

Gold as a Catalyst for the Ring Opening of 2,5-Dimethylfuran

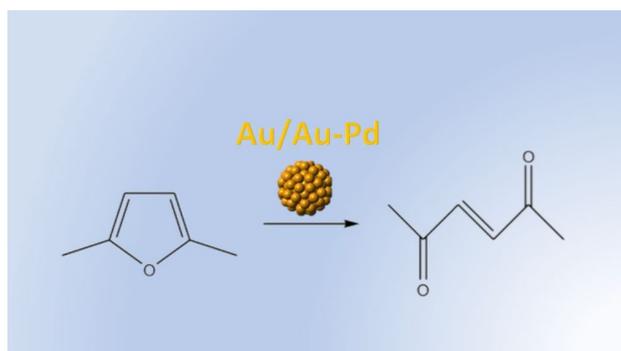
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Abstract

The epoxidation of 2,5-dimethyl furan leads to the production of hex-3-ene-2,5-dione via a ring opening rearrangement reaction. A second epoxidation reaction could then enable a further ring closing rearrangement to form 4-hydroxy-2,5-dimethyl-3-furanone (furanol). In this paper we report the use of gold and gold palladium supported on graphite and titania as catalysts for the ring opening reaction of 2,5-dimethyl furan. We show that by tuning the reaction conditions high selectivity towards hex-3-ene-2,5-dione can be achieved using green chemical methods and mild reaction conditions.

Graphical Abstract



Keywords 2,5 Dimethylfuran · Gold catalysis · Hex-3-ene-2,5-dione

1 Introduction

Recently there has been considerable interest in the use of supported gold as catalysts for oxidation reactions [1–6]. This is due to its high activity and the green nature of using

catalysis for chemical transformations. Studies have shown that cyclohexene and cyclooctene can be oxidised to their respective epoxides using supported gold catalysts [7]. High selectivity can be achieved to the epoxide by tuning the reaction conditions, primarily the solvent. Heterogeneous catalysis is a key process in the manufacture of a large range of bulk and fine chemicals. Since the discovery that supported Au nanoparticles can be used in catalysis [8, 9] there has been increased interest in the application of Au in oxidation catalysis. Supported gold catalysts have been shown to be highly stable under oxidation reaction conditions and nanoparticulate gold on a range of oxide supports has been used for a range of applications such as CO oxidation [10–12], CO oxidation in the presence of H₂, H₂O and CO₂ for fuel cells [13, 14], the oxidation of alkenes [15–18] and alcohols [19, 20], including polyols such as glycerol [21]. Gold

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supported on TiO_2 and TS-1 have been shown to be very active for the epoxidation of propene to propene oxide in the presence of H_2 and O_2 via the formation of a peroxy intermediate [22, 23]. However, the use of a sacrificial reductant is not ideal for green applications, and the use of pure O_2 is preferred. Caps and co-workers [24] have shown that supported gold catalysts can be used to convert trans-stilbene into trans-stilbene oxide in the presence of molecular oxygen. In this case titania was found to be the a better support than carbon or iron oxide in terms of epoxide yield.

The initial oxidation of 2,5-dimethylfuran to form hex-3-ene-2,5-dione has been reported using several different methods (Scheme 1). One of the most successful was reported by Adger et al. [25] who used dimethyldioxirane as an oxidant at room temperature using acetone as a solvent. With one equivalent of dimethyldioxirane quantitative yield of hex-3-ene-2,5-dione was obtained. Finlay et al. [26] found that methytrioxoruthenium in combination with urea hydrogen peroxide could also be used to ring open furan systems. The reaction was carried out at room temperature and gave a yield of 97% of hex-3-ene-2,5-dione. Massa et al. [27] used a $\text{Mo}(\text{CO})_6$ /cumyl hydroperoxide system to oxidise 2,5-dimethyl furan, 2 mmol of 2,5-dimethyl furan was converted by $\text{Mo}(\text{CO})_6$ in chloroform at 50°C with a yield of 94%. Wahlen et al. [28] used titanium silicate (TS-1) and hydrogen peroxide to oxidise various furan derivatives achieving 94% conversion with a selectivity of 85% to hex-3-ene-2,5-dione. While these processes give high yields of hex-3-ene-2,5-dione they are often carried out on a small scale, with large amounts of solvent and therefore cannot be called green processes. The further oxidation of hex-3-ene-2,5-dione could lead to 3,4-dihydroxyhexane-2,5-dione. Briggs et al. [29] have shown that 3,4-dihydroxyhexane-2,5-dione can be converted into furaneol; refluxing an aqueous solution of 3,4-dihydroxyhexane-2,5-dione for 7 days with piperidinium acetate resulted in the production of furaneol with a 48% yield. In this paper we show that by tuning the reaction conditions it is possible to achieve a high conversion and high selectivity towards hex-3-ene-2,5-dione while applying the principles of green chemistry using gold-containing heterogeneous catalysts.

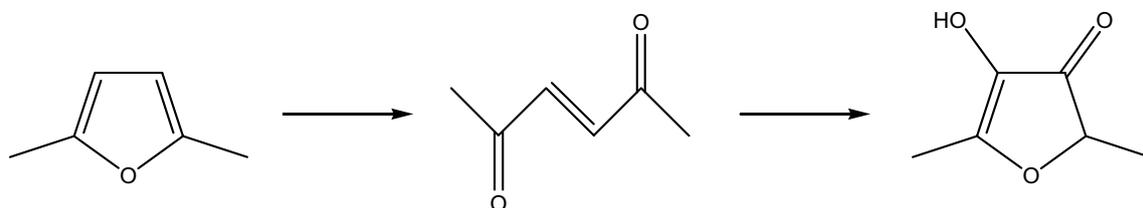
2 Experimental

2.1 Catalyst Preparation

Gold nanoparticle catalysts were prepared supported on titania (P25 Degussa) or graphite (Aldrich), using a wet impregnation technique. The monometallic 2.5 wt% Au and bimetallic 2.5 wt% Au–2.5 wt% Pd were prepared by impregnation of the support using aqueous solutions of palladium chloride (Johnson Matthey) and $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Johnson Matthey). The detailed procedure for the preparation of the 2.5 wt% Au–2.5 wt% Pd/support catalyst (2 g) is as follows: palladium chloride (83.3 mg) was dissolved in a stirred and heated aqueous solution (5 ml) of HAuCl_4 (5 g in 250 ml water). The resultant solution was added to the support (1.9 g) and stirred until it formed a slurry, this was dried at 80°C for 16 h. The resultant powder was ground and calcined (1 g, 15 cm quartz boat) in static air at 400°C for 3 h at a ramp rate of $20^\circ\text{C min}^{-1}$. We have previously reported the characterisation of Au–Pd catalysts prepared by this methodology, and have shown that the metal particles are bi-modal in their size distribution with the majority of metal particles in the < 15 nm range, but with a significant amount of the metal present as large particles 15–300 nm [30–32]. Catalyst recovery for resue testing was attempted however the catalyst proved disfficult to sperate from the product mixture.

2.2 Catalyst Testing

Catalyst testing was performed using a Parr Instruments stainless steel autoclave with a nominal volume of 50 ml and a maximum working pressure of 207 bar. The reactor was charged with 2,5-dimethyl furan (20 ml, Sigma Aldrich), catalyst and radical initiator (TBHP, when required, 70% in water, Sigma Aldrich). The autoclave was then purged three times with oxygen leaving the vessel at the desired pressure (5–30 bar). The pressure was maintained at a constant level throughout the experiment; as the oxygen was consumed in the reaction it was replenished. The effect of pressure during the reaction was studied by varying the initial O_2 pressure in the reactor. The reaction was carried out



Scheme 1 The preferred reaction scheme for the sequential oxidation of 2,5-dimethyl furan

at a number of temperatures (3–75 °C, temperatures > 85 °C resulted in exothermic reaction run-away). The stirrer speed was set at 1500 rpm and the reaction mixture was raised and maintained at the required temperature. Samples were taken from the final reaction mixture and analysed by GC (Varian star 3800) using a CP-Wax column. Carbon balances were calculated and for all the experiments reported were in the range of 80–120% except when reaction run away occurred where it is anticipated that it was significantly lower.

3 Results and Discussion

Following the work of Hughes et al. [7], who successfully demonstrated that 1%Au/graphite is an effective catalyst for the epoxidation of cyclohexene a 2.5%Au/graphite catalyst was used to investigate the oxidation of 2,5-dimethylfuran. Initial attempts to oxidise 2,5-dimethylfuran were carried out at low temperature, either ambient (23 °C) or cooled by ice (3 °C). Under these conditions, the conversion of 2,5-dimethylfuran was negligible after 2 h (Fig. 1).

When the temperature was raised to 50 °C, around 10% conversion was observed after 2 h, however, when the temperature was further raised to 75 °C almost complete conversion of the 2,5-dimethylfuran was achieved (Fig. 1). For all the reported temperatures the selectivity towards hex-3-ene-2,5-dione remained constant (around 60%). Above 85 °C reaction runaway occurred, resulting in a rapid and uncontrollable spike in temperature and pressure. The result

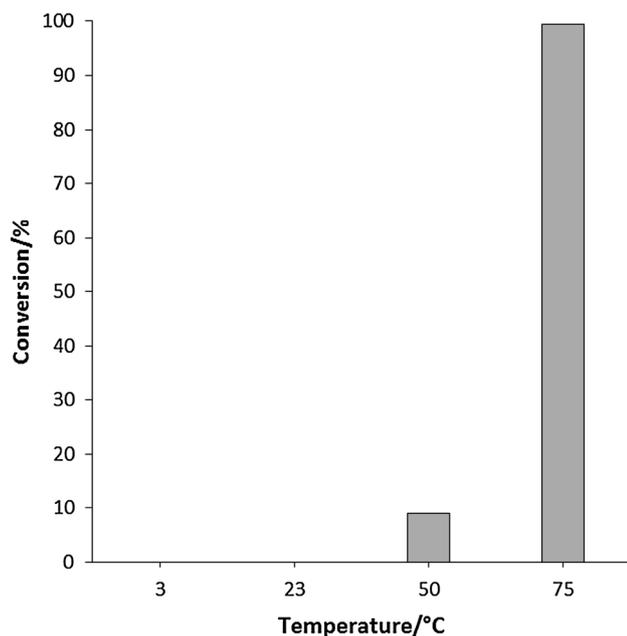


Fig. 1 The effect of temperature on the conversion of 2,5-dimethylfuran during the oxidation by 2.5 wt%Au/graphite (40 mg), 1500 rpm at different temperatures

of this experiment was a mixture of hex-3-ene-2,5-dione and a black tar-like substance. The tar-like substance was insoluble so could not be analysed, this also meant the mass balance could not be calculated in this experiment, however we anticipate it would be very low. Further reactions were restricted to a maximum temperature of 75 °C to avoid this problem. The formation of hex-3-ene-2,5-dione could occur if the initial oxidation reaction leads to the epoxidation of one of the double bonds in the furan. The epoxidation of cyclohexene by supported gold catalysts is a known reaction [7] and the epoxidation mechanism for this ring opening has been proposed by Whalen et al. [28] who used titania silicate as a catalyst and hydrogen peroxide as an oxidant to oxidise various furan derivatives.

As we have previously reported TiO₂ as an effective support for gold catalysts we also synthesised an analogous 2.5%Au/TiO₂ catalyst and contrasted this with the graphite supported gold. At 20 bar O₂ pressure and at 75 °C the initial activity of the 2.5 wt%Au/graphite catalyst was higher than the 2.5%Au/TiO₂, however, as shown in Fig. 2, at longer reaction times the activity of the TiO₂ increased and reached 97% 2,5-dimethylfuran conversion compared to 72% for the graphite supported catalyst. The initially slower reaction, followed by a faster reaction is indicative of a radical pathway occurring when the titania supported catalyst is used, while this leads to a higher activity at longer times the results are more variable, the selectivities towards hex-3-ene-2,5-dione (Fig. 3) of the two catalysts were similar, the differences between the selectivities can be attributed to the differences in

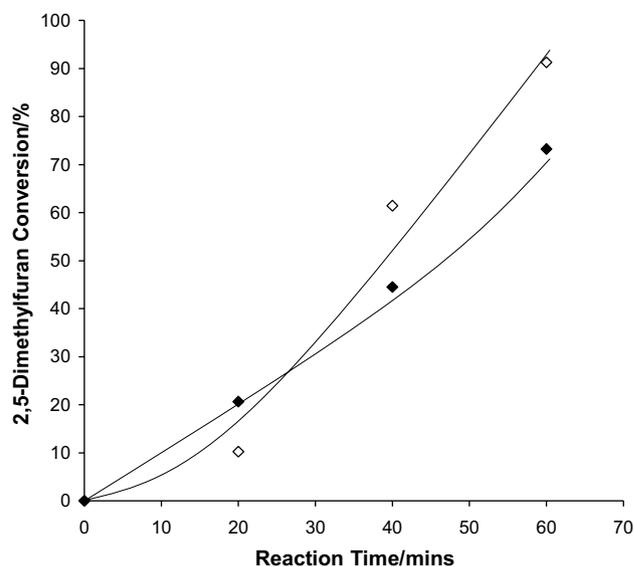


Fig. 2 The oxidation of 2,5-dimethylfuran by 80 mg 2.5 wt%Au supported on titania (opened rhombus) and graphite (filled rhombus) at 75 °C, 20 bar O₂ and 1500 rpm

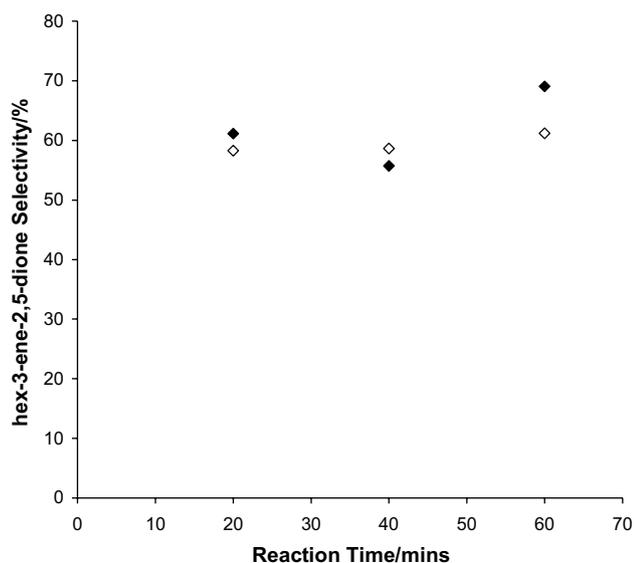


Fig. 3 The selectivity towards hex-3-ene-2,5-dione during the oxidation of 2,5-dimethylfuran by 80 mg 2.5 wt% Au supported on titania (filled rhombus) and graphite (open rhombus) at 75 °C, 20 bar O₂ and 1500 rpm

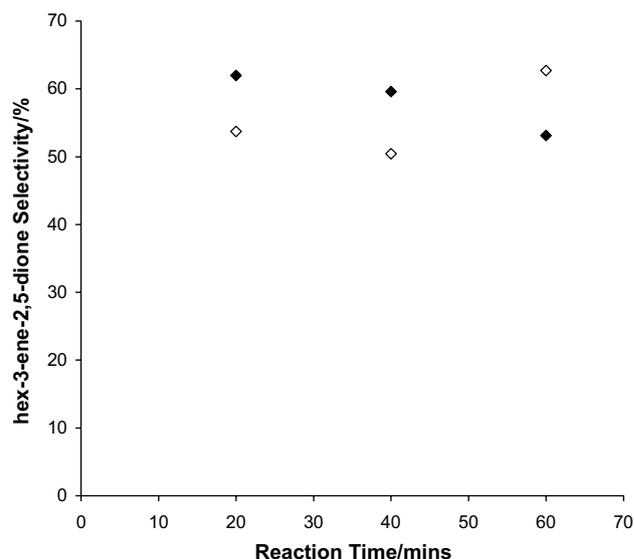


Fig. 5 The selectivity towards hex-3-ene-2,5-dione during the oxidation of 2,5-dimethylfuran by 80 mg 2.5 wt% Au + 2.5 wt% Pd supported on titania (filled rhombus) and graphite (open rhombus) at 75 °C, 20 bar O₂ and 1500 rpm

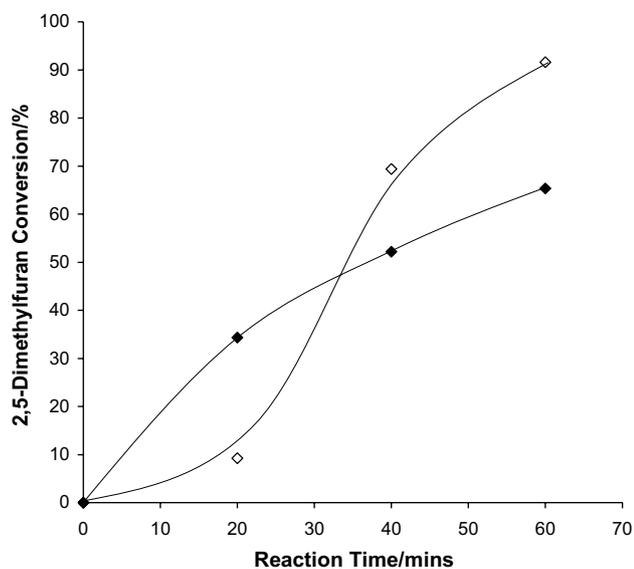


Fig. 4 The oxidation of 2,5-dimethylfuran by 80 mg 2.5 wt% Au + 2.5 wt% Pd supported on titania (open rhombus) and graphite (filled rhombus) at 75 °C, 20 bar O₂ and 1500 rpm

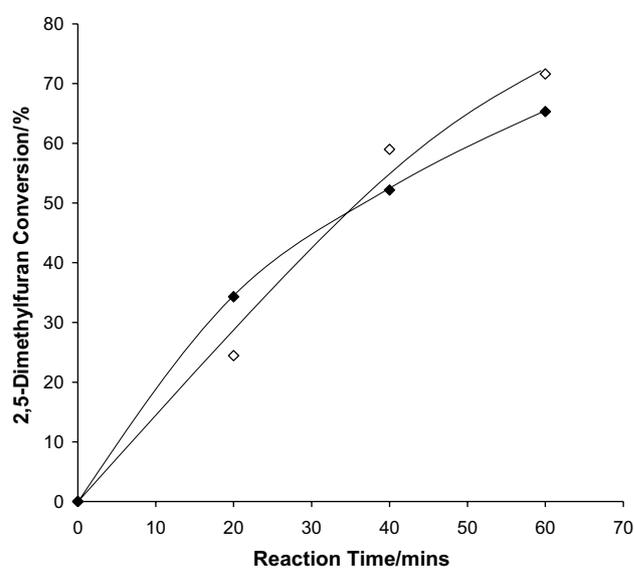


Fig. 6 The oxidation of 2,5-dimethylfuran by 80 mg 2.5 wt% Au + 2.5 wt% Pd supported on graphite (open rhombus) and with the addition of TBHP (0.116 cm³) (filled rhombus) at 75 °C, 20 bar O₂ and 1500 rpm

conversion in the sequential reaction shown in Scheme 1. At iso-conversion (20%) the selectivity towards 2,5-dimethylfuran is almost the same (~61%) suggesting that the same products are being formed whether there are radical pathways in operation or not.

We have previously reported a strong synergistic effect of combining gold and palladium, therefore 2.5% Au 2.5% Pd catalysts were prepared on both graphite and titania. The activity trend for the supports follows the same pattern as the monometallic gold catalysts (Fig. 4). Whilst the conversion after 1 h is similar the initial activity of the bimetallic

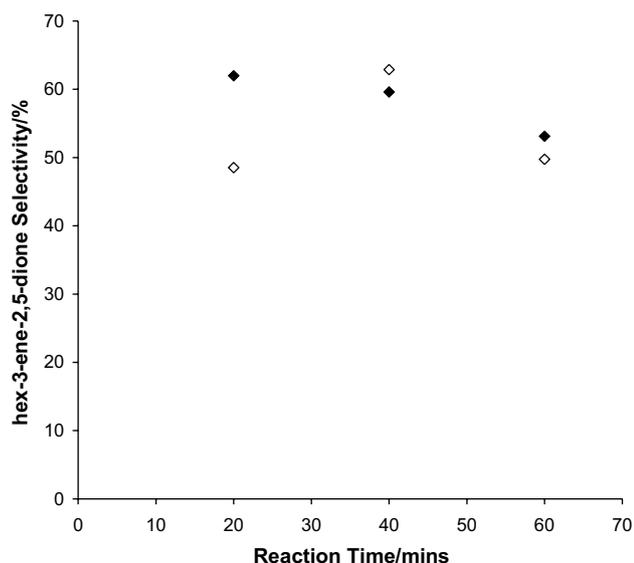
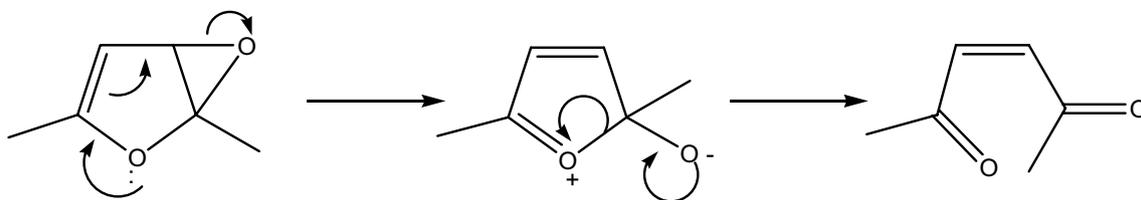


Fig. 7 The selectivity towards hex-3-ene-2,5-dione during the oxidation of 2,5-dimethylfuran by 80 mg 2.5 wt% Au + 2.5 wt% Pd supported on graphite (filled rhombus) and with the addition of TBHP (0.116 cm^3) (opened rhombus) at 75°C , 20 bar O_2 and 1500 rpm

catalysts is higher, suggesting there is some synergistic effect of combining the two metals. It is worth noting, that these catalysts contained more metal so higher activity would be expected in this case. The selectivity towards hex-3-ene-2,5-dione (Fig. 4) was similar to that observed with the monometallic catalyst, the small difference in selectivity is directly related to the difference in the conversion (Fig. 5).

In our previous work [7] we have shown that using a radical initiator can increase the initial rate of reaction. To investigate whether it is advantageous to use a radical initiator for this oxidation, reactions were carried out with the addition of tertiarybutylhydroperoxide (TBHP). As the AuPd catalyst had shown the highest activity this catalyst was selected for this study. The addition of TBHP [0.116 cm^3 , 205 mol/mol (substrate/TBHP)] led to an increase in the initial reaction rate for both the TiO_2 and graphite supported AuPd catalysts (Fig. 6), however, the conversion of 2,5-dimethyl furan over the 60 min reaction run the initiator did not lead to a significant improvement in the conversion of 2,5-dimethylfuran. In each case the selectivity towards hex-3-ene-2,5-dione was similar for each catalyst (Fig. 7; Scheme 2).



Scheme 2 The ring opening of the epoxide product from the oxidation of 2,5-dimethylfuran

The effect of oxygen pressure was studied next, however, to investigate the effects of pressure on the product selectivity of the sequential reaction longer timescale experiments were required, due to the previously described problems with exothermic reaction run-away, longer reactions were limited to 50°C . The catalyst selected for this study was 2.5% Au–2.5% Pd/graphite as this catalyst had displayed the highest initial activities in the previous reactions. Initially the oxygen pressure was increased to 20 and subsequently 30 bar, however, the selectivity towards hex-3-ene-2,5-dione decreased as the pressure increased (Fig. 8), most likely due to over-oxidation to form furaneol. The conversion of 2,5-dimethyl furan is shown in Fig. 9 and it is clear that increasing the pressure to 20 and 30 bar did not lead to an increase in the conversion. Subsequently the pressure of oxygen was reduced to 5 bar, again shown in Figs. 8 and 9.

The decrease in the oxygen pressure did not have a detrimental effect on the conversions of 2,5-dimethyl furan but did, however, have a positive effect on the selectivity towards hex-3-ene-2,5-dione with a maximum selectivity of $\sim 80\%$ towards hex-3-ene-2,5-dione achieved. In view of these results a longer reaction was carried out at 1 bar O_2 pressure (Figs. 10, 11), under these conditions the conversion of 2,5-dimethylfuran was almost complete after 24 h and the selectivity towards hex-3-ene-2,5-dione was consistently the highest displayed under any of the reaction conditions studied in this work suggesting that the ring opening reaction to give hex-3-ene-2,5-dione is zero order with respect to oxygen pressure but the subsequent sequential reaction to form furaneol is more favourable under high pressures of oxygen.

4 Conclusions

We have demonstrated that the ring opening oxidation of 2,5-dimethylfuran to yield hex-3-ene-2,5-dione can be carried out using various gold catalysts, most likely occurring via the epoxidation of one of the furan double bonds. By tuning the reaction conditions, specifically the use of different supports, the addition of a radical initiator and control of the oxygen pressure high selectivity to hex-3-ene-2,5-dione can be achieved. By using heterogeneous catalysts, solvent free conditions and eliminated sacrificial reactants

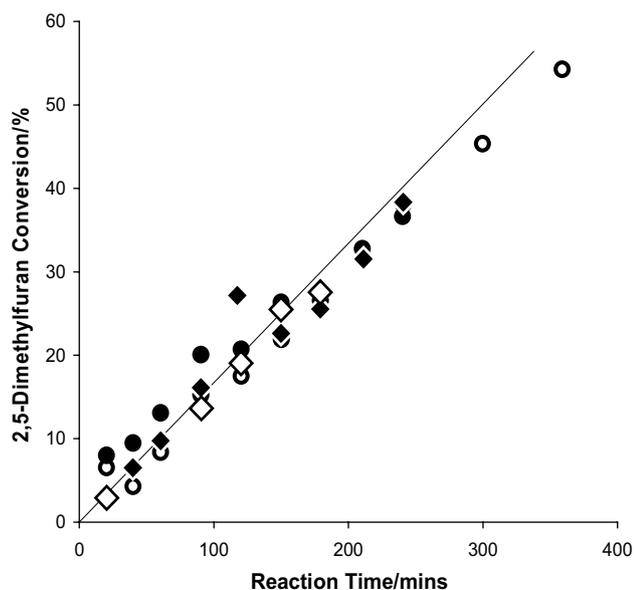


Fig. 8 The effect of O₂ pressure on the selectivity towards hex-3-ene-2,5-dione during the oxidation of 2,5-dimethylfuran by 2.5 wt%Au+2.5 wt%Pd/graphite at 50 °C, 1500 rpm, by 80 mg of catalyst at 5 bar (filled rhombus), 10 bar (opened rhombus), 20 bar (filled circle) and 30 bar (opened circle)

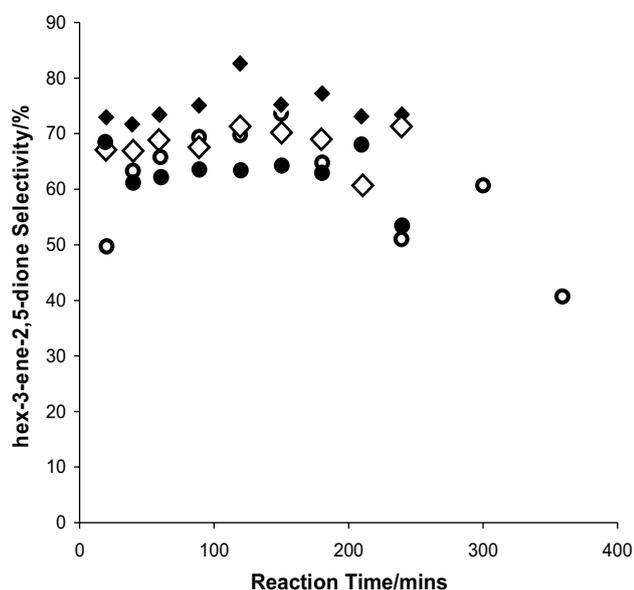


Fig. 9 The effect of O₂ pressure on the oxidation of 2,5-dimethylfuran by 2.5 wt%Au+2.5 wt%Pd/graphite at 50 °C, 1500 rpm, by 80 mg of catalyst at 5 bar (filled rhombus), 10 bar (opened rhombus), 20 bar (filled circle) and 30 bar (opened circle)

the reaction is considerably more environmentally benign than those that have been reported previously. The highest selectivity towards hex-3-ene-2,5-dione was achieved at the lowest pressure of oxygen, this suggests that the formation

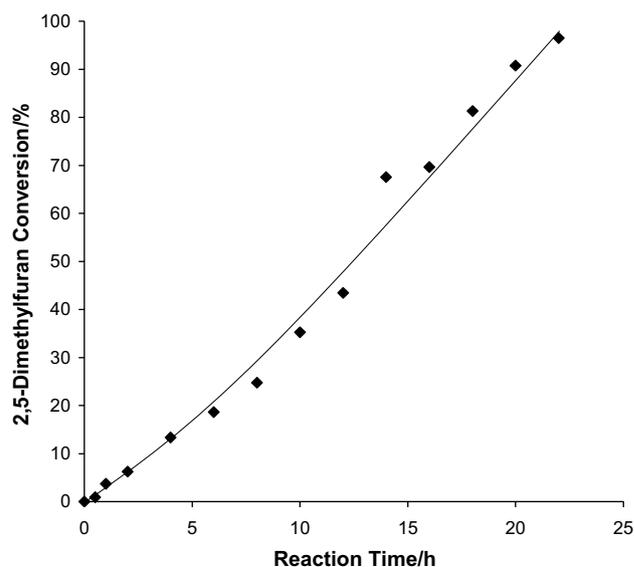


Fig. 10 The conversion of 2,5-dimethylfuran by 2.5 wt%Au+2.5 wt%Pd/graphite at 50 °C, 1500 rpm, by 80 mg of catalyst at 1 bar O₂

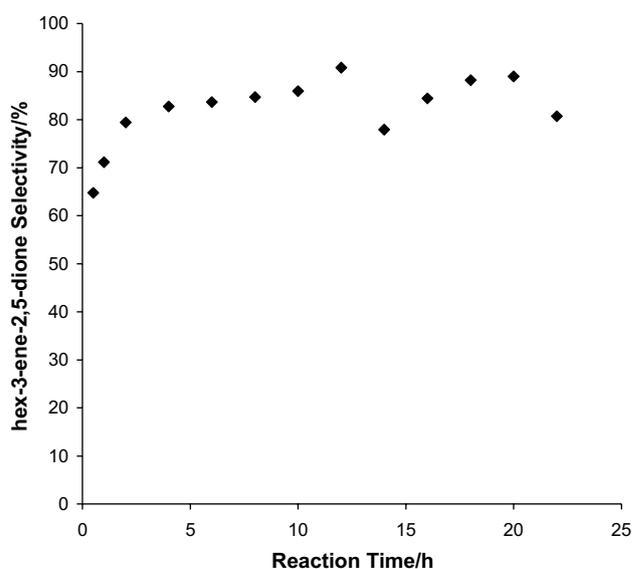


Fig. 11 The selectivity towards hex-3-ene-2,5-dione during the oxidation of 2,5-dimethylfuran by 2.5 wt%Au+2.5 wt%Pd/graphite at 50 °C, 1500 rpm, by 80 mg of catalyst at 1 bar O₂

of sequential oxidation products is more favourable at higher pressures.

Compliance with Ethical Standards

Conflict of interest There are no conflicts of interest.

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