). TiO₂ has good mechanical, thermal and anticorrosive properties, and it promotes the formation of a well-dispersed monolayer of the VOₓ active phase.⁹¹⁴ It was demonstrated that the addition of SO₄²⁻ species to TiO₂ enhanced the acidity and leaded to a higher activity in this reaction. The beneficial effect of the sulfated TiO₂ was due to an increase in the amount of BAS which promotes the adsorption of aromatics on the support. An increase in the LAS also improves the spreading of the VOₓ phase on the surface of the catalyst.⁷₂⁸,⁹¹⁵ Huang et al.⁹¹⁶ revealed that the addition of MoO₃ to V₂O₅/TiO₂ improved the catalyst redox properties and enhanced the CB oxidation activity at low temperatures. However, the formation of low amounts of polychlorinated compounds over V₂O₅-WO₃/TiO₂ and V₂O₅-MoO₃/TiO₂ was reported by Busca and co-workers.⁹¹⁷

Topka et al.⁹¹⁸ prepared monometallic noble metal (Pt or Au) catalysts supported on Ce-Zr mixed oxide by an impregnation method, and found that Pt catalysts were more efficient than Au analogues due to their superior redox property. The lower acidity of Pt catalysts was not found to be detrimental to their performance in CB oxidation. The catalytic oxidation of CB over Pt catalysts supported on H-ZSM-5 and H-Beta was studied by Crisafulli and co-workers.⁸⁸⁵ The results demonstrated that the activity of Pt/zeolite catalysts was higher for samples with lower SiO₂ : Al₂O₃ ratios (30 and 50). Different amounts of polychlorinated benzenes (PhClₓ) were produced on the catalysts in the order of Pt/H-ZSM5 < Pt/H-beta < Pt/γ-Al₂O₃. The smaller size of the zeolite channels hinders the chlorination of PhCl to PhClₓ. The formation of significant amounts of PhClₓ over Pd-based catalysts (especially at high temperatures) was also reported in the literature.⁷⁶⁶,⁸⁸⁶,⁹¹⁹
Ru-based catalysts were industrially implemented for the large-scale chlorine production via HCl oxidation (Deacon process) due to its higher reactivity, extraordinary stability (limited chlorination and resistance against HCl and Cl₂ exposure) and easier Cl₂ evolution. The catalytic oxidation of CB over Ru doped CeO₂ catalysts was investigated by Lu and co-workers. They revealed that the Ru/CeO₂ exhibited outstanding activity and stability. Subsequent work proposed that doping of Ti enhanced the activity and stability of Ru/CeO₂ catalysts in CB oxidation which was ascribed to a higher proportion of exposed oxygen vacancies and the high energy lattice plane of CeO₂.

3.5.6. 1,2-dichlorobenzene

1,2-dichlorobenzene (o-DCB) is a common industrial solvent for a range of applications such as wax, resin and rubber, as well as being used as a degreasant and cleaning agent. o-DCB has frequently been used in the literature as a model pollutant molecule because its structural similarity to 2,3,7,8-tetrachloro-dibenzodioxin (TCDD) which is the most toxic among a range PCDDs. The catalytic incineration of o-DCB is largely centred on V-, Fe-, Ti- and Mn-based oxides.

The catalytic oxidation of o-DCB was systematically investigated over a series of transition metal oxides (Cr₂O₃, V₂O₅, MoO₃, Fe₂O₃ and Co₃O₄) supported on TiO₂ and Al₂O₃. The results suggested that the TiO₂-supported catalysts are more active than the corresponding Al₂O₃-supported ones (except Co oxide catalysts), indicating that the metal oxide-support interactions are significant in this reaction. Among all catalysts, Cr₂O₃- and V₂O₅-based materials are the most active ones. Choi et al. reported that a vanadia-titania aerogel catalyst with a high surface area and chemical homogeneity possessed superior activity and thermal stability in o-DCB oxidation. Moon and co-workers reported that V₂O₅/TiO₂ catalysts synthesized by a thermal decomposition method showed a good performance in o-DCB decomposition at low temperature, with 95% of o-DCB converted at 200 °C (WHHSV of 18,000 mL·g⁻¹·h⁻¹). Albonetti et al. proposed that the LAS and BAS over V₂O₅/TiO₂ and V₂O₅-WO₃/TiO₂ had strong influences on their catalytic performance in this reaction (Fig. 24i). It was found that the BAS significantly increased the conversion of o-DCB but leaded to the formation of partial oxidation products such as dichloromaleic anhydride. The LAS were suggested to act as absorbing sites, promoting the
further oxidation of intermediates to CO and CO$_2$. The presence of water decreases $o$-DCB conversion but plays a positive role in CO$_x$ selectivity due to the reduction of BAS and the hydrolysis of the anhydride during wet oxidation tests.\textsuperscript{934}

It was reported that the Ca-doped Fe oxide catalysts exhibit higher catalytic activity in the decomposition of CVOCs compared with analogous single Fe oxide materials. This was attributed to the strong interaction between Fe$_2$O$_3$ and CaO which facilitates Cl$^-$ exchange between CaCO$_3$ and FeCl$_3$ (formed from the reaction of $\alpha$-Fe$_2$O$_3$ with $o$-DCB).\textsuperscript{935-937} CaCO$_3$/Fe$_2$O$_3$ nanocomposites were synthesized by Ma et al.\textsuperscript{938} adopting a one-pot method. The sample with 9.5 mol% Ca had the highest activity in $o$-DCB oxidation due to the easier formation of formate species on the surface which are then oxidised through to CO. However, the particle-like CaCO$_3$/Fe$_2$O$_3$ nanocomposite did not perform well under high water vapor content and at lower temperatures (< 350 °C). Based on these results, CaCO$_3$/Fe$_2$O$_3$ nanorods with excellent catalytic activity ($T_{100}$ = 350 °C for the sample with 2.8 mol.% Ca; GHSV of 88,000 h$^{-1}$), water-resistance and thermal stability were further obtained by Chen and co-workers.\textsuperscript{935} The authors attributed the excellent catalytic performance to the unique surface morphology and interfacial microstructure composed of CaCO$_3$ and $\alpha$-Fe$_2$O$_3$ nanorods. The morphology and microstructure of the catalysts plays an important role in the catalytic performance. Hollow microspheres with low density, high surface area, stability and excellent surface permeability have received increasing interest for application in heterogeneous reactions.\textsuperscript{939} Zheng and co-workers\textsuperscript{929} revealed that the optimal Ca-doped FeO$_x$ hollow microsphere (9.7 mol% Ca) exhibited not only excellent catalytic activity, water-resistant performance and stability, but low $E_a$ (21.6 kJ·mol$^{-1}$) in deep oxidation of $o$-DCB.

Mn-modified Co$_3$O$_4$ catalysts with spinel structure were prepared by Cai et al.\textsuperscript{807} using the co-precipitation method. The results revealed that the catalyst with a Co : Mn ratio of 9 : 1 presents the highest activity ($T_{90}$ = 347 °C; GHSV of 15,000 h$^{-1}$) and good stability which was ascribed to the synergetic effect between the activation of $o$-DCB on Co$^{2+}$ sites and subsequent oxidation by surface active oxygen in Co$_3$O$_4$ nanoparticles. Recently, Zhang and co-workers\textsuperscript{931} reported that addition of Ce or Ce+Fe into MnO$_x$ oxides promoted the formation of an amorphous powder rather than a crystalline material which enhanced their specific surface area and redox property, leading to an overall higher activity for $o$-DCB incineration.

Choi et al.\textsuperscript{940} reported that nano-sized Fe$_3$O$_4$@TiO$_2$ composites exhibited a higher $o$-DCB
oxidation activity than that of pure Fe$_3$O$_4$ and TiO$_2$. It was suggested that oxygen vacancies on Fe$_3$O$_{4+\delta}$ played an important role in the adsorption and reaction of CO, and TiO$_2$ provided oxygen to the Fe$_3$O$_{4+\delta}$ sites. Recently, Ce$_{1-x}$Ti$_x$O$_2$ mixed oxides with various Ti : (Ce+Ti) ratios were prepared by a sol-gel method and used in the catalytic oxidation of o-DCB. The results demonstrated that the incorporation of Ti distorted the crystal structure and thus greatly increased the acidity and oxygen mobility at high temperatures. The catalyst with a Ti : (Ce+Ti) ratio of 0.5 was shown to achieve the best performance in this reaction (Fig. 24ii). Ti improves the stability of Ce$_{1-x}$Ti$_x$O$_2$ catalysts by retarding the exchange of Cl with basic lattice oxygen and hydroxyl groups.

3.6. Nitrogen-containing VOCs

Nitrogen-containing VOCs (NVOCs) (e.g., acetonitrile, ethylenediamine, n-butylamine, pyridine and acrylonitrile) are widely used in industrial processes. For instance, acrylonitrile is used to make acrylic fibers, resins, and nitrile elastomers, and is employed as an intermediate in the production of adiponitrile and acrylamide. The crucial point for NVOCs catalytic oxidation lies in the control of NO$_x$ generation and prevention of secondary pollutants.

Guerrero-Pérez et al. indicated that the Sb-V-O/γ-Al$_2$O$_3$ catalyst synthesized via a tartrate method was a good candidate to eliminate NVOCs. This synthesis method provided dispersed Sb oxide and optimized the VSbO$_4$-Sb interphase, resulting in superior selectivity to N$_2$. PILC supported CrO$_x$-CeO$_2$ mixed oxides were studied in the oxidation of NVOCs. Na-montmorillonite and different pillared interlayered clay (Al-PILC, Zr-PILC, Ti-PILC and Al$_2$O$_3$/Ti-PILC) supported CrCe catalysts were reported by Zhou and co-workers in deep oxidation of n-butylamine and ethylenediamine. The results demonstrated that the mesoporous structure and the acid sites improved the catalytic activity of supported CrCe catalysts. CrCe/Ti-PILC and CrCe/Al$_2$O$_3$/Ti-PILC had higher catalytic activity than other catalysts. The strong adsorption of ethylenediamine on the acid sites led to a lower activity compared with n-butylamine. Subsequent work suggested that addition of an appropriate amount of CeO$_2$ enhanced the interaction between Cr and Ce, increasing the acid strength and mobility of active oxygen species on the catalyst. 8CrCe(6:1)/Ti-PILC exhibited the best catalytic performance and control of NO$_x$ in n-butylamine oxidation.
Nitrile gases such as acetonitrile and acrylonitrile are commonly classified as very toxic nitrogen-containing VOCs and can lead to serious environmental problems due to their hazardous properties. Noble metal (e.g., Pt and Pd) catalysts were found to be undesirable for nitrile oxidation due to the formation of NOx. Among transition metal-based catalysts, porous silica- or titania-supported copper catalysts have been reported to show the excellent performance in nitrile oxidation. A series of M/SBA-15 (M = Cu, Co, Fe, V and Mn) and noble metals (Pd, Ag and Pt) catalysts were prepared via the impregnation method and further used in acetonitrile oxidation by Chen and co-workers. Cu/SBA-15 was found to exhibit a near complete CH3CN conversion with a N2 selectivity of 80% at temperatures higher than 350 °C. Nanba et al. revealed that Cu/ZSM-5 with a Cu loading of > 2.3 wt.% show a high N2 selectivity (exceeding 90% above 350 °C) in acrylonitrile oxidation. The authors proposed that N2 formation from NH3 proceeds on Cu2+, resulting in the formation of Cu+ ions, which were then oxidized to Cu2+ at around 300 °C. Thus, a high N2 selectivity over Cu-ZSM-5 was attained over a wide range of temperatures by the reaction over the square-planar Cu2+. Subsequent work indicated that over Cu/ZSM-5 catalyst, acrylonitrile is mostly converted to isocyanate (-NCO), which was likely converted to adsorbed NH3 by hydrolysis. N2 was formed by the reaction of adsorbed NH3 and adsorbed nitrate or by oxidation of adsorbed NH3. It was reported that the presence of water suppressed the desorption of acrylonitrile and reduced the temperature of N2 evolution.

The high acrylonitrile decomposition activity of supported Ag catalysts was also reported by Obuchi and co-workers. Here, it was found that the activity was greatly influenced by the type of material used to support Ag, with TiO2 being described as an effective support. This Ag/TiO2 catalyst was composed of both metallic and oxidized Ag species. The metallic Ag exhibited a high acrylonitrile oxidation activity, whereas the oxidized Ag exhibited high acrylonitrile hydrolysis activity. The influence of the TiO2 crystal structure on acrylonitrile oxidation was also studied. The results indicated that the anatase phase of TiO2 favours the formation of ionic Ag, whereas the rutile phase favours that of metallic Ag. The Ag/anatase-TiO2 catalyst exhibited a high NH3 and N2 selectivity at low and high temperatures, respectively.

3.7. Sulfur-containing VOCs
3.7.1. Methyl mercaptan

Methyl mercaptan (CH$_3$SH) is a highly odorous sulfur-containing volatile organic compound (SVOCs) and is widely distributed in petroleum products and industry off-gases.$^{958-960}$ Even a small amount of CH$_3$SH in the atmosphere is harmful and can have adverse effects on humans.$^{961}$ The presence of CH$_3$SH is also a source of catalyst deactivation during many catalytic reactions such as synthesis of methanol and ammonia.$^{962}$ Catalytic abatement is regarded as an effective method for the complete removal of CH$_3$SH as it is both environmentally friendly and economically feasible. It produces low waste products and does not require the addition of any reagents during the desulfurization processes.$^{963-965}$

CeO$_2$ is well known as a major catalyst for CH$_3$SH catalytic decomposition.$^{966}$ CeO$_2$ nanoparticles were prepared by He et al.$^{967,968}$ using a convenient microwave-assisted sol-gel method. The results suggested that CeO$_2$-based catalysts are effective sulfur absorbents at high temperature. Various Ce-S compounds including cerium sulfide (Ce$_2$S$_3$) and cerium sulfate (Ce(SO$_4$)$_2$) are formed. The formation of Ce$_2$S$_3$ in the latter period of reaction causes a severe decline in the catalytic activity. Doping the surface with appropriate metal ions, especially some trivalent rare earth cations with different ionic radii, can enhance the stability of pure CeO$_2$. A series of rare earth (Y, Sm, and La) doped CeO$_2$ composite oxides were synthesized by He et al.$^{969}$ and evaluated in CH$_3$SH catalytic decomposition. A higher population of oxygen vacancies and increased basic sites were observed in the rare earth doped CeO$_2$ catalysts. A Y doped CeO$_2$ sample (Ce$_{0.75}$Y$_{0.25}$O$_{2-\delta}$) with a moderate increase in basic sites demonstrated a higher stability than CeO$_2$, while the La doped CeO$_2$ catalyst with highest alkalinity possessed the lowest stability. The superior stability of Ce$_{0.75}$Gd$_{0.25}$O$_{2-\delta}$ for CH$_3$SH oxidation was proposed in their recent work.$^{970}$

HZSM-5 zeolite was considered as a good candidate for catalytic decomposition of CH$_3$SH, over which complete decomposition to H$_2$S and some hydrocarbons (CH$_4$, C$_2$H$_6$ and C$_2$H$_4$) was achieved above 550 °C.$^{971,972}$ However, the stability of a pure HZSM-5 zeolite catalyst is not satisfactory, and serious deactivation of the catalyst can be observed. This is due to the presence of strong acid sites which usually promotes the formation of coke deposits.$^{24,973}$ Recently, HZSM-5 zeolite catalysts modified with various rare earth metals (Nd, Er, and Y) were prepared and used for CH$_3$SH catalytic decomposition.$^{960}$ The addition of rare earth metals significantly
improved the activity and stability of HZSM-5. A 13 wt.% Nd/ZSM-5 catalyst was found to exhibit the best performance. Characterization results revealed that the concentration of strong acid sites in the HZSM-5 catalysts decreased after rare earth metals addition, while the concentration of basic sites increased (displayed better adsorption ability to CH$_3$SH).\textsuperscript{960,974}

3.7.2. Dimethyl disulfide

Dimethyl disulfide (DMDS) is difficult to oxidize when compared with other SVOCs present in the waste gas streams. Moreover, DMDS is among the most odorous compounds due to its low human detection threshold (2.5 μg·m$^{-3}$),\textsuperscript{975} which makes its complete removal an important issue.

Wang \textit{et al.}\textsuperscript{976-978} reported that the addition of molybdenum promoted the catalytic activity of CuO/$\gamma$-Al$_2$O$_3$ in deep oxidation of dimethyl disulfide. The catalyst with a formula of 5 wt.% Cu-10 wt.% Mo/sulfated-$\gamma$-Al$_2$O$_3$ ($\gamma$-Al$_2$O$_3$ treated with sulfuric acid) was shown to have the best activity. The performance of a CuO-MoO$_3$/$\gamma$-Al$_2$O$_3$ catalyst was further promoted in subsequent work by the addition of Cr.\textsuperscript{979} A 5 wt.% Cu-6 wt.% Mo-4 wt.% Cr/sulfated-$\gamma$-Al$_2$O$_3$ sample was found to possess the highest DMDS oxidation activity and sulfur resistance.

Among transition and noble metals, Au shows the lowest reactivity towards sulfur which is ascribed to its high electronegativity. This result in Au is not readily reacting with other electronegative elements such as sulfur.\textsuperscript{980} Recently, Au, Cu and Pt catalysts supported on Al$_2$O$_3$, CeO$_2$ and CeO$_2$-Al$_2$O$_3$ were investigated in the oxidation of DMDS. The results demonstrated that the Au/CeO$_2$-Al$_2$O$_3$ catalyst had good stability during over a 40 h test. The presence of Cu resulted in the significant generation of formaldehyde instead of CO$_2$, and Pt catalysts exhibited over-oxidation or potential for deactivation when supported on Al$_2$O$_3$ and CeO$_2$-Al$_2$O$_3$.\textsuperscript{963} The stable and efficient DMDS incineration capability of a Au/TiO$_2$ catalyst was proposed by Keiski and co-workers.\textsuperscript{981}

It was reported that an amorphous SiO$_2$-Al$_2$O$_3$ support increases the material’s resistance against sulfur poisoning.\textsuperscript{982} Furthermore, the isoelectric point of SiO$_2$ can be enhanced by addition of Al$_2$O$_3$ as this improves the interaction between support and active metals.\textsuperscript{983} Darif \textit{et al.}\textsuperscript{984} found that the doping of SiO$_2$ led to a more selective and stable catalyst (Pt-Cu/(Al$_2$O$_3$)$_{0.8}$(SiO$_2$)$_{0.2}$), however the DMDS conversion over Pt-Cu/(Al$_2$O$_3$)$_{0.8}$(SiO$_2$)$_{0.2}$ was close to that of Pt-Cu/Al$_2$O$_3$. Recently, the sulfur deactivation process of Pt/Al$_2$O$_3$ catalyst was
further studied by Keiski and co-workers. They proposed that the decrease in the activity of industrially aged Pt/Al catalyst originated from a number of factors. The decrease in the active surface area due to support sintering, chemical poisoning from sulfate formation, increase in Pt particle size and formation of highly oxidized Pt(IV) species that were less tolerant against sulfur were all described as major issues. The addition of SiO₂ (20 mol%) into the Al₂O₃ support enhanced the stability and sulfur resistance of Pt catalyst (Fig. 25).

4. Monolithic catalyst for VOC destruction

For practical applications, the use of structured materials which exhibit good structural and thermal stabilities, induce only a minimal pressure drop, and possess a good tolerance to plugging are desirable properties for a catalytic reactor. For this reason, extruded materials such as monoliths are ideal structures for supporting catalysts as they are typically exhibit high surface areas and possess numerous parallel channels, which reduces pressure drops across the catalyst bed. They are also highly tunable; monoliths can be produced in many different sizes and shapes, and can be synthesized from lots of different materials, including; metal wires, meshes or foams, metallic or ceramic membranes, and cordierite honeycomb materials, which have attracted increasing attention due to their high mechanical strength and heat transfer capacity.

In general, wire-mesh structured monoliths possess high thermal conductivity and mechanical strength, making them applicable to several industrial and environmental processes. A great variety of wire-mesh monoliths currently exist and their applicability is typically determined by the diameter of their internal channels and the diameter and material of the wire used. The catalytic oxidation of n-hexane, acetyl acetate and toluene was investigated over Pt-CeO₂ deposited on monolithic stainless steel wire meshes (Fig. 26i). The results from these experiments confirmed that all of these VOCs could be completely oxidized at temperatures ranging from 200 to 350 °C. The excellent mechanical stability of these materials was confirmed by an ultrasound method. Li et al. demonstrated that a series of Pd-based FeCrAl wire-mesh monoliths could be prepared by an electroless plating methodology. The Pd/FeCrAl catalysts had no alumina
interlayers in their structure and consisted of between 0.3 and 0.4 wt.% Pd. These catalysts were calcined at 800 °C and determined to be highly active and stable for the total oxidation of toluene. The high activity and stability was suggested to be attributed to the in situ formation of a molten PdO phase (0.1-1 μm in diameter). Kuśtrowski and co-workers also confirmed that plasma-deposited cobalt oxide supported knitted wire gauzes were highly effective as for the oxidation of n-hexane (Fig. 26ii). The reaction was demonstrated to be first-order with an activation energy of 143.5 kJ/mol. A plug-flow reactor model was proved to reflect the real reactor performance with satisfactory accuracy.

Porous structured foams and membranes can increase turbulence and radial mixing in gas streams, which can reduce laminar flow and mass transfer issues in monoliths or honeycombs catalysts. Zhao et al. synthesized a white graphene foam (consisting of a low-dimensional boron nitride nanosheet; 3D BN) with multi-level pores, atomically thin walls and a specific surface area of 681 m²·g⁻¹ (Fig. 26iii). Ag was subsequently supported onto this material and tested for the oxidation of methanol. Over this catalyst, a 95 % methanol conversion was achieved at temperatures as low as 110 °C (GHSV of 40,000 h⁻¹); substantially lower than the T₉₀ observed over a Ag/γ-Al₂O₃ catalyst, which was also notably less stable. Ribeiro et al. explored how the method of preparing Pt zeolite coated cordierite foams affected catalytic performance in the oxidation of toluene. The authors revealed that the open structure of the foams, the formation of a homogeneous thin zeolite layer and the size of the deposited Pt particles were greatly affected by the dipping procedure used. Recently, a facile strategy for the in situ growth of hierarchical Co₃O₄ nanostructures on the surface of a 3D nickel foam was reported by Ye and co-workers (Fig. 26iv). The authors determined that materials with columnar Co₃O₄ nanoclusters on nickel foam exhibited excellent catalytic activities for the oxidation of toluene; with the best catalyst, full toluene oxidation was achieved at 270 °C with a GHSV of 20,000 h⁻¹ (50 °C lower than that of Co₂AlO₄ catalysts) (Fig. 26v and vi). Wang et al. revealed that a Mn/ZSM-5 membrane catalyst with a paper-like stainless steel fiber (PSSF) morphology could achieve 2-propanol conversion greater than 90% at 222 °C (GHSV of 7643 h⁻¹), which is a far lower temperature than that observed over a granular Mn/ZSM-5 catalyst (T₉₀ = 297 °C). Porous Cu/Mn binary oxide modified ZSM-5 catalyst were also prepared by the same group; the most efficient of these catalysts was a Cu-Mn(1:6)/ZSM-5/PSSF, which achieved a 2-propanol
conversion greater than 90% at 210 °C under the GHSV of 3822 h⁻¹. In a subsequent study, Yan et al.⁶³³ reported that over a Co/ZSM-5/PSSF catalyst, isopropanol conversions greater than 90% could be achieved at ca. 220 °C (GHSV of 7643 h⁻¹); similar to that observed over the Mn/ZSM-5/PSSF. This was achieved in a zeolite membrane reactor, which is much more efficient than a traditional particle fixed bed reactor. In addition, porous Co-Cu-Mn mixed oxide modified ZSM-5/PSSF catalysts were also confirmed to be efficient for the total oxidation of 2-propanol by the same researchers.¹⁰⁹ Huang et al.¹⁰⁰⁶ reported that 3D Co₀.₆⁵Mn₂₃₅O₄ (grown on carbon textile substrates) nanosheets exhibited remarkably long-term durability and high catalytic activity for the oxidation of formaldehyde; a full conversion was achieved at 100 °C with a GHSV of 120,000 mL·h⁻¹·g⁻¹. Recently, Chen and co-workers⁹⁹¹ prepared a series of monolithic Mn/Ce-based ceramic membrane (CM) catalysts (Fig. 27i). The catalysts were prepared using an impregnation method and characterization of these materials revealed that the fibrous CMs possessed a unique interconnected, uniform pore structure, and the MnOₓ-CeO₂ active phase was homogenously dispersed into the porous CMs support. A catalyst with a MnOₓ : CeO₂ ratio of 3 : 1 exhibited the highest activity for the total oxidation of benzene (T₉₀ = 244 °C; GHSV = 5000 h⁻¹) and was determined to be stable with up to 90 vol.% of water in the stream (20 °C). The high activity of this catalyst was associated with its good low temperature reducibility, abundance of active oxygen and a synergetic effect between MnOₓ and CeO₂.

Metallic monoliths are also considered to be promising catalysts for the oxidation of VOCs. This is typically attributed to their excellent heat transfer, good ductility and mechanical stability.¹⁰⁰⁷ However, the industrial application of these materials is often limited, due to their high cost, low chemical stability and difficulties associated with immobilizing catalysts on to them.⁹⁹⁹,¹⁰⁰⁸ Cordierite monoliths (2MgO-2Al₂O₃-5SiO₂) are highly porous, often have good thermal and chemical stabilities and exhibit excellent refractoriness and coating adherence. These materials typically have a high resistance to elevated temperatures and temperature shocks because of their low thermal expansion coefficient, making them suitable for application as a monolithic catalyst support.⁹⁹²,¹⁰⁰⁹,¹⁰¹⁰ It is often necessary to use an inorganic oxide pre-coat (washcoat), which can increase the surface area of the material and act as a secondary support for the active phase. The most common washcoat material is γ-Al₂O₃, but numerous other materials such as La₂O₃, CeO₂, ZrO₂, carbons and zeolites have also been investigated.⁵⁵⁷,⁵⁷₃,⁷₅₈,⁹₉₃,¹⁰¹¹-¹⁰¹₃
The method used for the deposition of the secondary support can also influence the resultant catalytic performance. Various strategies have been implemented for the initial coating of the monolith, which is generally followed by the subsequent deposition or immobilization of the active phase.\textsuperscript{1014}

Huang \textit{et al.}\textsuperscript{1011} investigated the catalytic combustion of toluene over cordierite-supported Ni-Mn composite catalysts, which were prepared by a wet impregnation method. The authors reported that the catalytic activity of the synthesized materials was strongly dependent on a number of factors, which included; the molar ratio of Ni/Mn, the loading of the Ni-Mn oxide and the calcination temperature. A catalyst with a Ni/Mn ratio of 0.5 displayed the highest activity for the oxidation of toluene; a 92.1% conversion of toluene was observed at 300 °C. This catalyst had a 10 wt.% Ni/Mn loading and was calcined at 400 °C. Azalim \textit{et al.}\textsuperscript{1012} proposed that the high activity of Mn-Ce-Zr/cordierite catalysts for the oxidation of \textit{n}-butanol was heavily dependent on the method used to immobilize the active phase. In this study, corresponding Mn-Ce-Zr/cordierite catalysts were synthesized by one-pot precipitation (Ce, Mn and Zr nitrates mixed together) and impregnation (Mn loaded over the Ce-Zr washcoated phase). The catalysts prepared in the one pot precipitation were determined to be significantly more active than the corresponding impregnated catalysts. The notable differences in performance were attributed to the former method producing a highly active thin layer of Mn-Ce-Zr, which exhibited a high specific surface area and was easily reducible.

Jin and co-workers\textsuperscript{993} prepared a series of Pd/Ce\textsubscript{x}Y\textsubscript{1-x}O\textsubscript{δ}/cordierite honeycomb catalysts and determined that the Ce\textsubscript{x}Y\textsubscript{1-x}O\textsubscript{6} washcoat exhibited a better adhesion and had a higher vibration- and heat-resistance when compared to other conventional washcoats. The formation of CeO\textsubscript{2}-Y\textsubscript{2}O\textsubscript{3} and PdO phases at high calcination temperatures resulted in increased thermal stability. The highest catalytic activity for the oxidation of toluene was exhibited by a Pd/Ce\textsubscript{0.8}Y\textsubscript{0.2}O\textsubscript{δ}/cordierite honeycomb catalyst; full oxidation of toluene was observed at 210 °C. Carbon-coated monoliths have also been considered as catalyst supports for industrial applications due to their mechanical resistance, and desireable chemical and textural properties.\textsuperscript{557,1015} Carbon nanofiber (CNF)-coated monoliths with a very thin, homogeneous, well-adhered CNF layer were investigated as supports by Morales-Torres \textit{et al.}\textsuperscript{1013} for the decomposition of ethylene over Ni particles. These catalysts were determined to be more active.
for the oxidation of benzene than toluene or m-xylene, which was ascribed to a better aromatic-support dispersive interaction. The study indicated that the CNF-coated monoliths were also more affective supports than alumina for Pt or Pd catalysts in the gas phase catalytic combustion of BTX at low temperatures; the CNF surface is more hydrophobic than that of \( \gamma\)-Al\(_2\)O\(_3\).\(^{1013}\)

The structure of the support on the monolith can also influence the resultant activity in VOC oxidation reactions. Pérez-Cadenas et al.\(^{1016}\) investigated how the pore structure of carbon-based monoliths effected the performance of Pd supported catalysts. For this, a number of different monoliths were used; a classical square channel cordierite modified with \( \alpha\)-Al\(_2\)O\(_3\) to block any macroporosity in the cordierite and round the channel cross-sections (HPM); a composite carbon/ceramic monolith with micropores (WA); and a monolith consisting of mesopores (WB) (Fig. 27ii). The activity of these catalysts was determined to decreases in the order of Pd/WB > Pd/WA > Pd/HPM. The notable difference in the activity of these catalysts evidenced the influential effect of the surface area. In another study, monolithic cordierite catalysts with Au nanoparticles supported on Ce\(_{0.5}\)Zr\(_{0.5}\)O\(_2\) were prepared by washcoating with powdered gold/ceria-zirconia (AuCeZr) and by deposition of gold on the monolith washcoated with ceria-zirconia (Au/CeZr). Characterization of these materials indicated that the Au/CeZr catalyst exhibited a smaller mean Au particle size (ca. 6.7 nm) and was more active for the oxidation of ethanol \((T_{50} = 80 ^\circ C)\) than the AuCeZr catalyst, which had a mean Au particle size of ca. 13.2 nm \((T_{50} = 120 ^\circ C)\).\(^{1017}\) Recently, Lu and co-workers\(^{1018}\) reported an efficient, economic and simple strategy for the synthesis of Pt/TiO\(_2\) monolith catalysts, which involved spraying a dispersed Pt/TiO\(_2\) liquid on different substrates (Fig. 28). This study revealed that a Pt/TiO\(_2\) cordierite monolithic catalyst, which had a Pt loading of 0.1 wt\%, exhibited excellent catalytic activity \((T_{90} = 212 ^\circ C; \text{GHSV of } 3000 \text{ h}^{-1})\) and stability (without deactivation during a 120 h test) for the oxidation of toluene. This catalyst also displayed good vibration resistance; a mass loss of only 0.11% was reported after 1 h of ultrasonic vibration under experimental conditions.

When designing catalytic systems for total oxidation reactions, detailed data concerning the effects of mass and heat transfer on the catalytic reaction rates should be considered carefully.\(^{1019}\)

In the case of fixed beds with small catalyst particles, both interparticle and intraparticle
diffusional limitations are minimized when a highly turbulent flow is employed, but comes at the cost of a high pressure drop. With honeycomb monoliths, the flow inside the channels is deeply laminar, but the pressure drop is negligible, which is a prerequisite for many environmental processes.\(^{551}\) When the monolith is operated at low temperatures, catalytic reaction rates are typically slow, which ultimately limits the overall conversion of the reactant. At higher temperatures, mass transfer typically has a much weaker dependence on temperature than reaction rates and is therefore, more likely to become rate-limiting.\(^{1020}\) The correct interpretation of the mass transfer phenomena occurring in the oxidation process is essential to define operating conditions for the affective removal of VOCs.\(^{1021}\)

Hayes et al.\(^{1020}\) studied the influence of the washcoat and channel shape on mass transfer and concluded that for non-uniform washcoats, the Sherwood numbers and hence the mass transfer coefficient, varies along the gas solid interface. The authors determined that the washcoat thickness, channel radius and angular diffusion in the washcoat; caused by variable thickness in non-symmetrical geometries, were the three predominant factors that determined mass transfer in this system. Hayes et al.\(^{1022}\) subsequently used a 2D finite element monolith reactor model to study external and internal heat transfer in ceramic monoliths for the catalytic oxidation of propane. The authors determined that heat radiation and conduction effected the outlet temperature, with axial conduction resulting in the most significant effects. A separate study invoked the use of a 2D heterogeneous model to also investigate behavior in monolithic reactors.\(^{1023}\) The authors reported that both inter- and intra-phasic diffusion limitations had to be considered when modeling complex reactor configurations like monolith reactors, especially given that monoliths with thicker catalytic layers are typically operated at higher temperatures. The authors concluded that the 2D model was suitable to describe the overall behavior of the monolith reactor and in particularly, assisted with identifying the effect of every single process; the interphasic mass transfer, the chemical reaction and the intraphasic mass transfer. Similar results were also put forth by Rodríguez and Cadús,\(^{1024}\) who explored the catalytic oxidation of oxygenated VOCs (ethanol and acetaldehyde) over manganese-copper mixed oxide catalysts in a monolithic reactor using an isothermal 1D heterogeneous model. This study revealed that the overall rate of the process was, under some reaction conditions limited by internal diffusion (e.g., thick washcoats and high conversions of VOCs); however, the overall process rate was limited by
external mass transfer resistance to the catalyst at high temperatures and/or monoliths with poor interfacial areas.

The washcoat often has a non-uniform thickness, as coatings often tend to accumulate on corners which has a detrimental effect on catalyst performance. It is therefore vitally important that such factors are incorporated into models for mass transfer resistances to ensure that the performance of monolithic reactors are accurately assessed.\textsuperscript{1025} The effect of catalyst accumulation at the corners of a square section channel was investigated by Borio and co-workers.\textsuperscript{1026} Non-uniform coatings resulted in a considerable deterioration in the averaged effectiveness factors of two reactions; the catalytic oxidation of ethanol and acetaldehyde. The decrease in the reactor performance, resulting from the catalyst accumulation, was magnified as the feed concentration increased. Due to the reduction in performance, higher feed temperatures and/or lower space velocities were necessary to ensure the complete destruction of the VOC was achieved.

Klenov \textit{et al.}\textsuperscript{1027} studied the influence of flow rate on heterogeneous reactions over porous honeycomb monoliths with triangular channels. It was determined that there was no stabilization of the reacting flow over the whole of the channel length under the reaction conditions used in this study (Fig. 29i). The most radical changes of the gas streams appeared near the channel inlet, which caused the highest localized rates of interphase exchange processes; the resultant difference in rates observed was up to two orders of magnitude different (Fig. 29ii). A higher reaction rate existed in the initial section due to penetration of the feed components into the catalyst channels through the frontal surface, leading to an increase in the effectiveness factor (Fig. 29iii). The reaction rate limitation by the transport of reagents inside porous wall was observed along the monolith length.

5. Influence of reaction conditions

Based on the results reported in the literature, it can be concluded that the reactivity of VOCs over catalysts generally follows the order of alkanes < arenes < esters < ketones < alcohols < aldehydes,\textsuperscript{15,194,382,579,1028-1030} and heteroatom (S/Cl)-containing hydrocarbons are usually more stable than those of aliphatic hydrocarbons and arenes.\textsuperscript{408,1031} However, the oxidation behavior of VOCs is also greatly influenced by reactant composition and reaction conditions.
5.1. Effect of water vapor

Water is often present in flue gases emitted from various industries and is also one of the products of VOC catalytic oxidation. The effects of water vapor on catalytic activity were explored and reported, and the role of water in VOC catalytic oxidation is very complex, depending on many factors such as catalyst component, VOC type and reaction conditions. In most cases, water vapor is found to act as an inhibitor for VOC oxidation. Marécot et al.\textsuperscript{1032} reported that the presence of water inhibited the oxidation of propane and propene over Pd and Pt supported Al\textsubscript{2}O\textsubscript{3} catalysts due to decreasing of active surface for the reactions. The inhibition effects of catalytic deep oxidation of ethylacetate to CO\textsubscript{2} over Pt/\gamma-Al\textsubscript{2}O\textsubscript{3} and Pt/TiO\textsubscript{2}-WO\textsubscript{3} catalysts were also found by Verykios and co-workers.\textsuperscript{1033} It is interesting to note that the water promotes the decomposition of ethylacetate, which hydrolyzes to ethanol and acetic acid. However, the obvious inhibition effect of water on conversion of ethylacetate over cryptomelane-type Mn oxide was also reported recently.\textsuperscript{1034}

The inhibition effects of water on the catalytic oxidation of aromatic hydrocarbons (e.g., benzene, toluene, o-xylene and styrene) were also investigated. Park and co-workers\textsuperscript{537} proposed that the presence of water vapor in the feed had a negative impact on the activity of 1.0 wt.% Pt/HRM(400) catalyst (HRM(400): acid-treated red mud calcined at 400 °C) in the oxidation of benzene, toluene, o-xylene and hexane. Similar results were also found over a Ru-5Co/TiO\textsubscript{2} catalyst in benzene oxidation at low temperature (210 °C), whereas the catalytic efficiency was barely influenced at higher temperature (230 °C).\textsuperscript{1035} Pan et al.\textsuperscript{1036} revealed that presence of water vapor had a significant and negative effect on the catalytic activity of CuO/\gamma-Al\textsubscript{2}O\textsubscript{3}, CuO/SiO\textsubscript{2} and CuO/TiO\textsubscript{2} catalysts in styrene oxidation due to the competitive adsorption of water molecules. Among them, CuO/TiO\textsubscript{2} exhibited the best durability to water vapor, while CuO/\gamma-Al\textsubscript{2}O\textsubscript{3} had the poorest. Further studies revealed that the presence of water vapor had a negative effect on toluene oxidation activity over CuMn-based catalysts due to the competition of water and toluene molecules for adsorption on surface active sites.\textsuperscript{1037} Similar results were also reported by Verykios and co-workers.\textsuperscript{1038} Recent work reported by Li et al.\textsuperscript{381} suggested that the water vapor had a significant negative influence on the activity of mesoporous Co\textsubscript{3}O\textsubscript{4} catalysts in toluene oxidation (toluene conversion dropped from 90% to 61% in the presence of 5 vol.% of water vapor at 225 °C), while this effect could be fully eliminated after removing the water. The
inhibition effect of water vapor on toluene oxidation over CeO$_2$ hierarchical microspheres was also reported by Li and co-workers.$^{1039}$

The inhibition effects of water vapor on CVOCs were reported by different researchers. Bertinchamps et al.$^{1040}$ indicated that water had two negative effects on VO$_x$/TiO$_2$, VO$_x$-WO$_y$/TiO$_2$ and VO$_x$-MoO$_y$/TiO$_2$ catalysts in CB oxidation, that is, the reduction of the V phase and decrease in the number of strong BAS which were involved in the adsorption of CB. Dai et al.$^{1041}$ reported that the presence of water not only obviously inhibited the oxidation of 1,2-DCE over VO$_x$/CeO$_2$ materials mainly due to the blockage or competitive adsorption of active sites, but had retarding effect on strong Brønsted acid sites from VO$_x$ species. Their following work indicated that the presence of water also dramatically inhibited the activity of CeO$_2$@HZSM-5 for 1,2-DCE oxidation; however, water also completely suppressed the formation of PCHs by-products.$^{824}$ A high Si : Al ratio can also improve the water-resistance due to the increase in hydrophobicity. Analogous results were obtained in 1,2-DCE and TCE incineration over Ce-Cr supported catalysts and Ce-Zr mixed oxides.$^{830,837,1031}$

Although water is commonly regarded as a poison in the catalytic oxidation of VOCs, in some cases, the presence of water vapor may be beneficial. Kullavanijaya et al.$^{1042}$ reported that water enhanced the catalytic oxidation of cyclohexene over Pt and Rh catalysts on CeO$_2$-Al$_2$O$_3$ supports, possibly due to high activity of Rh and Pt for steam reforming. Dai and co-workers.$^{501}$ proposed that the enhancement in catalytic activity for toluene oxidation over 0.27 wt.% Pt/3DOM 26.9CeO$_2$-Al$_2$O$_3$ in the presence of moisture could be ascribed to an enhanced reoxidation of reduced CeO$_2$ by water. Subsequent work from the same group also suggested that the presence of water vapor had a positive effect (beneficial to oxygen activation) and a negative effect (competitive adsorption of water and reactant molecules) on toluene oxidation over the Au-based catalysts.$^{528}$ The positive effects of water vapor on the catalytic oxidation formaldehyde were reported. Wang et al.$^{1043}$ indicated that both surface bound water and atmospheric water compensated the consumed hydroxyl groups to sustain the oxidation of formaldehyde over birnessite. Additionally, atmospheric water stimulated the desorption of carbonate via a water competitive adsorption, leading to a recovery in the birnessite activity. Leung and co-workers$^{1044}$ reported that hydroxyl radicals (·OH) from water vapor dissociation favored the adsorption and transfer of oxygen on the Pd/TiO$_2$ catalysts, which enhanced formaldehyde oxidation.
For catalytic incineration of CVOCs, many researchers have demonstrated the positive role water can play in removing Cl⁻ from the active sites which prevents the deactivation of catalysts. Zhang et al. revealed that a Pt-structured anodic Al₂O₃ catalyst also demonstrated a high chlorine-resistance under moisture atmospheres, as water promoted the reaction of DCM transformation to clean chloride by-products from active sites. H-zeolites were strongly hydrated restoring hydroxyl groups to maintain their activities under wet conditions.

Water vapor can act as hydrolysing agent and a source of hydrogen to help decrease by-product formation. Abdullah et al. proposed that the presence of water increased the CO₂ yield in TCE oxidation over a H-ZSM-5 catalyst by supply of hydrogen and suppressing chlorine-transfer reactions. López-Fonseca et al. stated that the presence of water in the gaseous stream exhibited substantial beneficial effects on the performance of noble metal supported zeolite materials since water acted as an efficient cleaning agent for chlorine species from the surface of the catalysts. Furthermore, the addition of water was also important for producing the desired HCl rather than Cl₂, and the formation of tetrachloroethylene also considerably decrease. Analogous results were also reported by González-Marcos and co-workers, who found that the presence of water could promote complete oxidation of TCE to CO₂ and greatly improved HCl selectivity over Pt/Al₂O₃ and Pd/Al₂O₃ catalysts, while the selectivities to C₂Cl₄ and Cl₂ were greatly reduced.

In order to avoid the inhibition effect of water, hydrophobic supports have been utilized to expel water from catalyst surface. Wu and Chang reported that the use of a Pt/SDB (SDB: porous styrene divinylbenzene copolymer) catalyst produced better result for toluene oxidation in presence of water, over which 100% conversion of toluene could be achieved at 150 °C (GHSV of 21,000 h⁻¹), much lower than other catalysts (Pt/AC01 and Pt/AC03) with less hydrophobic supports. Xia et al. revealed that the hydrophobicity and hydrothermal stability of Pt/MCM-41 catalysts could be increased when the MCM-41 was prepared in a fluoride medium, and found that this catalyst shows remarkable hydrothermal stability for toluene oxidation in the presence of 21,000 ppm of water. Chen et al. suggested that the Pt-R/Meso-KZSM-5 catalyst was extraordinarily stable and exhibited negligible inhibition by water during toluene oxidation which was assigned to the good hydrophobicity of zeolite with a high Si : Al ratio. Similar results for toluene oxidation over hydrophilic SiO₂-supported NiO or NiO-TiO₂ were reported by Kim and
co-workers.\textsuperscript{303} AC has also been reported to be a suitable support for catalysts in the complete oxidation of VOCs due to its hydrophobic character. For example, the activity of Pt-10Ce/C catalyst in ethanol and toluene oxidation is only slightly influenced by water vapor due to the hydrophobic character of AC support, which prevents the adsorption of water.\textsuperscript{631}

The role of water vapor in the catalytic oxidation of VOC is rather complex, particularly at low temperatures. As a consequence, the effect of water vapor on specific VOC-containing catalytic oxidation should be considered in the design of industrial pilot plants and practical applications.

5.2. Promotion effect of ozone

The use of ozone in catalytic oxidation is a promising new technology for VOC elimination as higher conversions can be achieved at lower reaction temperatures when compared with those conducted with molecular oxygen.\textsuperscript{1049-1051} Ozone-induced active oxygen species on the surface of catalysts plays a significant role in VOC oxidation.\textsuperscript{1052} Previous work has indicated that using ozone can reduce the temperature required for oxidizing VOCs by approximately 200 K, and thus leading to increased energy efficiency.\textsuperscript{1053} There are many examples which focus on the low-temperature oxidation of typical VOC pollutants (e.g., benzene,\textsuperscript{1054-1056} toluene,\textsuperscript{1057-1059} chlorobenzene,\textsuperscript{1060,1061} 1,2-dichloroethane,\textsuperscript{1062} dimethyl sulfide\textsuperscript{1063,1064} and naphthalene\textsuperscript{1065}) in ozone catalytic oxidation system.

SiO\textsubscript{2}-supported catalysts are effective for ozone utilization because the catalysts exhibit a low ozone/VOC decomposition ratio compared with other supported catalysts. 5 wt.% Mn oxide supported on SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2} and ZrO\textsubscript{2}, with 1000 ppm of ozone has been used to completely decompose 100 ppm of benzene at temperatures lower than 100 °C. Herein, SiO\textsubscript{2} was found to be the most efficient support.\textsuperscript{1056} An excellent activity in the catalytic oxidation of benzene with ozone and a superior efficiency for ozone utilization was recently reported over a Mn/SiO\textsubscript{2} catalyst.\textsuperscript{1066} Similar results were also revealed by Huang et al.\textsuperscript{1067,1068} in the catalytic ozonation of benzene. Catalyst surface area was found to be an important factor in obtaining high catalytic activity.\textsuperscript{1056,1069} Einaga \textit{et al.}\textsuperscript{1070} reported that manganese oxides dispersed on USY zeolite can completely oxidize benzene to CO and CO\textsubscript{2} in the presence of water vapor at room temperature. The high activity of Mn in the oxidation of VOCs can be attributed to the better capability for decomposition of ozone among transition metal oxides.\textsuperscript{1071} As a result of the decomposition of
ozone on Mn oxides, highly active oxygen species (peroxide and atomic oxygen) are formed which can contribute to oxidation of VOCs at low temperatures. Teraoka and co-workers further proposed that the addition of Cu, Ni and Fe (especially Cu) to Mn oxides enhanced the activity and stability of the Mn/SiO$_2$ catalyst in benzene oxidation with ozone.

The effect of Mn loading (1, 5, 10 or 20 wt.%) on the total oxidation of toluene by ozone using Al$_2$O$_3$ supported manganese oxide catalysts was studied by Chen and co-workers. It was suggested that lower Mn loadings possess higher activity in the oxidation of toluene. Ozone decomposition was more facile over these materials resulting in higher rate of toluene oxidation. It is reported that the combination of transition metal oxides and noble metals can lead to an enhancement in overall catalytic activity in the oxidation of VOCs by oxygen. Rezaei’s additional work found that the addition of Pt improves activity of Mn oxides, leading to complete conversion of toluene at 70 °C (WHSV of 300 L·g$^{-1}$·h$^{-1}$). However, Pd is found to be ineffective in enhancing activity of Mn oxides, mainly due to a lack of atomic interaction between Pd and Mn. They proposed that the interaction between Pt and Mn occurred via the surface oxygen of Mn oxide clusters. The increasing dispersion of Pt atoms in the presence of Mn, and interaction with Mn increased the electron occupancy of Mn 3d orbital, which was more favorable for the decomposition of ozone and consequently oxidation of toluene. Teramoto et al. combined the advantageous of a ZrCeO$_3$ solid solution (superior oxygen storage capacity) and SiO$_2$ (large surface), and found that Zr$_{0.77}$Ce$_{0.23}$O$_2$-SiO$_2$ provides the best resulted in terms of toluene conversion and CO$_2$ selectivity. The authors indicated that the catalyst performance in toluene decomposition significantly depended on the capability of catalyst to retain the active oxygen species formed by ozone.

CNTs have been reported to be an excellent VOC adsorbent and the addition of CNTs into metal oxide catalysts can promote VOC oxidation. MnO$_x$/CNTs materials were prepared by an impregnation method and their catalytic oxidation performances of CB with the assistance of ozone were investigated. The results suggested that ozone efficiently promoted CB catalytic oxidation over MnO$_x$/CNTs, and CO$_2$ selectivity above 95% could be achieved at 80 °C (GHSV of 36,000 h$^{-1}$). Moreover, MnO$_x$/CNTs catalysts showed good stability and resistance to chlorine poisoning in presence of ozone. The promotion effect of ozone on CB oxidation over CuO$_x$/CNTs was also reported.
5.3. Existence of NOx

Berinchamps et al.\textsuperscript{1077,1078} reported that the presence of NO induced an increase in CB conversion over VO\textsubscript{x}/TiO\textsubscript{2}, VO\textsubscript{x}-WO\textsubscript{x}/TiO\textsubscript{2} and VO\textsubscript{x}-MoO\textsubscript{x}/TiO\textsubscript{2} catalysts. CB conversion continued to increase dramatically when a higher NO concentration was implemented. They proposed that the vanadia phase firstly gave its lattice oxygen to oxidize CB following the Mars van Krevelen mechanism. In parallel, the NO was oxidized into NO\textsubscript{2} principally on the doped phase of WO\textsubscript{x} or MoO\textsubscript{x}. The \textit{in situ} produced NO\textsubscript{2} was then able to replace or assist O\textsubscript{2} in the reoxidation of the reduced vanadia sites, leading to the regeneration of active vanadia sites. These could once again relinquish their lattice oxygen atoms leading to the liberation of NO in the same amount as it had been introduced in the stream. This higher oxidation capacity of NO\textsubscript{2} than O\textsubscript{2} in the reoxidation of the vanadia reduced sites induced a speeding up of the oxidation cycle in the first step, which corresponds to the increase in CB conversion.\textsuperscript{1078} Zhang and co-workers\textsuperscript{1079} proposed that the existence of NO\textsubscript{x} could dramatically promote the oxidation of methanol as demonstrated by the reduced reaction temperature and significantly enhanced CO\textsubscript{2} selectivity.

Mrad et al.\textsuperscript{1029} found that the existence of NO can compete with propene for the active metal sites causing a reduction in propene conversion over CuMgAlFeO\textsubscript{x} hydrotalcite-like catalysts. Similar results were also obtained by Samojeden and co-workers\textsuperscript{1080} who revealed that the conversion of ethanol on the modified layered aluminosilicates decreases slightly in the presence of NO\textsubscript{x}. However, the presence of NO\textsubscript{x} in the reaction mixture does not affect the stability of the used catalysts.

5.4. Mutual effect of miscellaneous VOCs

Generally, industrial flue gas streams contain a mixture of VOCs with different physical and chemical properties (Table S3) rather than a single compound. Special attention has been paid to the relatively few scientific studies involving mixtures of VOCs since the catalytic reaction of a component in a mixture cannot be predicted solely from the behavior of the individual components. To understand the mutual effects of representative VOCs contained in industrial exhausts is extremely important especially when one component of a gas stream is significantly more toxic than other components, and research on its behavior in mixtures is not available.

The presence of other molecules usually inhibits the oxidation of VOCs attributed to the
competition among different VOC pollutants and reaction intermediates for adsorption sites. In the vast majority of cases, aromatic hydrocarbons demonstrate significant inhibition effects on aliphatic hydrocarbons. Burgos et al. found that catalytic oxidation rate of 2-propanol over a Pt-Al₂O₃/Al monolith significantly decreased in the presence of toluene and MEK due to the competitive adsorption over Pt sites. Similarly, the inhibition effect of o-xylene on the catalytic oxidation of isopropanol over NaX zeolite was reported by Magnoux and co-workers. The authors demonstrated that the concentration of o-xylene influenced the formation of secondary products (e.g., propene and coke) resulting from the isopropanol transformation. More recently, a significant inhibition effect of o-xylene in the oxidation of cyclooctane was proposed by Bozga and co-workers. Santos et al. reported that toluene inhibited both EA and ethanol oxidation (especially for EA) over a cryptomelane catalyst. On the contrary, toluene oxidation is only slightly inhibited by the presence of EA, while the presence of ethanol has a promoting effect. Co-existence of EA and ethanol has a mutual inhibitory effect on each other, which is more evident in the case of EA. Reciprocal inhibition effects of EA and ethanol as well as the suppressive effect of toluene on EA and ethanol over MnOₓ/γ-Al₂O₃ catalyst were also revealed by Cadús and co-workers. Our previous work demonstrated that propanal oxidation over CuCeOₓ mixed oxides could be remarkably suppressed by introduction of toluene, while the presence of propanal had a negligible effect on toluene oxidation (Fig. 30). Dangi et al. found that methyl tert-butyl ether conversion was distinctly inhibited by benzene over a monolith Pt/Al₂O₃ catalyst, while no inhibition effects were seen for methyl tert-butyl ether on benzene.

The co-existence of aromatic hydrocarbons can lead to the inhibition of each other when they reacted together. Ordóñez et al. reported that the presence of both benzene and toluene inhibited the conversion of each other over Pt/γ-Al₂O₃ catalyst. In addition, n-hexane did not affect the conversion of benzene and toluene, while the presence of benzene or toluene inhibited the oxidation of n-hexane. Similar results regarding the mutual suppressive effects of benzene and toluene were also reported in our previous work. It was found that EA demonstrated a clear inhibitory effect on benzene oxidation, while EA had a promoting effect on toluene conversion.

The existence of hydrogen-containing aliphatic/aromatic hydrocarbons has different effects on the oxidation of CVOCs. Gutiérrez-Ortiz et al. proposed that 1,2-DCE, TCE, and n-hexane
inhibited each other over Ce\textsubscript{x}Zr\textsubscript{1-x}O\textsubscript{2} mixed oxides due to competitive adsorption. Additionally, selectivity to HCl during the oxidation of 1,2-DCE or TCE was noticeably enhanced when \textit{n}-hexane was co-fed into the reaction. Similar results were also found using other H-rich additives such as toluene and water in 1,2-DCE or TCE oxidation\textsuperscript{953,955}. Wang \textit{et al.}\textsuperscript{774} found that the addition of toluene had no effect on the decomposition of CH\textsubscript{2}Cl\textsubscript{2}, although it suppressed CH\textsubscript{3}Cl formation.

The catalytic oxidation of CB on a Pt/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst in binary mixtures with various hydrocarbons (e.g., toluene, benzene, cyclohexane, cyclohexene, 1,4-cyclohexadiene, 2-butene and ethene) was explored. Herein, it was found that the addition of hydrocarbons increases the rate of conversion of CB. The co-feeding of hydrocarbons invariably reduces the output of polychlorinated benzenes, especially for toluene, ethene, and 2-butene\textsuperscript{1088}. Similarly, the promotion effects of other VOCs (e.g., toluene, ethanol and acetone) on the catalytic oxidation of TCE and trichloromethane over Pt-Pd-based catalysts have been reported\textsuperscript{1089}. Musialik-Piotrowska and Mendyka\textsuperscript{1090} stated that both hydrocarbons and ethanol enhanced CB oxidation over Pt-based catalyst, while 1,2-DCE conversion was inhibited in the presence of these additives. The promotional effects seen with the presence of heptanes in CB oxidation over Pt/\gamma-Al\textsubscript{2}O\textsubscript{3} catalysts were also reported by Brink \textit{et al.}\textsuperscript{1091} and Jong \textit{et al.}\textsuperscript{1092}. Magnoux and co-workers\textsuperscript{1093} revealed that the presence of benzofuran in a benzofuran/\textit{o}-DCB mixture clearly improved the conversion of chlorinated compounds, decreased the production of chlorinated by-products and enhanced the selectivity to CO\textsubscript{2}.

The mutual effect of VOC mixtures is also dependant on catalyst type and component. Activity of two noble metal catalysts (Pt and Pd) supported on a metallic monolith and perovskite (La\textsubscript{0.5}Ag\textsubscript{0.5}MnO\textsubscript{3}) on a cordierite monolith was comprehensively tested in the oxidation of toluene, \textit{n}-heptane, ethanol, ethyl acetate, acetone, MEK and TCE\textsuperscript{1081}. The results indicated that each compound in the reaction mixtures strongly enhances TCE oxidation only over Pt catalyst. Alternatively, the promoting effect on TCE oxidation over Pd catalysts is only observed for toluene and ethanol. Over La\textsubscript{0.5}Ag\textsubscript{0.5}MnO\textsubscript{3} supported catalyst, all non-chlorinated compounds are found to inhibit TCE oxidation. The presence of TCE is found to inhibit the oxidation of all compounds added over both noble metal catalysts; however, it has no influence on ethanol, ethyl acetate, acetone, and MEK oxidation over the perovskite supported catalyst\textsuperscript{1081}. 

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The above results demonstrate that it is necessary to carefully select not only the catalyst to be used but also the reaction conditions when treating industrial flue gases containing different mixtures of organic compounds and chlorinated hydrocarbons.

6. Catalyst deactivation and regeneration

6.1. Catalyst coking, poisoning and sintering

A promising catalyst for industrial applications should present not only high catalytic activity, but also good stability and durability. However, most catalysts suffer from different kinds of deactivation such as coking, poisoning and thermal sintering under operating conditions of catalytic VOC oxidation. Carbonaceous deposits (coking) on the catalyst often occur with the oxidation of VOCs and can lead to a loss in oxidation activity of the catalysts. Active sites poisoned by chloride, sulfide, nitride, bromide or other reaction intermediates have been widely reported and studied in VOC oxidation, especially for the heteroatom-containing VOCs. Coking and poisoning can disable active sites and/or obstruct the pores of catalyst. The selectivity in oxidation reactions may also be altered as the former may decrease the effective diffusivity of reactants and products while the latter may reduce the intrinsic rate of formation of reaction products. A catalyst can also be deactivated by the loss of active sites or a change in relative distribution of active sites due to the structural changes of the catalyst caused by thermal sintering.

Intermediates produced during VOC oxidation are one of the major sources of catalyst deactivation (coking). Ihm et al. found that the deactivation during oxidation of \(n\)-hexane over \(\text{Pd/Al}_2\text{O}_3\) was mainly due to the formation of carbonaceous intermediates. Antunes et al. reported that the carbonaceous deposits, mainly composed of aromatic hydrocarbons and oxygenated aromatic compounds (the latter being predominant at low temperature), were usually found inside the pores of \(\text{Cu/NaHY}\) catalysts during the deep oxidation of toluene. The increase of Cu content promoted the oxidation of toluene and facilitates the removal of coke. Dégé et al. proposed that the formation of coke over \(\text{Pd/HFAU}\) catalysts in xylene oxidation was attributed to the acidic properties of catalyst (the lower the number of acid sites and the slower the coke formation). Our previous work also found that the zeolites with higher acidity facilitated the formation of coke in deep oxidation of benzene, toluene and EA. Two types of coke, that is,
“light coke” (monoaromatic polysubstituted compounds) and “hard coke” (polyaromatic compounds), were revealed by Ribeiro and co-workers in the deep oxidation of methyl cyclohexane with HUSY zeolites. Similar results were also reported by Hosseini et al. for propene and toluene oxidation over Au-Pd loaded TiO2 catalysts.

The influence of chlorine on catalysts is a major problem leading to deactivation in the oxidation of CVOCs. The majority of catalysts used for the oxidation of CVOCs were deactivated to different extents by chlorine attack. Zeolites with high specific surface areas, variable pore structures and remarkable acidic properties present excellent catalytic performance for CVOC oxidation. However, zeolite catalysts are usually subjected to coking and/or chlorine poisoning during the oxidation processes. The effect of coking on the stability of H-zeolites depends strongly on their pore channel structure. The detrimental effect chlorine, specifically over the BAS, is most severe when oxidizing molecules with a H : Cl ratio < 1, since the hydrogen atoms present are not sufficient to restore the consumed hydroxyl groups. Wu and co-workers found that coking was the primary reason for Fe-O/HZSM-5 catalyst in the oxidation of DCM which was attributed to its lower oxidation capacity toward the intermediate products. Cu-O/HZSM-5 catalyst was found to be severely poisoned by chlorine species owing to the formation of stable Cu(OH)Cl species. Aranzabal et al. revealed that both coke formation and chlorine poisoning were the causes of H-zeolites (H-ZSM-5, H-MOR and H-BEA) rapid deactivation during TCE oxidation. Chlorine atoms cause the irreversible deactivation of zeolites by attacking the BAS, leading to structural changes. Subsequent work confirmed that the deactivation of H-zeolites in TCE oxidation leads to a decrease in the selectivity to HCl and CO2, and an increase in the selectivity to tetrachloroethylene and tetrachloromethane.

Sulfur-containing VOCs may deactivate the catalyst and reduce the efficacy of catalytic incineration. It is reported that the poisoning effects of sulfur is more apparent for Al2O3-supported catalysts than those of silica-supported catalysts. Yu et al. attributed the poisoning effect of sulfur on Pd/Al2O3 to the formation of aluminum sulfate above 473 K. Chu et al. also concluded that (CH3)2S and C2H5SH had poisoning effects on Pt/Al2O3 catalyst, especially at low temperatures. Darif et al. revealed that doping of SiO2 over Al2O3 leaded to a more selective and stable catalyst for dimethyl disulfide oxidation. Recently, their additional work has confirmed that sulfate formation during dimethyl disulfide oxidation was one of the most
important contributing factors in the deactivation of industrially aged Pt/Al₂O₃ catalyst.⁹⁷⁵

Catalysts can also be deactivated by thermal sintering, which re-disperses active sites and alters the physicochemical properties of catalysts.⁸⁷,⁷⁵³ Catalytic oxidation of benzofuran and a benzofuran/o-DCB binary mixture over zeolite catalysts was investigated by Magnoux and co-workers.¹⁰⁹³ It was found that 1.2 wt.% Pt/HY catalyst initially deactivated during the first 24 h reaction due to Pt sintering, leading to a collapse of the cristallinity of the zeolite. Zhang et al.⁸³⁹ proposed that the coking and chlorine attack were not the main reasons for LaMnO₃ catalyst deactivation in VC oxidation, but rather parameters such as lower specific surface area, weakened low-temperature reducibility, lower Mn⁴⁺/Mn³⁺ molar ratio and inhibited surface oxygen mobility of the used catalyst caused by sintering.

Catalyst deactivation can also be attributed to the presence of water in exhaust gases or water formed in situ during VOC oxidation reactions. However, water can also play a positive role in the case of CVOC oxidation, namely, removing deposited chlorine on catalyst surface as well as reacting with chlorine to produce HCl by the Deacon reaction.⁸⁷⁴,⁹³² Dai et al.⁸⁵⁴ reported that trichloroethylene oxidation was inhibited at lower water concentrations (3%), but enhanced to a certain extent at higher water concentrations (12%). Additionally, HCl selectivity was much improved with the addition of water to the feed by combination of hydrogen species with surface bound chlorine. Wu and co-workers⁹⁰⁹ found that the presence of water could not only protect the active sites of Mn₀.₈Ce₀.₂O₂ from accumulated chlorine poisoning, but acted as H·and OH·radical source to deeply oxidize CB over Mn₅Ce₁.₅O₂/H-ZSM5. Guillemot et al.¹¹⁰³ proposed that water vapor played an important role in tetrachloroethylene oxidation and limited catalysts (Pt/HY, Pt/NaY, and Pt/NaX) deactivation by acting as metallic site cleanser.

### 6.2. Catalyst regeneration

The economical feasibility of any industrial catalytic process is based on the catalyst activity, selectivity, and durability, but also on the possibility of regeneration (or reactivation) and reuse. The ability to regenerate a catalyst depends upon the reversibility of the deactivation process. Several approaches, such as heat treatment, ozone oxidation, chemical regeneration and oxygen plasma treatment, are available for the regeneration of catalysts.

Carbonaceous deposits are relatively easily removed through gasification with H₂, O₂, water or
The temperature required to gasify these deposits varies with the type of gas, the structure and reactivity of the deposits, and the activity of catalyst. In general, carbonaceous deposits can be rapidly removed with oxygen at moderate temperatures (400-600 °C). Kim and Shim found that the air pretreatment significantly enhanced the catalytic activity of the spent Fe-based catalysts in toluene oxidation at 400 °C. However, their results indicated that the hydrogen pretreatment had a negative effect on catalytic activity due to the formation of metallic Fe. Han et al. proposed that the NiO/SiO₂ catalyst in toluene oxidation could be regularly regenerated under reaction conditions at 450 °C. Duprez and co-workers also indicated that the carbonaceous deposits over a PtCe catalyst could be totally removed by diluted oxygen at moderate temperature. Deactivated industrial catalysts (by carbon or coking) were usually regenerated in air. However, because of the exothermic nature of the combustion reaction, particular attention must be given to regeneration conditions, that is, oxygen should be diluted with an inert gas and the regeneration temperature should be carefully controlled to prevent overheating and subsequent thermal degradation of the catalyst. Alternatively, regeneration by ozone is an attractive low temperature process for coke removal due to the high oxidizing activity of this compound. For instance, Copperthwaite et al. showed that an ozone-enriched oxygen treatment could restore activity of deactivated ZSM-5 zeolite under mild conditions (150 °C), while a temperature of about 450 °C was necessary with oxygen only.

Catalyst sintering is generally irreversible. However, metal redispersion is possible under certain conditions in selected noble metal systems. The reactivation of thermally sintered Pt/Al₂O₃ catalysts used in the simultaneous oxidation of CO and propene has been achieved by an oxychlorination treatment. The redispersion mechanism of Pt clusters is broadly accepted on an atomic scale by the formation of chloride-containing surface complex [Pt⁴⁺OₓClₓ]ₜ. Some poisons such as chlorine can be selectively removed by chemical washing or heat treatments. Vu et al. reported that the activity of a partially deactivated MnCuOₓ/TiO₂ catalyst (due to the formation of oxychlorinated Cu and Mn species) during CB oxidation could be recovered by treatment in air at 350 °C. Gallastegi-Villa et al. proposed that wet air was more effective (especially at higher temperature) than dry air to regenerate catalytic activity of H-Beta in 1,2-DCE and TCE oxidation as it aided both coke and chlorine removal.
6.3. Anti-deactivation catalysts

The stability of the catalyst is clearly a determining factor in industrial applications. Chen et al.\textsuperscript{1120} reported a porous Co-Cu-Mn/ZSM-5 membrane/PSSF catalyst. It was found that the catalyst possessed an excellent reaction stability, demonstrated by a high catalytic activity (90\%) during the 550 h long-term catalytic oxidation of 2-propanol. The superior catalytic stability of 1.6Au/\text{CeO}_2 catalyst for 2-propanol oxidation at different reaction temperatures (120 and 150 °C) was reported by Liu and Yang.\textsuperscript{636} Abdelouahab-Reddam et al.\textsuperscript{631} revealed that the Pt-10Ce/Carbon catalysts showed no deactivation during a test for 100 h in ethanol and toluene oxidation. Furthermore, humid conditions had an insignificant influence on this catalyst. Recently, Ye and co-workers\textsuperscript{502} presented a highly stable Pt/\text{CeO}_2-1.8 catalyst, which could work properly for 120 h with different toluene inlet concentrations and be completely negligible for 5 vol\% water vapour at 155 °C. Other catalysts such as Au/3DOM LaCoO\textsubscript{3} and Co\textsubscript{3}O\textsubscript{4}/3DOM La\textsubscript{0.8}Sr\textsubscript{0.2}CoO\textsubscript{3} with satified reaction stability in the oxidation of toluene were also reported.\textsuperscript{395,436} Rei and co-workers\textsuperscript{1121} proposed that the Pt/h-BN (hexagonal boron nitride) was a very active and stable catalyst for VOC oxidation even under a high temperature environment (500 °C) owing to the high thermal conductivity and water resistant ability of h-BN.

Chlorine attack is a primary reason for catalyst deactivation during CVOC oxidation. In recent years, several kinds of catalysts with high resistance to chlorine poisoning and coking were reported. Liu and co-workers\textsuperscript{418} indicated that the SnO\textsubscript{x}-MnO\textsubscript{x}-TiO\textsubscript{2} catalysts had excellent anti-deactivation ability during CB oxidation due to the lower average energy required to desorb Cl species and to the absence of MnO\textsubscript{x}Cl\textsubscript{y} on the active sites during the reaction. Wu et al.\textsuperscript{910} developed a Mn-Ce-Mg/Al\textsubscript{2}O\textsubscript{3} catalyst which presented high CB oxidation stability at 400 °C (no deactivation could be found during 1000 h reaction). Besides, the superior catalytic stability of MnO\textsubscript{x}/TiO\textsubscript{2},\textsuperscript{881} MnCeLaO\textsubscript{x},\textsuperscript{905} and Ru/Ti-CeO\textsubscript{2}\textsuperscript{887} for CB destruction were reported. Recently, Dai et al.\textsuperscript{824} developed a sandwich-structured CeO\textsubscript{2}@HZSM-5 core-shell composite, and found that this catalyst had good activity and resistance to coking and chlorine poisoning in catalytic oxidation of 1,2-DCE (Fig. 31i and ii). This was due to the formed non-activated coke species and polyaromatic species being more easily removed via an in situ oxidation by the active oxygen species from CeO\textsubscript{2}. The exposed HZSM-5 is also tolerant to the chlorination of acid sites and prevents the direct adsorption of HCl on CeO\textsubscript{2}. Zhou and co-workers\textsuperscript{1122} revealed that the addition
of CeO$_2$ or/and CuO obviously improved the durability of USY material in 1,2-DCE long-term oxidation because of the slight coke deposition and preserved high density of acid sites (Fig. 31iii). In their following work, the authors proposed that the strong interaction between Cr$_2$O$_3$ and CeO$_2$, along with the synergy between Cr$_2$O$_3$-CeO$_2$ and USY zeolite resulted in less coke deposit and slight HCl attack on the Cr$_2$O$_3$-CeO$_2$/USY catalysts and improved resistance to chlorination of active components. Similar synergistic effects among CeO$_2$, Cr$_2$O$_3$, and HZSM-5 zeolite in the oxidaiton of CVOCs (1,2-dichloroethane, dichloromethane, and trichloroethylene) were also proved by the same group. 

7. Oxidation kinetics and mechanism

7.1. Kinetic models

In general, three models are adopted to explain the mechanism of deep catalytic oxidation of VOCs, that is, the Langmuir-Hinshelwood (L-H) model, Eley-Rideal (E-R) model, and Mars-van Krevelen (MVK) model. The validity of each model strongly depends on the characteristics of catalysts as well as the nature of the VOCs being studied. Amongst, the MVK model has been widely used for kinetics modeling of hydrocarbon oxidation reactions, especially over metal oxide catalysts.

The L-H model assumes that the reaction occurs between the adsorbed oxygen species and adsorbed VOC molecules, and the controlling step of this model is the surface reaction between these two adsorbed molecules. The L-H model can be respectively subdivided into the single site L-H model and duel site L-H model according to VOC molecules and oxygen species adsorb on analogous active sites or different active sites. Hosseini et al. reported that the oxidation reaction of toluene and propene over Pd-Au/TiO$_2$ catalysts followed the L-H model where the molecules of oxygen and VOC were in competition for adsorption on the surface of catalyst. Tseng and Chu proposed that the catalytic oxidation of styrene over MnO/Fe$_2$O$_3$ could be described by the L-H model. Garetto and Apesteguia found that benzene oxidation on Pt/Al$_2$O$_3$ catalyst proceeded via an L-H mechanism, and similar results were also obtained by Danciu and co-workers for methyl isobutyl ketone oxidation. Tseng et al. revealed that the kinetic behavior of methyl isobutyl ketone oxidation could be accounted for by the MVK model and L-H model (molecular oxygen adsorption). Heynderickx et al. compared the L-H, E-R, and MVK
models for predicting the oxidation kinetics of propane over CuO-CeO$_2$/γ-Al$_2$O$_3$ catalysts, and found that the L-H rate equation provided the best description of the experimental data. Oxidation of propane was also studied by Kaichev et al.$^{123,1128}$ over a nickel foil. The team proposed that the oxidation over metallic Ni surface occurred via the L-H mechanism, whereas the MVK mechanism prevailed when the reaction proceeded over NiO. Todorova et al.$^{1129}$ reported that the oxidation of $n$-hexane over single component manganese and bi-component Co-Mn catalysts proceeded through the MVK mechanism, while the L-H mechanism was more probable for the Co sample.

Based on the E-R model, the oxidation reaction occurs between adsorbed oxygen species and gas phase reactant molecules (or between adsorbed reactant and gas phase oxygen). The controlling step of the E-R model is the reaction between an adsorbed molecule and a molecule from the gas phase. The E-R rate expression was found to be appropriate to describe the kinetics of cyclohexane oxidation over Co/AC catalysts.$^{218}$ Aranzabal et al.$^{1130,1131}$ proposed that a five-step reaction network scheme, based on the E-R model, provided an accurate correlation of the experimental data for TCE oxidation over Pd/Al$_2$O$_3$ catalyst. Recently, Bozga and co-workers$^{1083}$ revealed that cyclooctane oxidized over Pt/γ-Al$_2$O$_3$ followed the E-R type mechanism, whereas the $o$-xylene combustion was explained by the L-H scheme.

The MVK model (two-step redox model) assumes that the reaction occurs between the oxygen-enriched sites of catalyst and adsorbed VOC molecules. The adsorbed VOC molecules react with oxygen species in the catalyst, resulting in the reduction of the metal oxide. And then, the reduced sites are reoxidized immediately by the gas phase oxygen present in the feed. The reduction and oxidation rates must be equal in a steady state, and the VOC oxidation rate can be expressed by the following equation according to the MVK model:

$$-r_V = \frac{K_0 K_V P_0 P_V}{P_0 P_V + \delta K_0 K_V}$$

where, $-r_V$: reaction rate (mol·m$^{-3}$·s$^{-1}$); $K_0$, $K_V$: rate constant of catalyst reoxidation and VOC oxidation, respectively; $P_0$, $P_V$: reaction partial pressure of O$_2$ and VOC reactant, respectively; $\delta$: stoichiometry coefficient of O$_2$ in VOC oxidation.

Kinetic behaviors of VOC oxidation over metal oxide-based catalysts are usually described by the MVK model. Genuino et al.$^{541}$ indicated that catalytic oxidation of benzene, toluene,
ethylbenzene and xylenes over Mn oxide and Cu-Mn mixed oxide proceeded via the MVK mechanism. Similar results were obtained by Kim and Shim\textsuperscript{1132} for catalytic oxidation of benzene, toluene, and α-xylene over Ce-Cu/γ-Al\textsubscript{2}O\textsubscript{3} catalysts. Catalytic oxidation of EA and toluene over Cu-Ce-Zr-ZSM-5/TiO\textsubscript{2},\textsuperscript{382} Au/MO\textsubscript{x} (M = Cu, Fe, La, Mg, Ni, and Y)\textsuperscript{516} or Pd/ZSM-5\textsuperscript{1087} obeyed the MVK scheme. In addition, the catalytic oxidation behaviours of toluene over Ce-Co/La-Co mixed oxides,\textsuperscript{429} Co\textsubscript{3}O\textsubscript{4}/La-CeO\textsubscript{2}\textsuperscript{1133} and Cu-Mn spinels\textsuperscript{1134} can be interpreted by the MVK model. Li et al.\textsuperscript{1135} revealed that the catalytic combustion of benzene over the NiMnO\textsubscript{2}/CeO\textsubscript{2}/Cordierite catalyst obeyed the MVK mechanism. Arzamendi et al.\textsuperscript{1136} found that the catalytic oxidation of MEK over Pd-Mn/Al\textsubscript{2}O\textsubscript{3} catalysts could be explained by the MVK model. The applicability of MVK model in complete combustion of propane and MEK over Cr/ZrO\textsubscript{2} was proved by Choudhary and Deshmukh.\textsuperscript{1137} Catalytic oxidation of propene over Au-MO\textsubscript{x}/Al\textsubscript{2}O\textsubscript{3} (M = Ce, Mn, Co, and Fe),\textsuperscript{235} Cr/saponite\textsuperscript{1138} or α-Fe\textsubscript{2}O\textsubscript{3} films\textsuperscript{1139} followed the MVK mechanism, and the destruction behaviours of other oxygen-containing hydrocarbons (dimethyl ether over transition metals (Fe, Co, Ni, Cu and Cr) cryptomelane-type manganese,\textsuperscript{1140} methanol over Pd/Y\textsuperscript{598} and 2-propanol over Cu-Co mixed oxides\textsuperscript{643} and alkanes (isobutene over Au-MO\textsubscript{x}/CeO\textsubscript{2} (M = Mn, Fe, Co, and Ni)\textsuperscript{88} and n-hexane over γ-MnO\textsubscript{2}\textsuperscript{1141}) are also proved to be reasonably fitted by the MVK model.

### 7.2. VOC oxidation mechanism

Confirmation of the surface oxidation mechanisms of VOCs over heterogeneous catalysts is of great importance to supplement catalyst design. However, many factors such as the catalyst elemental composition, the catalyst physicochemical properties, the pollutant composition and reaction condition can all drastically influence the surface mechanisms taking place. Below are some pertinent examples of reaction mechanism determined over various catalysts for a range of different VOCs.

#### 7.2.1. Aliphatic and aromatic hydrocarbons

**7.2.1.1. Propane**

Garetto et al.\textsuperscript{157} reported on the catalytic oxidation mechanism of propane over Pt/zeolite (HY, ZSM-5, Beta and KL) catalysts (Fig. 32i). It was proposed that the rate-determining step was the dissociative chemisorption of propane on Pt, which involved the cleavage of the weakest C-H
bond followed by its subsequent interaction with oxygen atoms adsorbed on adjacent sites. In a parallel oxidation pathway, propane was adsorbed and activated on surface sites in the metal-oxide interfacial region and reacted with oxygen spilled-over from Pt.

7.2.1.2. Ethylene and propene

A generalized mechanism for the catalytic oxidation of ethylene over Ag/zeolite (ZSM-5, Beta, Y and Mordenite) catalysts was proposed by Yang et al. In this mechanism, it was proposed that the overall reaction occurs in four steps: (1) the adsorption and activation of ethylene on a Brønsted acid site in the Ag/zeolite catalyst, leading to the formation of an adsorbed ethylene species; (2) the attack of an active oxygen species on this adsorbed ethylene species; (3) C-C cleavage in the adsorbed ethylene species to produce formaldehyde; (4) oxidation of these surface-bound formaldehyde species into carbonic acid, which undergoes sequential oxidation to CO$_2$ and H$_2$O.

The mechanisms of propene oxidation over various catalysts (Pt/Al$_2$O$_3$, Pt/BaO/Al$_2$O$_3$ and Pt/SO$_4^{2-}$/Al$_2$O$_3$) were proposed by Weng and co-workers. In this study, it was proposed that propene adsorbed on Pt/Al$_2$O$_3$, proceeds from acrylates to carboxylates and formates, before finally undergoing oxidation into CO$_2$ and H$_2$O. Over Pt/BaO/Al$_2$O$_3$ however, BaO modification leads to the formation of a more reactive enolic species, making sequential oxidation more favourable. The formation of active oxygen species was also observed at the Pt-Ba interface, leading to an increase in the oxidation rate of CO. For the Pt/SO$_4^{2-}$/Al$_2$O$_3$ sample, di-σ bonded propene was strongly adsorbed on the catalytic surface, leading to a suppression in the oxygen activation on Pt. Therefore, initial oxidation occurred through the consumption of S=O bond to provide necessary O atoms. The intermediate CO resulted in Pt poisoning, blocking the Pt sites for further propene oxidation, until operating at high reaction temperature (Fig. 32iii).

7.2.1.3. Benzene and toluene

The reaction mechanism for benzene oxidation over a MnO$_x$/TiO$_2$ catalyst was studied by Zhu and co-workers, the observations of which were acquired from in situ FTIR experiments. As shown in Fig. 33, benzene first reacts with the active Mn center, giving a phenolate species with two conjugated structures. The oxygen-containing group was considered to act as an electron-donator and ortho-para positioned director; the phenolate species could be easily oxidized...
into \( o \)-benzoquinone and \( p \)-benzoquinone. Following this, the ring opening occurred with the catalyst promoting and the attack of the active oxygen species, affording the small molecule intermediates such as maleate and acetate species before undergoing sequential oxidation to (CO, CO\(_2\), and H\(_2\)O).

Liao et al.\(^{51}\) reported that toluene adsorbs on the surface of polyhedra MnO\(_x\) catalysts and is partially oxidized to benzyl alcohol, which can transform into benzaldehyde and benzoic acid. By increasing the reaction temperature, the benzene ring opens to form maleic anhydride, which can then undergo sequential oxidation to CO\(_2\) and H\(_2\)O.

7.2.3. Heteroatom-containing VOCs

7.2.3.1. Ethanol and 2-propanol

Zhou et al.\(^{618}\) suggested that ethanol could be oxidized to produce acetaldehyde and acetic acid over nano-CeO\(_2\) catalysts because of the existence of surface active oxygen species (O\(^*\)). In addition to various condensation products such as ethyl acetate, acetal and ethyl ether were also detected, the formation of which was attributed to the presence of acid/base sites (A/Bc) on the surface catalyst. It was confirmed that ethanol, the oxidation intermediates and condensation products could all be oxidized to produce CO\(_2\) in air; a high CO\(_2\) selectivity was therefore observed (Fig. 34i).

A reaction mechanism for the oxidation of 2-propanol over Au/CeO\(_2\) catalysts was proposed by Liu and Yang (Fig. 34ii).\(^{636}\) The authors indicated that the mechanism begins with the dissociative adsorption of gaseous 2-propanol to produce 2-propoxide surface species. From this intermediate, it was postulated that 2-propoxide either undergoes dehydration to propene over strong acid sites or dehydrogenation over moderate/weak acid sites or strong basic sites. In this example, the former reaction is dominant.

7.2.3.2. Formaldehyde and acetaldehyde

The mechanism for the catalytic oxidation of formaldehyde over TiO\(_2\) supported with Pt, Rh, Pd and Au catalysts was proposed by Zhang and He.\(^{658}\) It was determined that that formaldehyde is first oxidized into surface dioxymethylene species and subsequently, formate species, which decompose to form surface-bound CO species (rate-determining step in the formaldehyde oxidation mechanism) before finally being oxidized to CO\(_2\) (Fig. 35i). In our previous work, we
determined that $\text{Co}_3\text{O}_4\{110\}$ facets composed mainly of $\text{Co}^{3+}$ cations over $\text{Au/Co}_3\text{O}_4$ and $\text{Au/Co}_3\text{O}_4-\text{CeO}_2$ catalysts were the active site in formaldehyde oxidation, over which formaldehyde could be oxidized to formate, further oxidized to carbonate and is finally dissociated to CO$_2$ (Fig. 35ii). Liu et al. demonstrated that formic acid and formate are the primary intermediates for formaldehyde oxidation. The formate can then undergo transformation into the corresponding carbonate and hydrocarbonate, which can also lead to incomplete oxidation and the deposition of carbon on the surface of CeO$_2$ support (Fig. 35iii).

Tada and co-workers proposed a reaction mechanism for the total oxidation of acetaldehyde over Au/TiO$_2$ materials (Fig. 36). They demonstrated that acetaldehyde and O$_2$ were firstly adsorbed at the dual perimeter sites of Au/TiO$_2$ catalyst, over which acetaldehyde was thermocatalyzed by adsorbed O$_2$, yielding acetic acid. The formed acetic acid moved to the TiO$_2$ surface where surface Ti$^{4+}$ ions and bridged oxygen can act as a Lewis acid or base sites. The acetate ion and proton derived from the dissociation of acetic acid is strongly adsorbed on surface Lewis acid and base sites. Upon heating to 548 K, the adsorbed acetic acid undergoes decomposed to CO$_2$ and H$_2$O via a gold ketenylidene intermediate species by thermocatalysis over Au/TiO$_2$.

7.2.3.3. Methyl ethyl ketone

We have previously reported on the reaction mechanism for the oxidation of methyl ethyl ketone (MEK) over Pd/ZSM-5 and Pd-Ce/ZSM-5 (PC$_x$Z) catalysts. We determined that the introduction of CeO$_2$ increased the number of by-products formed in the reaction. Ce-containing catalysts promoted the dehydration of a reaction intermediate (3-hydroxybutan-2-one) to form acetaldehyde, which lead to the formation of numerous secondary products such as acetone, 1-penten-3-one and 3-buten-2-one, 3-methyl.

In more recent work, we have investigated the catalytic oxidation of MEK over Pt/K-Al-SiO$_2$ nanorods (Fig. 37). The MEK molecules firstly adsorb onto Brønsted acid sites on the catalyst surface, before the monodispersed metallic Pt located in close proximity to surface K, interacts with the MEK leading to its oxidation. MEK was converted into 2,3-butandiol and diacetyl via 2-butanol and acetoin intermediates. The 2,3-butandiol intermediate was oxidatively cleaved to form acetaldehyde and the diacetyl was cleaved to form acetaldehyde and acetic acid.
Acetaldehyde and acetic acid were considered the primary C₂ scission product of MEK oxidation, which further converted into formaldehyde and formic acid over the Brønsted acid sites and finally were sequenitally oxidized to CO₂ and H₂O.\(^\text{740}\) We have also investigated the catalytic oxidation of MEK over Mn₃O₄ metallic oxide catalysts; the results of which suggested that MEK oxidation to CO₂ predominantly proceeds via a diacetyl intermediate species.\(^\text{1142}\)

**7.2.3.4. Dichloromethane and tetrachloromethane**

Oxidation mechanisms of CVOCs have also been extensively studied and discussed in the literature. It is generally agreed that dissociation of the C-Cl bond occurs first and is the rate-determining step. Hindermann and co-workers\(^\text{1147}\) indicated that adsorbed dichloromethane (DCM) molecules could react with surface hydroxyl groups in a γ-Al₂O₃ catalyst to yield chloromethoxy species. The sequential reaction of this species leads to the formation of a chemisorbed formaldehyde analogue and formed methoxy or formate groups. The Cl from DCM is released as HCl and/or reacted with γ-Al₂O₃ to form aluminum chloride. Recently, a two-stage Ce/TiO₂-Cu/CeO₂ catalyst with separated catalytic functions was designed and adopted as a catalyst for the removal of DCM by Wu and co-workers.\(^\text{788}\) The cleavage of the C-Cl and the total oxidation of CO were physically isolated in the two-stage system, which avoided not only the decrease of acid sites on Ce-Cu/TiO₂ catalyst, but also avoided the chlorine poisoning of TiO₂ due to the strong adsorption of Cl on CuO. A three-step degradation mechanism was proposed, which consisted of the adsorption and cleavage of the C-Cl bonds, the deep oxidation of C-H bonds in the intermediate species and finally, the oxidation of CO to CO₂ (Fig. 38).

In another study, the catalytic activity and selectivity of four zeolite-Y catalysts (H-Y, Co-Y, Na-Y, and Co-Y/CA) were investigated for the total oxidation of dichloromethane (DCM) and tetrachloromethane (TCM).\(^\text{1146}\) With DCM, it was proposed that the proton from the hydroxyl group in the BAS is dissociated to form the corresponding carbonium ion (CH₂Cl₂H⁺). This is then undergoes a sequential reaction to form the corresponding carbenium ion by abstraction of a molecule of HCl. The carbenium ion interacts with the O⁻ at the cationic site to form a COHCl intermediate species, which subsequently dissociates into COₓ and HCl and results in the restoration of the proton on the BAS.\(^\text{1059}\) The researchers confirmed that there are major differences between TCM and DCM oxidation mechanisms under dry conditions, which was
attributed to the absence of a hydrogen source in the former. Following the abstraction of a molecule of HCl from the carbonium ion, it is proposed that the C⁺Cl₃ species interacts with another BAS. This leads to the dissociatively adsorbed oxygen on the cationic site to form phosgene, releasing another molecule of HCl. The phosgene molecule adsorbed on an adjacent BAS forms an unstable positively charged haloacylium ion, which chlorinates the zeolitic structure to form AlOCl and releases a molecule of CO. Further adsorption of phosgene on the AlOCl site results in the formation of CO and AlCl₃ (Fig. 39).

7.2.3.5. 1,2-dichloroethane and trichloroethylene

The catalytic oxidation of 1,2-dichloroethane (1,2-DCE) over CeₓZr₁₋ₓO₂ mixed oxides in dry air was studied by Gutiérrez-Oritiz and co-workers.⁸²⁸ They postulated that the oxidation of 1,2-DCE proceeds via dehydrochlorination into vinyl chloride (VC) in the presence of acid sites. In the presence of OH surface species, these sites are protonated leading to the formation of carbonium ions, which can be readily attacked by nucleophilic oxygen species from the catalyst to form chlorinated alkoxide species. These intermediates readily decompose to generate acetaldehyde, which could be further oxidized to acetates and finally degraded to COₓ (Fig. 40i).

Similar processes were proposed by Feijen-Jeurissen et al.¹¹⁴⁸ for 1,2-DCE oxidation over Al₂O₃; in this case, 1,2-DCE is activated via HCl elimination to VC, which is followed by an attack from a hydrogen and a surface oxygen on the double bond resulting in the formation of acetyl chloride. Acetyl chloride can then be transformed to acetaldehyde by dechloridation, which can subsequently undergo a series of oxidative reaction to produce acetate before decomposes to COₓ and H₂O.

The complete catalytic oxidation of trichloroethylene (TCE) over Pd/Al₂O₃ was investigated by González-Velasco and co-workers.¹¹³¹ In this reaction, its proposed that gas phase oxygen molecules are dissociatively adsorbed onto active sites and gaseous TCE reacts directly with adsorbed oxygen, leading to CO and CO₂ according to the E-R mechanism. The oxidative decomposition of TCE involved C-Cl bond dissociation by chemical interaction of the halogen with the precious metal and the support. This resulted in precious metal (oxide)-chloride species, [M(Oₓ)Clᵧ], on Al₂O₃ and aluminum chloride. The [M(Oₓ)Clᵧ] species then directly decomposes to molecular chlorine (Cl₂) and also reacts with additional TCE in the feed by transferring
chlorine (Cl$_2$) to the double bond. The pentachloroethane intermediate species was spontaneously dehydrochlorinated by HCl elimination, resulting in the formation of the more stable tetrachloroethylene. CO and C$_2$Cl$_4$ were also assumed to react in the gaseous phase with adsorbed atomic oxygen (Fig. 40ii).

Miranda et al. proposed that the oxidation of trichloroethylene over a Ru/Al$_2$O$_3$ catalyst proceeds via at least three reaction pathways: (1) trichloroethylene reacts with oxygen, yielding deep oxidation products (CO$_2$, Cl$_2$ and HCl) directly; (2) the chlorine formed in the first step reacts with the double bond yielding pentachloroethane or leads to an elimination reaction yielding tetrachloroethene and hydrogen chloride; (3) the pentachloroethane or tetrachloroethene reacts with additional chlorine, yielding tetrachloromethane and trichloromethane (Fig. 40iii). Finally, all the chlorinated by-products formed can react with oxygen to yield the deep oxidation products.

**7.2.3.6. Chlorobenzene and 1,2-dichlorobenzene**

Chlorobenzene (CB) oxidation mechanisms over CeO$_2$ and Ru/CeO$_2$ were proposed by Lu and co-workers. The authors suggested that the C-Cl bond in CB was dissociated with relative ease over Ce$^{3+}$/Ce$^{4+}$ active sites. It is suggested that this is then followed by its oxidation to CO$_2$ and H$_2$O by reactive surface oxygen or lattice oxygen. The adsorption of chlorine species on the active sites results in the rapid deactivation of the catalyst due to the blocking of the active sites. It was proposed that such deactivation can be prevented by the addition of Ru, which catalyzed the removal of adsorbed chlorine species via the Deacon reaction (Fig. 41i).

The catalytic oxidation of 1,2-dichlorobenzene (o-DCB) in wet air was investigated over protonic zeolites (HFAU, HBEA, HMFI, HMCM22 and ITQ2). The results from this study indicated that the oxidation pathways proceed through a concerted six centered mechanism, where two o-DCB molecules react over the BAS. The first molecule reacts directly with protonic center to give HCl, and second one reacts with the first o-DCB molecule to give CB and other adsorbed surface species on the framework oxygen of zeolite. It proposed that these adsorbed species can then be oxidized by oxygen with the participation of H$_2$O to produce CO$_2$, CO, HCl; regenerating the protonic sites of the zeolite. Albonetti et al. concluded that both LAS and BAS acted as adsorption sites and that chloroaromatics adsorbed via chlorine abstraction on the LAS
and hydrogen abstraction on BAS (Fig. 41ii). However, the presence of numerous BAS ultimately led to the incomplete decomposition of chlorobenzene.

7.2.3.7. Acrylonitrile

Obuchi and co-workers demonstrated that acrylonitrile decomposition over Cu-ZSM-5 catalysts is initiated by the oxidation of the vinyl group to form gaseous HCN, NO\textsubscript{x}, surface \textbf{-NCO}, and nitrate species. The isocyanate species is hydrolyzed to NH\textsubscript{3} and N\textsubscript{2} was formed by the reaction between adsorbed NH\textsubscript{3} with nitrate and by the oxidation of adsorbed NH\textsubscript{3} (Fig. 42i). Poignant et al. suggested that AN decomposition over Cu-ZSM-5 proceeded via AN adsorption $\rightarrow$ Cu\textsuperscript{+}-CN $\rightarrow$ Cu\textsuperscript{+}-NC $\rightarrow$ Cu\textsuperscript{+}-NCO $\rightarrow$ Cu\textsuperscript{+}-NH\textsubscript{3} and that the adsorbed NH\textsubscript{3} subsequently reacts with NO to form N\textsubscript{2}.

The oxidation pathway of AN over Ag-based catalysts was reported by Obuchi and co-workers. They indicated that AN oxidation proceeds on Ag\textsubscript{2}O species and NH\textsubscript{3} and acrylic acid intermediates were respectively oxidized to N\textsubscript{2} and CO\textsubscript{x} over metallic Ag. The direct oxidation of AN over large metallic Ag particles in Ag/ZrO\textsubscript{2} and Ag/MgO formed large amounts of NO\textsubscript{x} and N\textsubscript{2}O. For Ag-ZSM-5, AN was decomposed into nitrogen-containing products and some hydrocarbons over Ag\textsuperscript{+}, Ag\textsubscript{n}\textsuperscript{δ+} and Ag\textsubscript{n} clusters (Fig. 42ii).

8. Typical catalytic reactor and oxidizer

Many different types of reactors (e.g., fixed-bed reactors and fluidized-bed reactors) have been reported in the literature for the catalytic oxidation of VOCs. Fixed-bed reactors can be subdivided into continuous flow fixed-bed reactors and membrane reactors. A series of structured catalysts such as monolithic honeycomb catalysts and foam catalysts (detailed research progresses can be found in section 4), have been designed to replace conventional granular catalysts with high diffusion resistance in the continuous flow fixed-bed reactor, which can improve gas-solid contact, enhance the attrition resistance of a given catalyst and reduce pressure drops across the system. Recently, Nigar et al. developed a microwave-heated adsorbent-reactor system containing an adsorptive DAY zeolite and PtY zeolite (Fig. 43). The reactor was used to investigate the continuous oxidation of \textit{n}-hexane (500 ppm). The zeolites were selectively heated by short periodic microwave pulses, which resulted in the desorption of \textit{n}-hexane and its catalytic combustion. The authors found that the reactor was highly efficient, even under realistic humid
gas conditions, as these conditions favored more intense microwave absorption, producing a faster heating of the adsorptive and catalytic beds. Under these conditions, the continuous removal of gaseous VOCs could be achieved with short (3 min, 30 W) microwave heating pulses (5 min).

Catalysts and porous membranes can be combined in different ways (extractor, distributor and contactor) depending on the required applications in a given membrane reactor (Fig. 44i). Membrane reactors operating in the Knudsen regime under a flow-through configuration, is typically adopted for VOC removal as this type of gas-solid contactor provides an intimate contact between the molecules and the wall of the pores, thus minimizing any diffusive resistance. The configuration of the reactor can also have a significant influence on the performance of catalysts for the oxidation of VOCs. Fiaty and co-workers compared the behavior of a Pt/Al₂O₃ catalyst in a conventional monolithic reactor and a flow-through membrane reactor (contactor type) for the oxidation of propene. It was determined that flow-through membrane reactor performs better due to the high contact efficiency between the propene, O₂ molecules and catalytic active sites (Fig. 44ii). This was subsequently evidenced further by Kajama et al., who also observed that the contactor flow-through membrane reactors were highly effective for this reaction.

Most of the published work investigating the catalytic oxidation of VOCs employs the use of continuous flow fixed-bed reactors. As such, it is important to consider that when supported metal catalysts are investigated, much of the reactor volume is occupied by the catalyst support, rather than the active catalytic species itself. Syed-Hassan and Li recently proposed an alternative approach for the aerobic catalytic oxidation of ethane, which utilized a nanoparticle fluidized-bed reactor (Fig. 45). This novel approach benefits from many different merits which include; a low pressure drop, good dispersion of the active species, a uniform temperature distribution inside the catalyst bed and an absence of intra-particle mass transfer barriers. The preliminary results were exceptionally positive and indicated that the fluidized NiO nanoparticles exhibited very different characteristics when it was compared with a traditional NiO/SiO₂ catalyst. It was determined that the lack of a rigid porous structure in the fluidized NiO nanoparticles facilitated the desorption of ethyl radicals from the surface of the NiO nanoparticles into the gas phase, which was suggested...
to initiate further gas-phase radical reactions. This ultimately led to an enhancement in the reaction rate over the NiO nanoparticles.

Catalysis has been widely used for industrial pollution control, which is likely to be attributed to the high activities and selectivities which can be achieved at relatively low reaction temperatures. Regenerative catalytic oxidizers (RCOs) and recuperative catalytic oxidizers (COs) are of two main catalytic technologies in industrial VOC control. The RCO technique developed by Boreskov and Matros\textsuperscript{1158} in the mid-1970s combines the advantages of catalytic oxidation with a thermal recovery system, obtaining high treatment efficiency, low operational temperature, low fuel cost and low selectivity to harmful by-products. The combination of these two technologies is very much considered to be an energy-efficient method for eliminating VOCs.\textsuperscript{1159-1161}

In an RCO system, chambers of inert regenerative materials with high specific heat capacities (800-1000 J·kg\textsuperscript{-1}·K\textsuperscript{-1}) are utilized to heat the VOC stream by cooling burnt gases, through reverse flow operation, which can dramatically cut fuel costs. In such systems, catalysts are used to reduce the required reaction temperatures and increase the overall efficiency of the VOCs oxidation.\textsuperscript{1162,1163} As shown in Fig. 46, a two bed RCO is predominantly composed of ceramic layers, catalyst layers, a natural gas burner/electrical heater (for heat storage), reaction media and heat supply. The entry direction of the VOC flow turns over with four combined valves switching every 1-2.5 min. The VOC flow is preheated by the ceramic layer when passing through ceramic chamber A. Most of the heat can be reserved in the ceramic heat storage media (thermal recovery efficiency ≥ 95\%) when the reacted flow proceeds down through to ceramic chamber B, and is ready to preheat the inlet VOCs for the next cycle.\textsuperscript{7,1163}

It is also important to note that there are some other distinct advantages of using RCO besides the merits mentioned above: (1) long characteristic cooling times and short characteristic heating times for RCOs ensure a stable autothermal operation, despite inlet parameters fluctuating greatly; (2) fast start-ups are possible with RCOs as the catalyst temperature does not need to exceed 250-350°C and this procedure typically only requires between 1 to 3 h operation time, even when the catalyst bed is cold; (3) the RCOs purification unit can be used as a source of secondary high-potential energy such as steam, hot water and hot gas when the VOC content in the gas mixture is higher than 2.5-3.0 g·m\textsuperscript{-3}. For these conditions, the released heat can be removed from
the hottest area of the packed bed. In some cases, this actually makes the process of gas purification profitable.\textsuperscript{1164,1165}

Compared to RCOs, COs have space advantages as only a tubular/plate heat exchanger is used to replace regenerative thermal ceramic heat storage layers. However, the thermal recovery efficiency of a normal CO is generally below 70\%, which is attributable to the simpler heat exchanger configuration. As such, COs are not suitable to use in large volume industrial streams with low VOC concentrations.\textsuperscript{1166} Taking into account the low initial investment and high flexibility, COs are suitable for treating VOC streams with low flowrate ($< 5000 \text{ m}^3\text{h}^{-1}$). However, its important to note that the use of RCO and CO systems may not always be beneficial: (1) the presence of organometallic or inhibiting compounds may reduce catalytic performance; (2) certain compounds such as C\textsubscript{2} to C\textsubscript{5} paraffins, cannot be easily oxidized effectively at temperatures lower than 430 °C; (3) emissions should be considered when operating with low VOC concentrations and large flowrates.\textsuperscript{1159} Some new or coupled treating technologies have also been developed in an attempt to side-step the disadvantages of single RCOs or CO systems. These systems include; photocatalytic oxidation, adsorptive concentration-catalytic oxidation, regenerative thermal catalytic combustion and non-thermal plasma assisted catalytic oxidation.

9. Conclusions and perspectives

 Catalytic oxidation is one of the most promising technologies for VOC removal; it is more effective and economical than the conventional thermal incineration techniques, especially for application in low concentration pollutant streams ($< 0.5 \text{ vol.\%}$). This article summarizes the progress made on the catalytic oxidation of VOCs over the past two decades from a visual approach; focusing on the differing pollutant types and sources. The effects of reaction conditions on oxidation efficiency and the causes for catalysts deactivation and protocols for their subsequent reactivation were discussed. Kinetic models and oxidation mechanisms for representative VOCs were considered and typical catalytic reactors and oxidizers for industrial VOC destruction were reviewed.

 Noble metal supported catalysts generally exhibit a superior activity to metal oxide catalysts; a trend which is perhaps most pertinent in the total catalytic oxidation of alkanes, alkenes and oxygen-containing VOCs. Amongst these, Pt and/or Pd supported catalysts are the most
extensively studied, which is likely to be attributable to their high efficiency for the removal of VOCs at relatively low temperature. The activity of supported noble metal catalysts is mainly governed by the intrinsic properties of the active phase and support, active metal precursor, total metal loading, preparation method and status of metal active sites (dispersion, size, morphology, and valence). Although noble metal based catalysts often have a higher activity than metal oxide catalysts, in general they suffer from several disadvantages, such as; the expense of the metal precursors and its poor natural abundance, high volatility and low resistance to heteroatom poisoning such as Cl and S; Ru is somewhat an exception to this does, as it has a relatively higher tolerance to Cl than other noble metal catalysts. By comparison, the efficiency of single metal oxide catalysts for the removal of VOCs is usually considerably lower than that of noble metal supported catalysts, but they are typically more tolerant to poisoning. In general, the most active single metal oxide catalysts for the complete oxidation of VOC are oxides consisting of Mn, Co, Cr, Fe, Ni, and Cu, as these are reducible and can strongly adsorb organic compounds at anionic oxygen sites in oxide lattices, leading to the activation of VOC molecules, formation of intermediate species and promoting the subsequent complete oxidation. In the field of CVOC treatment, especially under humid atmosphere, catalytic hydrolytic oxidation has been happened. The metal oxide catalysts (e.g., CrO$_x$ and VO$_x$) with high Cl resistance have distinctive advantages over noble metal supported catalysts. Similar results are reflected from the decompositon of NVOCs (selective catalytic oxidation in general) as the amount of NO$_x$ by-product over noble metal based materials, is typically much higher than that over transition metal catalysts such as Cu-ZSM-5. Great efforts have been made to develop more efficient catalysts based on transition metal oxides for the catalytic oxidation of VOCs, the primary aim of which is to improve the low-temperature efficiency and ultimate exhibit activity which is competitive with that observed over noble metal supported catalysts. Mixed metal oxides have significantly different properties (morphology, texture, redox and acid-base) than the single metal oxides, which makes mixed metal oxides such as NiMnO$_x$, CuMnO$_x$, and CoMnO$_x$ in general, possess higher catalytic activities than their analogous single metal oxide forms. Monolithic catalysts are highly suited for large scale applications such as the industrial abatement of VOCs. Their desirability in such applications is attributed to the low-pressure drop they provide and their excellent mass and heat transfer performance. Moving forwards, we consider it to be crucial that
data concerning mass and heat transfer effects on catalytic reaction rates is carefully considered when designing monolithic systems for the catalytic oxidation of VOCs.

Water vapor is commonly present in industrial flue gase streams. These streams can often also consists of various mixtures of VOCs rather than just a singular pure component. Co-occurrence of water vapor in VOCs mixture should have the activity effect on a given catalyst. In most cases, water vapor acts as an inhibitor in VOC oxidation due to competitive adsorption and reaction of water molecules and reactants on catalytic active sites. The use of hydrophobic supports seems be an effective protocol to alleviate such inhibition. The presence of water vapor is however in some cases, is beneficial for the oxidation of some VOCs. Water can assist with oxygen activation and replenish consumed hydroxyl groups on a given surface. For the catalytic destruction of CVOCs, water vapor can also play a positive role in removing Cl\textsuperscript{-} from active sites and can prevent catalytic deactivation. Moreover, water can also act as a hydrolysis agent and source of hydrogen, which in some cases, can decrease by-product (e.g., poly-chlorinated hydrocarbons, PCHs) formation.

The rates of reaction for a given compound in a stream containing mixtures of VOCs cannot be predicted solely from the behavior of the individual components, as mutual effect and reactivity of VOC mixtures is related to many parameters such as the catalyst type, pollutant component and reaction conditions. In the vast majority of cases, aromatic hydrocarbons have significant inhibition effects on aliphatic hydrocarbons, while the inhibition effects of aliphatic hydrocarbons on aromatic hydrocarbons are relatively weak. The co-existence of aromatic hydrocarbons can also inhibit each other. The existence of aliphatic/aromatic hydrocarbons has different effects on the oxidation of CVOCs as the hydrocarbon additive can compete with CVOC molecules for adsorption sites. In addition to this, they can act as a source of H, which can reduce the generating of hydrocarbon by-products and enhance the selectivity to HCl and CO\textsubscript{2}. Therefore, special attention should be paid to understand how different VOCs can affect the reactivity of one another over different catalysts.

Despite the progress made in this field, many issues remain and must be resolved to meet the stringent emission standards in an economical and effective manner. Moving forward, we consider that future efforts should focus on the following aspects: (1) developing efficient catalysts with highly dispersed active phase or highly exposed reactive facets, abundant defect
sites and strong interfacial interactions, for instance, hierarchical porous materials, skeleton/channel-confined materials, core-shell structured materials and single-atom catalytic materials; (2) designing highly active, universally applicable and stable catalysts, with a strong resistance to poisons (particularly for halogenated or sulfur-containing organic pollutants) as the practical reaction environments are usually very complicated and trace pollutants including water vapor, ammonia and sulfur containing compounds may co-exist in these streams; (3) exploit the developments made in the field of molecular modelling; use of theoretical calculations and models to simulate mass and heat transfer effects and predict the reaction behavior of given systems/reactors, especially for mixed VOCs catalytic destruction; (4) demonstrate how bond cleavage and oxidation mechanisms of VOCs are influenced by reaction conditions or time at the molecular level. This can be achieved through application of in situ/operando characterization techniques such as FTIR, synchrotron radiation, isotopic tracer techniques and highly sensitive real-time monitoring techniques such as proton transfer reaction-mass spectrometry; (5) establish how different catalytic active sites (i.e., redox center, noble metal active sites and acidic/basic center) activate the VOC and intermediate species in order to develop a deeper understanding of desirable properties to aid future catalyst design; (6) derive a greater understanding of the deactivation or poisoning mechanisms of different catalysts. This can be achieved by establishing correlations between the material surface chemistry and its catalytic performance, and through exploration of effective regeneration methods (in particular, in situ regeneration) for deactivated catalysts, to reduce the operating cost and ultimately, increase industrial viability; (7) development of coupling technologies such as adsorptive concentration-catalytic oxidation, regenerative thermal catalytic combustion, non-thermal plasma assisted catalytic oxidation, ozone-catalytic oxidation and photo induced catalytic oxidation to enhance VOC removal in a more efficient and cost-effective way.

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References


(18)Tokumura, M.; Nakajima, R.; Znad, H. T.; Kawase, Y. Chemical Absorption Process for


(67) Baran, R.; II Kaminska; Srebowata, A.; Dzwigaj, S. Selective Hydrodechlorination of


(149) Nitadori, T.; Misono, M. Catalytic Properties of $\text{La}_{1-x}\text{A'}_x\text{FeO}_3$ ($\text{A'} = \text{Sr, Ce}$) and $\text{La}_{1-x}\text{Ce}_x\text{CoO}_3$. *J. Catal.* **1985**, *93*, 459-466.


(205) Brunelle, J. P.; Delmon, B.; Grange, P.; Jacobs, P.; Poncelet (Eds.), G. *Preparation of Catalysts II*, Elsevier: Amsterdam, 1999; p 211.


(208) Gluhoi, A. C.; Bogdanchikova, N.; Nieuwenhuys, B. E. Total Oxidation of Propene and
Propane over Gold-Copper Oxide on Alumina Catalysts: Comparison with Pt/Al\textsubscript{2}O\textsubscript{3} Catal. Today 2006, 113, 178-181.


(212) Chzhu, D. P.; Tsyrul'nikov, P. G.; Kudrya, E. N.; Smolikov, M. D.; Borbat, V. F.; Bubnov, A. V. Effect of Thermal Activation of Supported Catalysts Pt/MeO\textsubscript{x}, Where MO\textsubscript{x} = Al\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}, La\textsubscript{2}O\textsubscript{3}, and ZrO\textsubscript{2}, for Complete Oxidation. Kinet. Catal. 2002, 43, 379-383.


(253) Najafishirtari, S.; Guardia, P.; Scarpellini, A.; Prato, M.; Marras, S.; Manna, L.; Colombo,


(299) Hou, J. T.; Li, Y. Z.; Liu, L. L.; Ren, L.; Zhao, X. J. Effect of Giant Oxygen Vacancy


(314) Mo, S. P.; Li, S. D.; Li, J. Q.; Peng, S. P.; Chen, J. Y.; Chen, Y. F. Promotional Effects of


Kim, I. H.; Park, E. J.; Park, C. H.; Han, S. W.; Seo, H. O.; Kim, Y. D. Activity of Catalysts Consisting of Fe$_2$O$_3$ Nanoparticles Decorating Entire Internal Structure of Mesoporous Al$_2$O$_3$


(402) Li, J. J.; Li, L.; Wu, F.; Zhang, L.; Liu, X. M. Dispersion-Precipitation Synthesis of


(417) Li, W.; Chu, W.; Zhuang, M.; Hua, J. Catalytic Oxidation of Toluene on Mn-Containing


(432) Jiang, S. J.; Song, S. Q. Enhancing the Performance of Co₃O₄/CNTs for the Catalytic


(470) Hosseini, S. A.; Salari, D.; Niaei, A.; Oskoui, S. A. Physical-Chemical Property and Activity Evaluation of LaB$_{0.5}$Co$_{0.5}$O$_3$ (B= Cr, Mn, Cu) and LaMn$_x$Co$_{1-x}$O$_3$ (x = 0.1, 0.25, 0.5) Nano Perovskites in VOC Combustion. *J. Ind. Eng. Chem.* **2013**, *19*, 1903-1909.


149-160.


(481) Wang, Y. Q.; Xue, Y. F.; Zhao, C. C.; Zhao, D. F.; Liu, F.; Wang, K. K.; Dionysiou, D. D. Catalytic Combustion of Toluene with La$_{0.8}$Ce$_{0.2}$MnO$_3$ Supported on CeO$_2$ with Different Morphologies. *Chem. Eng. J.* 2016, 300, 300-305.


(491) Bendahou, K.; Cherif, L.; Siffert, S.; Tidahy, H. L.; Benaïssa, H.; Aboukaïs, A. The Effect of the Use of Lanthanum-Doped Mesoporous SBA-15 on the Performance of Pt/SBA-15 and


Ce$_{0.6}$Zr$_{0.3}$Y$_{0.1}$O$_2$ Nanorod Supported Gold and Palladium Alloy Nanoparticles: High-Performance Catalysts for Toluene Oxidation. *Nanoscale* **2015**, *7*, 8510-8523.


*Environ. 2012, 127, 77-88.*


Xia, Y. S.; Dai, H. X.; Jiang, H. Y.; Zhang, L. Three-Dimensional Ordered Mesoporous


(612) Aguero, F. N.; Scian, A.; Barbero, B. P.; Cadús, L. E. Influence of the Support Treatment on


(628) Jiratova, K.; Mikulova, J.; Klempe, J.; Grygar, T.; Bastl, Z.; Kovanda, F. Modification of


(673) Bai, L.; Wyrwalski, F.; Safaramin, M.; Bleta, R.; Lamonier, J.-F.; Przybylski, C.; Monflier,


2015, 119, 7724-7733.


(719) Lin, L.-Y.; Bai, H. Promotional Effects of Manganese on the Structure and Activity of


(747) Tsoncheva, T.; Issa, G.; Nieto, J. M. L.; Blasco, T.; Concepcion, P.; Dimitrov, M.; Atanasova,


(807) Cai, T.; Huang, H.; Deng, W.; Dai, Q.; Liu, W.; Wang, X. Catalytic Combustion of...


(832) de Rivas, B.; López-Fonseca, R.; Gutiérrez-Ortiz, M. A.; Gutiérrez-Ortiz, J. I. Impact of Induced Chlorine-Poisoning on the Catalytic Behaviour of Ce$_{0.5}$Zr$_{0.5}$O$_2$ and Ce$_{0.15}$Zr$_{0.85}$O$_2$ in the Gas-Phase Oxidation of Chlorinated VOCs. *Appl. Catal. B: Environ.* **2011**, *104*, 373-381.


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(867) Lee, D. K.; Yoon, W. L. Ru-Promoted CrO$_x$/Al$_2$O$_3$ Catalyst for the Low-Temperature


(963) Nevanperä, T. K.; Ojala, S.; Bion, N.; Epron, F.; Keiski, R. L. Catalytic Oxidation of Dimethyl Disulfide (CH₃SSCH₃) over Monometallic Au, Pt and Cu Catalysts Supported on


(977) Wang, C. H.; Weng, H. S. Promoting Effect of Molybdenum on CuO/γ-Al2O3 Catalyst for the


(993) Luo, M. F.; He, M.; Xie, Y. L.; Fang, P.; Jin, L. Y. Toluene Oxidation on Pd Catalysts


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