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CO and O₂ Adsorption on K/Pt(111)

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Abstract. We have investigated CO and O₂ on K promoted Pt(111) using mainly molecular beams and TPD. Surprisingly, CO adsorption is little affected by the presence of potassium on the surface up to around 1/6th of a monolayer promoter coverage (half of the maximum), even though the chemisorbed state in TPD is more strongly adsorbed. This is because the adsorption is dominated by the precursor state kinetics which are little affected by the K. However, as the K coverage increases and the layer changes from ionic to metallic, then the adsorption of CO diminishes to zero, since both CO and K are electron donors. In contrast the opposite is the case for oxygen adsorption. The sticking probability on the clean surface is very low, but is enormously enhanced at even low coverages of K, and oxygen can adsorb strongly onto the metallic layer to high coverage. A number of oxygen states can be identified in TPD, those desorbing in the same temperature range as for clean Pt, those associated with Pt affected by K at low coverage of the latter, and those on the metallic layer. The former is dissociated oxygen while the latter is molecular peroxide.

Introduction. Transition metal catalysts often have sub-monolayer amounts of alkali metals incorporated due to the ability of the alkali metal to alter the adsorption characteristics of the catalyst. This is believed to occur via the low ionisation potential of the alkali metal leading to the transference of a valence electron from the alkali metal to the transition metal, which sets up a localised dipole. This transfer of electronic charge is normally evidenced by a marked decrease in the work function of the transition metal surface. The first demonstration of this effect was the observation of a significant enhancement in electron emission from the transition metal surface upon alkali adsorption¹. The adsorption of the alkali metal onto a metal crystal surface hence normally results in a range of altered properties such as differing adsorption kinetics, differing vibrational frequencies of adsorbed species and different adsorption sites becoming available. This effect is most pronounced in heterogeneous catalysis where alkali metal promotion is used to increase the activity of the catalyst and/or the selectivity towards certain products. For instance, in ammonia synthesis it enhances activity of pure iron surfaces, whereas in ethene epoxidation it enhances selectivity. It must be remembered that in catalytic systems the potassium is present in the K⁺ ionic form, associated with anions such as O, OH or CO₃, depending on the reaction system.

Clean Pt(111) has been found to adsorb CO with a high initial sticking probability (S_0)²⁻⁵, although the exact value determined varies. The coverage is a strong function of temperature, but at ambient temperature it is reported to be between 0.3 and 0.5. In contrast to this oxygen has great difficulty in dissociating with S_0 , being low (<0.06) and variable^{4,6-9}, perhaps because dissociation occurs mainly at steps on the surface, the density of which vary from one sample to another. This, of course, implies a high activation barrier to dissociation on pure Pt(111) itself, as described by Luntz et al⁹.

Contaminant-free potassium adlayers have been found to be hexagonally ordered on Pt(111) for potassium coverages of $\theta = 0.9-1$ ¹⁰. A complete monolayer of potassium, $\theta = 1$, is reported to be ~36% of the surface density of platinum atoms or 5.4×10^{14} atoms cm⁻². The ordering of the surface was only visible at low temperature and at room temperature more than one complete monolayer of potassium was not

attainable. The potassium layer could, however, be thermally stabilised by exposure to oxygen¹⁰.

Early models of potassium adsorption onto the Pt(111) surface assumed the charge transfer model as proposed by Gurney¹¹, in which the adsorbing potassium donates electron density to the surface from an s-orbital. Repulsion between the resulting dipole species formed leads to the adsorbate being spread evenly over the surface rather than clumping into islands. In this model potassium atoms adsorb with a sticking probability that is independent of coverage and at a constant rate¹².

The adsorption of potassium onto Pt(111) has been shown to reduce the work function of the surface greatly, due to the ionic nature of potassium at low coverages^{12,13}. Early work by Kiskinova and colleagues showed that the decrease in work function (~ 6 eV for clean Pt(111)) reaches a minimum of 1.4 eV at 0.5 ML, whereafter it increases to almost that of bulk potassium (~ 2.2 eV) at 1 ML (as defined by the authors, where 1 ML = 1 complete adlayer).¹⁴ The point at which the minimum occurs in the workfunction curve was disputed in a following paper by Lehmann and colleagues, who placed the minimum work function much closer to the point of monolayer formation.¹⁵ As the coverage of alkali metal increases metallization and the formation of ordered overlayers are observed^{16,17} as the potassium becomes more neutral due to depolarisation effects^{10,13}. Many early studies have claimed that potassium adsorbs on the surface with a sticking coefficient that is independent of coverage^{12,18} however later work has suggested that the rate of potassium adsorption is much more rapid at lower coverages.^{12,13,19}

Lehmann et al¹⁵ and Hannon et al²⁰ have suggested that for low coverages of potassium (less than 0.2 ML) potassium is absorbed into sub-surface sites and migrates to the surface upon adsorbing above a critical amount. While Lehmann states that all potassium is absorbed below 0.22 ML coverage with no measurable activation energy barrier, Muller has observed initial adsorption of potassium up to 0.1 ML (where 0.33 ML is equal to a complete adlayer being deposited) on the surface, after which there is a migration to subsurface sites in the second layer on the Pt crystal. The fact that there have been LEED observations of a (3x3) pattern at low coverages and that there is no evidence of potassium incorporation below the surface at 100 K would seem to argue against the proposals by Lehmann and co-workers.

This incorporation of potassium has been confirmed by scanning tunnelling microscopy experiments that show a potassium-induced reconstruction of surface steps with some buckling outwards of localised surface regions²⁰. This is supported by cantilever bending measurements in AFM. Room temperature adsorption of potassium onto Pt(111) causes a compressive surface stress, whereas at lower temperatures the tensile stress of the surface was found to increase, the compressive and tensile stresses created being due to incorporated K atoms and surface-bonded atoms respectively²¹

If we consider CO adsorption on the K dosed surface, some authors have reported a marked decrease in the sticking coefficient of CO as potassium coverage increases past a certain limit^{14, 24}. Whether this is due to an increase in potassium radius with an associated increase in site blocking of platinum CO adsorption sites, or to a change in the lifetime of a precursor state¹⁴ remains to be seen. Below this limit ($\theta_K = 0.19$) the initial sticking coefficient is independent of K coverage. It is worth noting that although the initial sticking coefficient changes from almost 1 to less than 0.25 as this threshold is passed the saturation coverage of CO still remains high and in fact appears to increase with increasing potassium coverage¹⁴.

It has been shown that the co-adsorption of potassium and carbon monoxide increases the heat of adsorption of CO and causes a decrease in the strength of the C-O double bond^{22,23}. This is in agreement with observations that the increased temperature of desorption observed in temperature programmed desorption experiments with potassium was due to an increased C-Pt bond strength²⁴. This C-O bond weakening has been shown to be caused by the potassium which enhances electron back-donation from the platinum surface into $2\pi^*$ antibonding orbitals on the CO with simultaneous strengthening of the C-Pt bond^{14,25}. The decrease in the strength of the C=O bond results in an increased dissociation probability²⁶. In apparent contradiction to this, dissociative adsorption of CO on K covered Pt(111) is reported not to occur at ambient temperature and that CO adsorption on the potassium adatoms does not occur¹⁴.

It has frequently been found that the presence of oxygen, either bonded as an oxide or coadsorbed with the alkali metal, is able to accentuate the catalytic effect of the catalyst¹⁶. Oxygen adsorbs very readily on this potassium monolayer and induces

a contraction, making the potassium coverage higher in the local vicinity when co-dosing. Exposure to oxygen makes a layer of adsorbed potassium (provided coverage > 0.2 ML) more thermally stable, reflected in an increase in the heat of desorption¹⁰ (105 kJ mol⁻¹ for a monolayer of pure potassium to 209 kJ mol⁻¹ for the same coverage after exposure to oxygen).

Two adsorbed oxygen states are commonly observed, a potassium-oxygen bonded state and a more loosely held platinum-oxygen state. Temperature programmed desorption studies have shown a simultaneous desorption of molecular oxygen and potassium with low potassium coverages also producing some weakly bound oxygen¹⁰. The Pt-O state is similar to that obtained for chemisorbed O₂ on Pt(111) and it has been claimed that that the K-O state is not K₂O¹⁶. However adsorption stoichiometries of 2:1 are observed and other groups suggest the existence of K₂O species for potassium coverages of less than a monolayer¹⁰. The work of Brodén *et al*¹⁶ shows that potassium oxide does not exist at monolayer coverages. They theorize that oxygen is chemisorbed to the substrate and incorporated into the substrate lattice or present as a substrate-metal oxide.

In addition to this, the work of More *et al* shows that substitutional or subsurface incorporations do not occur at reduced temperatures²⁷. Pirug *et al*¹⁶ also noted that exposure to oxygen caused the ($\sqrt{3} \times \sqrt{3}$)R30° LEED pattern to disappear, with greater exposures also causing a weakening of the Pt(111) substrate spots and an increase in background, indicating a loss of surface order. However annealing this layer brought an ordering of the surface with a (4 x 4) LEED pattern being observed. It has been suggested that in addition to potassium-bonded species being formed the potassium is able to reduce the dissociation barrier of O₂ resulting in atomic oxygen being created and spilling over to free platinum binding sites¹⁶.

Oxygen monolayers form much more readily on potassium-dosed platinum than on platinum alone. Pirug *et al* report an increase from very low values of S₀ on the clean surface to near unity with a monolayer of K¹⁶.

It was our aim to study the interaction of the K layer on Pt(111) with CO and oxygen more completely by examining the adsorption characteristics in more detail using molecular beam methods, and to clear up some of the inconsistencies described above.

Experimental. The experiments were carried out in an instrument described in more detail previously^{28,29}. Briefly it consists of a UHV system equipped with a thermal molecular beam system²⁸, facilities for TPD, both of these using a Hiden Hal200 quadrupole mass spectrometer for background molecular detection. Also present was a VG retarding field analyser used for Auger analysis. Background pressures in the machine were $\sim 1 \times 10^{-10}$ mbar. The sample was cleaned by Ar ion bombardment, and gases were 99.99% pure. The K was evaporated from an SAES getter source, and deposition of the K was followed by Auger electron spectroscopy, as reported in the supplementary material.

Results and Discussion

The details of formation of the K layer are given in the supplementary section.

Adsorption of CO on the K/Pt(111) surface

CO adsorbs with high initial sticking probability $S_0 = 0.55 \pm 0.03$ on clean Pt(111) at 25 °C, figure 1. Others have reported values of 0.4-0.9²⁻⁵ However, we have found that that S_0 on high doses of potassium is negligibly small.

Figure 1 indicates that surface doses of potassium up to 120 s appear to adsorb roughly the same amount of CO as the clean surface, have similarly shaped uptake curves, and saturate at about the same coverage. As the potassium surface dose is increased further there is a large decrease in the saturation coverage and sticking coefficient until no CO adsorption is visible at 360 s of potassium surface dose. This decrease in CO sticking with increased potassium surface dosage has been reported in the literature, with a reduction in measured sticking coefficient but with a relatively stable total saturation CO coverage. However, the authors note that much greater CO exposures are required to reach these coverage than at lower θ_K ¹⁴. All the sticking profiles have an initial plateau followed by a steep decrease indicating that precursor kinetics are important. To aid analysis of the growth of the potassium on the surface the initial sticking coefficient, S_0 , was plotted against time of dose and figure 2 clearly shows a transition in behaviour after 120 s, when S_0 and coverage diminish rapidly with increasing K dose. The decrease continues until both properties are near zero.

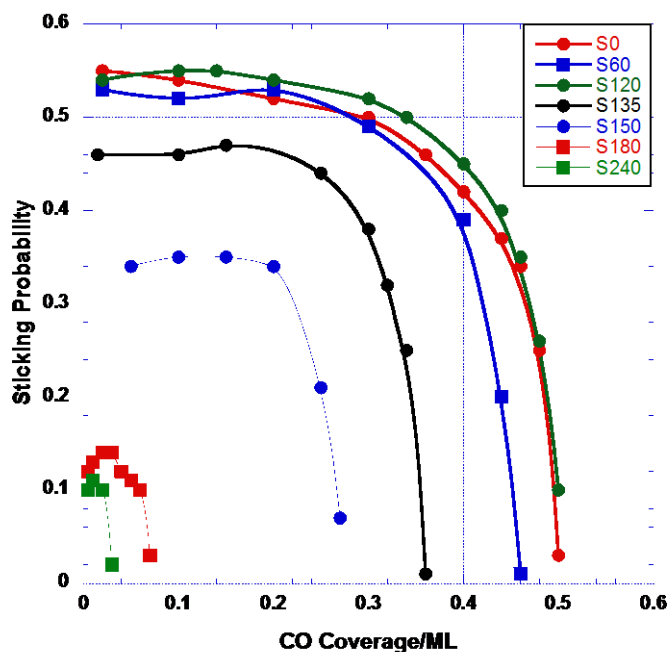


Figure 1 – The variation in the sticking probability of CO with CO coverage for increasing K doses on the Pt(111) crystal surface.

This behaviour has been noticed by other groups, with Liu and co workers observing that the CO adsorption at K coverages in excess of a full layer ($\theta_K = 0.49$, where $\theta_K = 0.33$ is defined by them as complete K coverage of the Pt(111) surface) is extremely slow. This is rationalised as the reluctance of CO to adsorb on potassium that is metallic in character³⁰. This then in turn leads us to consider that 1/3rd of a monolayer, considered by others to be the saturation coverage for K, appears to be the saturation of these effects occurring at ~ 180 - 240 s K dosing time, while the transition at ~ 120 s is at ~ 0.2 monolayer coverage.

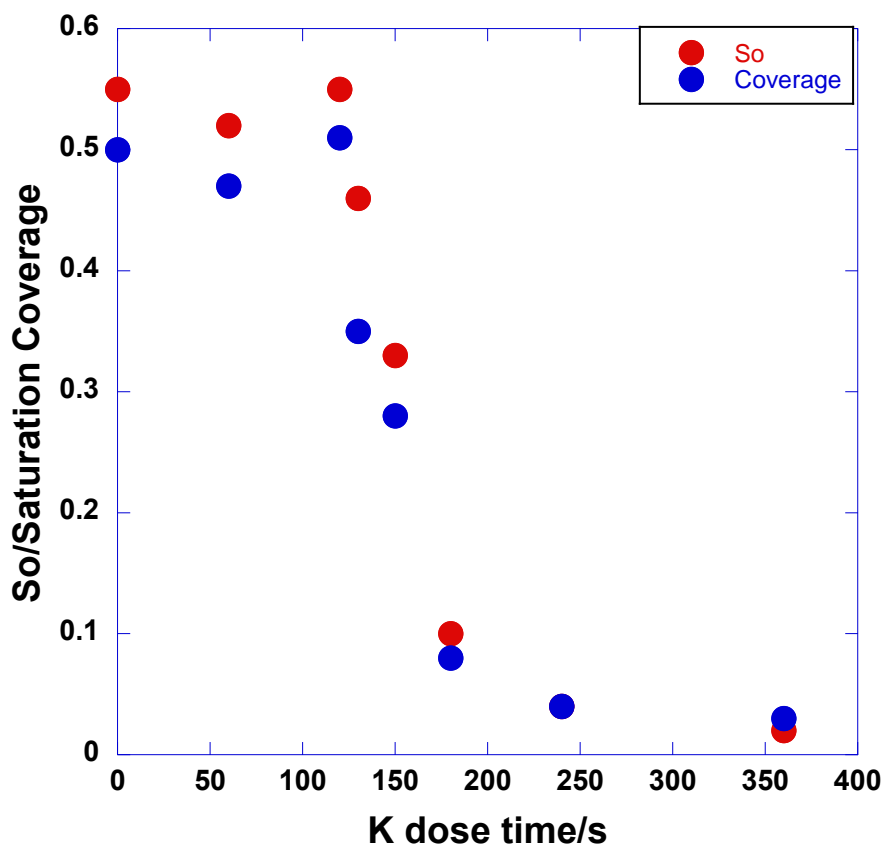


Figure 2 – The initial sticking probability of molecular beams of CO plotted against time of potassium dose of Pt(111) crystal surface.

The plateau of constant sticking probability with increasing initial potassium surface coverage has been noted by Kiskinova and co-workers¹⁴ who have postulated that it is due to a potassium-induced increase in the lifetime of the CO precursor species. However, we see little change (within error) of the shape of the CO sticking curve with increasing dose up to 120 s, which would not support this claim. The authors also ascribe the sudden drop in the sticking coefficient to be due to a change from ionic potassium to metallic potassium, which induces a drop in the precursor state lifetime. However, it is clear from figures 1 and 2 that sites are becoming blocked as the surface coverage increases and these are necessary for strong CO chemisorption. It has been observed in the literature that no CO dissociation occurs

on K-promoted Pt(111)¹⁴. The shape of figure 2 appears to be related to the changes in work function observed when dosing potassium onto the Pt(111) surface. Both Windham¹² and Pirug³¹ have observed a decrease in workfunction with increasing potassium up to half a complete monolayer of potassium, after which the workfunction increases to resemble that of bulk potassium. The rise from the minimum in the workfunction curve reported by Kiskinova and colleagues¹⁴, at which point metallic potassium begins to form, is likely to be at a point co-incident with the fall in sticking probability in figure 2. It therefore appears that the decrease in sticking probability of CO is caused by the beginning of the formation of metallic potassium. The fall then is most likely due to the blocking of CO adsorption sites on the Pt(111) both because of the increasing coverage and the increased size of metallic K atoms (~ 0.2 nm covalent radius³²) compared with K ions (~ 0.14 nm radius³²). K seems to be inert to CO, as might be expected since there are no room temperature-stable K-CO compounds, because CO is a both sigma donor and a pi acceptor, but K has no orbitals of appropriate symmetry for bonding and is not an electron acceptor. No doubt there is a physisorbed state which can adsorb on this K layer, but it is not stable at ambient temperature.

It is a little surprising that there is so little effect of K dosing on the CO curves at low coverage of K up to 120s dosing. The minor change in adsorption profiles and sticking probabilities of CO could perhaps be explained by invoking the sub-surface adsorption model of K as described by Hannon³³ and Lehmann¹³ in which the initial adsorbed potassium migrates to sub-surface sites, leaving CO adsorption sites unobstructed for adsorption. At these low coverages K is in the ionic state and, at least in Madelung terms, the radius of this species is reduced, but K ions in crystals are actually relatively large, at ~ 0.14 nm ionic radii. It certainly appears that K^+ does not block Pt adsorption sites at these coverages, and that the adsorption profile is not affected, even though surface electronic structure is, as evidenced by the large work function changes at low coverage^{13,14}. This is probably because the precursor adsorption kinetics dominate and the barriers between precursor and chemisorbed CO, and the heat of adsorption of physisorbed CO are not significantly affected by the K. Nevertheless, the binding of chemisorbed CO to the surface certainly is affected, as shown below.

The temperature programmed desorption spectra recorded after the molecular beam experiments (figure 3) show several interesting features that help to clarify the adsorption processes that are occurring in this system. With no potassium surface coverage there is just a single CO desorption environment at relatively low temperature (~ 120 °C), characteristic of CO desorbing from clean Pt(111)²³. Already at 60 s K dosing there is a clear change in CO desorption with several states apparent including new CO desorption peaks at 180 °C and 220 °C. The magnitude of the desorption peak associated with clean Pt(111) has decreased and when potassium is dosed onto the surface for 120 s this peak has essentially disappeared and the CO desorption has shifted to one main higher temperature peak at 300 °C. This then shifts slightly higher in temperature and with decreased integral up to the maximum dose. Note that the TPD after molecular beam dosing shows some desorption, whereas the sticking curves show a very low sticking probability. TPD from the molecular beam patch is not ideal, since it is only a small part of the surface (~ 7 mm² vs ~ 110 mm² for the whole crystal), and so the high K dose TPD may represent a low coverage of CO over the whole crystal surface, rather than from just the beam patch. This feature has been observed by Somorjai and co-workers, however they have interpreted it as being a gradual shift of the potassium-influenced CO-Pt rather than as a K-CO species²⁶. Crowell *et al.*¹ observed that no CO adsorption took place on multilayer potassium.

Kiskinova and co-workers have observed, using ultraviolet photoelectron spectroscopy and x-ray photoelectron spectroscopy, two separate CO environments when adsorbing CO on potassium pre-covered Pt(111). They state that the initial CO adsorption takes place into a potassium-influenced site on the platinum, followed by adsorption on the clean platinum. The potassium-influenced adsorption sites have a greater adsorption energy than the platinum sites alone (~ 200 kJ mol⁻¹ compared to 138 kJ mol⁻¹ for CO on clean Pt(111)). They also observe exchange in the relative populations of clean and potassium-influenced sites as the surface potassium coverage increases¹⁴. These conclusions aid rationalization of figure 3. At 60 s dose two separate CO environments are visible, a lower temperature desorption peak at 125 °C resulting from CO adsorption on Pt(111), and a higher temperature CO desorption peak at 183 °C that is therefore due to the adsorption of CO on the

electronically perturbed platinum immediately adjacent to potassium. As the surface dose is increased to 120 s both of these environments are drastically reduced in size and a new desorption peak at 290 °C, that is obviously due to CO adsorption affected by K, has appeared. All potassium doses greater than this lack the lower temperature desorption peaks associated with CO on clean Pt(111) and only show the single higher temperature desorption peak associated with potassium. It is likely that these various high temperature states are due to CO interactions with different ensembles of K⁺, perhaps isolated K ions (180 °C peak), multiple K⁺ ions (210 °C peak), and perhaps isolated Pt sites in a sea of K ions (300 °C peak). Note that peak appears rather large compared with what would be expected from the molecular beam data, but it is likely to be due to a small coverage of CO all over the catalyst surface, as described above. Note that this model would then explain the apparent contradiction of high CO binding induced by K, yet low coverages being reported^{1, 14}.

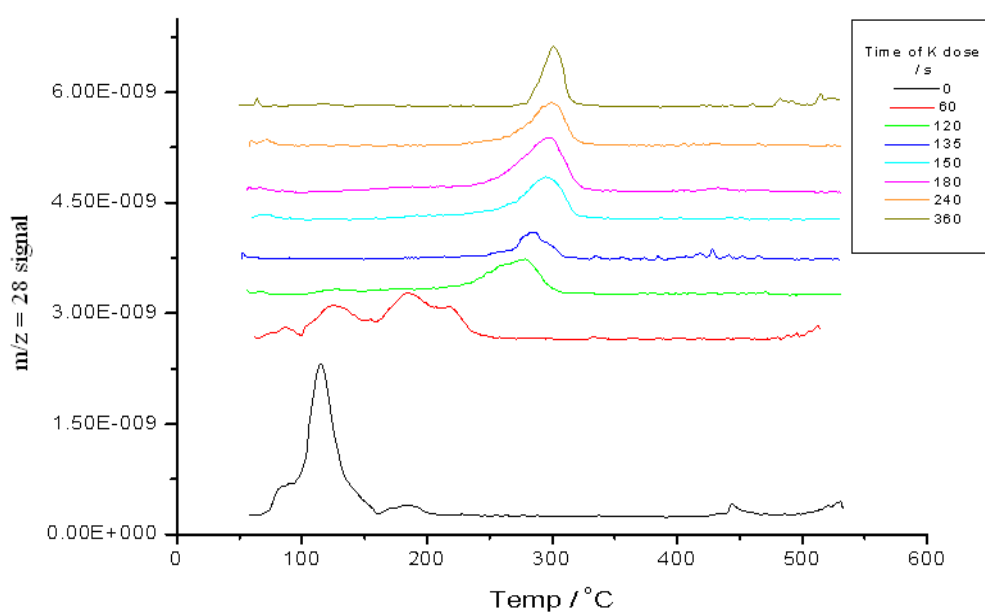


Figure 3 – Temperature programmed desorption of the crystal surface following the molecular beam experiments shown in figure 1.

Sticking of O₂ on K dosed Pt(111)

O₂ adsorbs with a low initial sticking probability on pure Pt(111) at ambient temperature ($S_0 \sim 0.06$, due to the highly activated nature of oxygen adsorption on this surface reported by others³⁴⁻³⁶). However it was found that the addition of potassium to the surface could vastly improve the affinity of oxygen for the surface as shown in figure 4, as also reported by Brown and Luntz³⁵, though they only reported initial sticking probabilities, ranging from ~ 0.04 at zero K coverage, to ~ 0.9 at 0.33 ML for low beam energies.

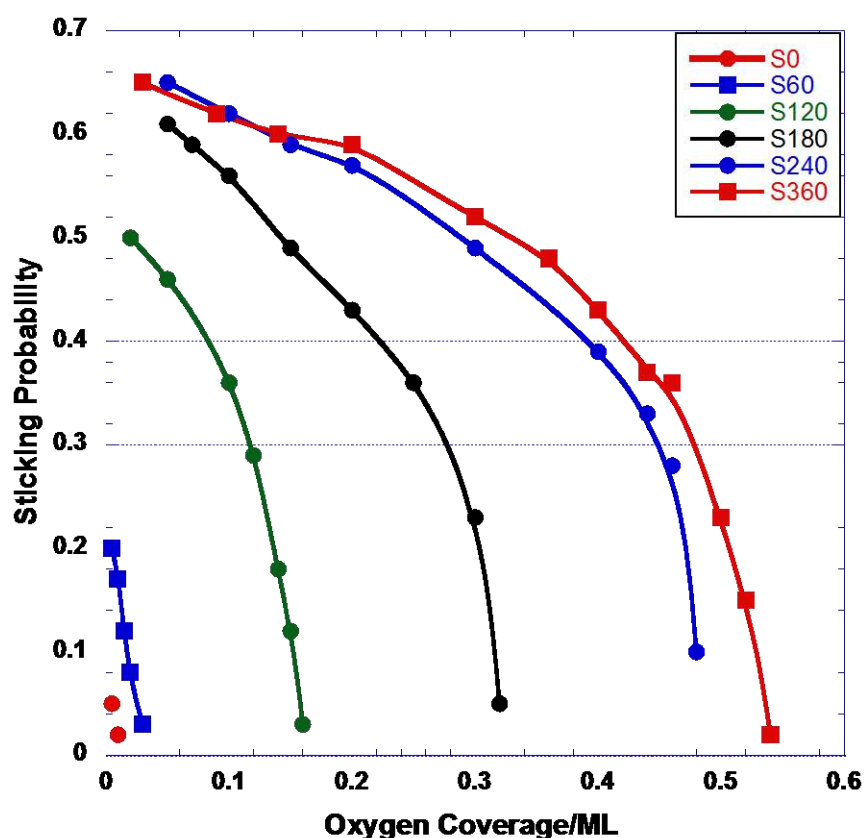


Figure 4 – The sticking probability of a molecular beam of O₂ and its dependence on O₂ coverage for increasing time of K surface dose.

As figure 4 and 5 show, the initial sticking probability of oxygen rises with increasing potassium dose up to a maximum of $S_0 = 0.65 (\pm 0.03)$ at 180 s of dosing time. Above this there is no further increase in the initial sticking probability of oxygen but the saturation oxygen coverage continues to increase up to a maximum of ~ 0.5 ML at 360 s K dose time. The initial sticking probability and saturation coverage dependence on the time of the potassium dose are given in figure 5 below.

In contrast to the behaviour of CO adsorption, low coverages of K have a huge effect on O_2 adsorption. This is due to the promotional effect of K, altering the electronic structure of the Pt adjacent to it, which reduces the activation barrier to dissociation on the surface³⁵. Effectively polarisation of the incoming molecule by the presence of K enables easier electron transfer into the incoming molecule, which is much more difficult on the clean surface.

This increase in sticking is clearly near complete by 120 s in fig. 5, close to the point at which CO sticking starts to diminish, which we have proposed above is due to a change in the nature of the K layer, from ionic to metallic-like. However, unlike for CO, coverage of oxygen is high on these surfaces, even on the metallic-like layer, which implies that there is intrinsic reactivity of the K layer itself. That the coverage in fig. 5 increases beyond the sticking maximum is probably due to two processes occurring with increasing coverage; i) enhanced adsorption onto Pt at low K coverage, increasing as K coverage increases in the K^+ state, followed by ii) direct adsorption onto the K metallic layer. Note that although there is a transition from ionic to metallic K, the latter still has a very low work function ($2\text{eV}^{13,14}$) thus enabling easy electron transfer into the incoming O_2 molecule. It is, of course, very likely to be the case that, even after the metallic K layer has been formed, it returns to the ionic state when oxygen is adsorbed, and can create extra 'room' for incoming oxygen. The XPS described below and in the supplementary section, figure S2, confirms this.

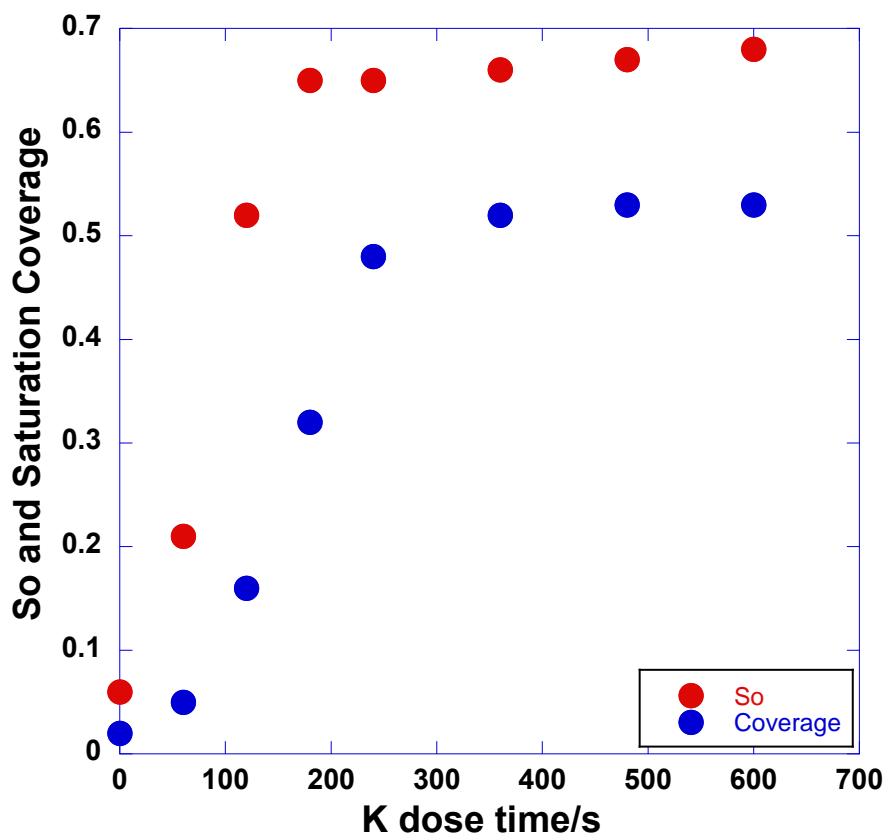


Figure 5 – A plot of initial sticking probability and saturation coverage of O₂ against the time of potassium dose of the Pt(111) crystal surface.

The work of Pirug¹⁶ has shown that potassium adatoms induce O₂ dissociation with atomic oxygen binding on the Pt(111) surface rather than with the potassium. However Brodén has provided evidence that dosing oxygen onto the surface of a complete layer of potassium disrupts the monolayer (and induces a contraction) and that although oxygen is stored, it is not stored as platinum oxide¹⁶. Together, this indicates that the adsorption of O₂ on K/Pt(111) is not simple, with multiple adsorption mechanisms being responsible for the oxygen adsorption.

To complement the molecular beam work, temperature programmed desorption experiments were carried out following the experiments in figure 4 (figure 6). With

no potassium present on the surface, due to the very low initial sticking coefficient of O_2 on Pt(111), no O_2 desorption is evident. As O_2 has a finite adsorption coefficient on Pt(111) ($S_0 < 0.06$) it seems likely that the lack of a desorption peak, which should appear for Pt(111) at ~ 420 °C is due to a clean-off reaction with the low level of background CO^{36} . However, with 60 s potassium dosed onto the surface there is a desorption peak at 310 °C with a higher temperature shoulder. Increasing the potassium surface coverage resolves this shoulder and shifts it to higher temperatures. With three minutes of potassium dose another oxygen desorption peak at 480 °C becomes visible. It is likely that the initial $m/z = 32$ desorption peak at 325 °C is a result of the desorption of atomic oxygen created by a potassium-induced reduction in the barrier to O_2 dissociative adsorption (this peak is noted in temperature programmed desorption spectra of potassium oxide by Somorjai *et al.*¹⁰, who also note that it disappears for potassium coverages of greater than a monolayer). The fact that this peak does not disappear in the temperature programmed desorption experiments shown in figure 6 is due to a difference in experimental procedure – in our experiments the potassium layer was deposited before oxidation by the molecular beam. This peak is therefore evidence of the contraction that occurs when oxidising a layer of potassium (a contraction in a complete monolayer of potassium of the magnitude described by Brodén and co-workers would leave 25% of the underlying platinum surface exposed)¹⁷ This chemisorbed oxygen-platinum species has also been noted by Bonzel *et al.*¹⁶ when examining oxygen adsorption on potassium-covered Pt(111). The smaller size of the oxide allows atomic oxygen adsorption on the exposed Pt(111). Garfunkel and Somorjai also note that potassium desorption occurs at the same temperature as the highest temperature oxygen desorption peak, making it likely that the peak at ~ 480 °C is due to a potassium oxide species decomposition, and we see some K desorption too²⁵. If so, it is worth noting that this species only occurs after a complete monolayer of potassium has been deposited, indicating that the potassium oxidation does not occur if the potassium is ionic in character. However, Brodén and co-workers have provided evidence that potassium oxide does not form on Pt(111). They theorise that this state is due to oxygen incorporation into the platinum surface¹⁷. It seems likely that, as they deposited the potassium at 600 K, only sub-monolayer coverages of

potassium were formed; these were shown to be reluctant to oxidise (making the sticking observed in the early parts of figures 4 and 5 to be likely to be due to K-induced O_2 dissociation and spillover of atomic oxygen to nearby K-affected platinum adsorption sites). The mid-temperature peak is likely to be due to a substrate-metal-oxide species as theorised by Brodén *et al*¹⁷. The formation of potassium oxide at half-monolayer coverages has been proven by Cassuto and co workers. Using UPS they proved that molecular oxygen adsorbs via dissociative adsorption on a potassium-promoted Pt(111) surface and that the atomic oxygen produced either chemisorbs on the potassium/platinum or forms potassium oxide³⁸. They also formed potassium peroxide and superoxide species at 95 K. O_2 molecularly adsorbs in the form of O_2^- on Pt(111) as a precursor to dissociative adsorption. The adsorption is facilitated by partial transfer of electronic charge into a π^* antibonding orbital on the oxygen molecule. It is therefore to be expected that the enhanced back-donation from the platinum as a result of increased local electron density provided by adsorbed potassium would reduce the barrier to sticking by stabilising the precursor state as a species and reducing the barrier to dissociation. This is evidenced by the increased sticking of O_2 that is visible with low coverages of surface potassium and the temperature programmed desorption experiment.

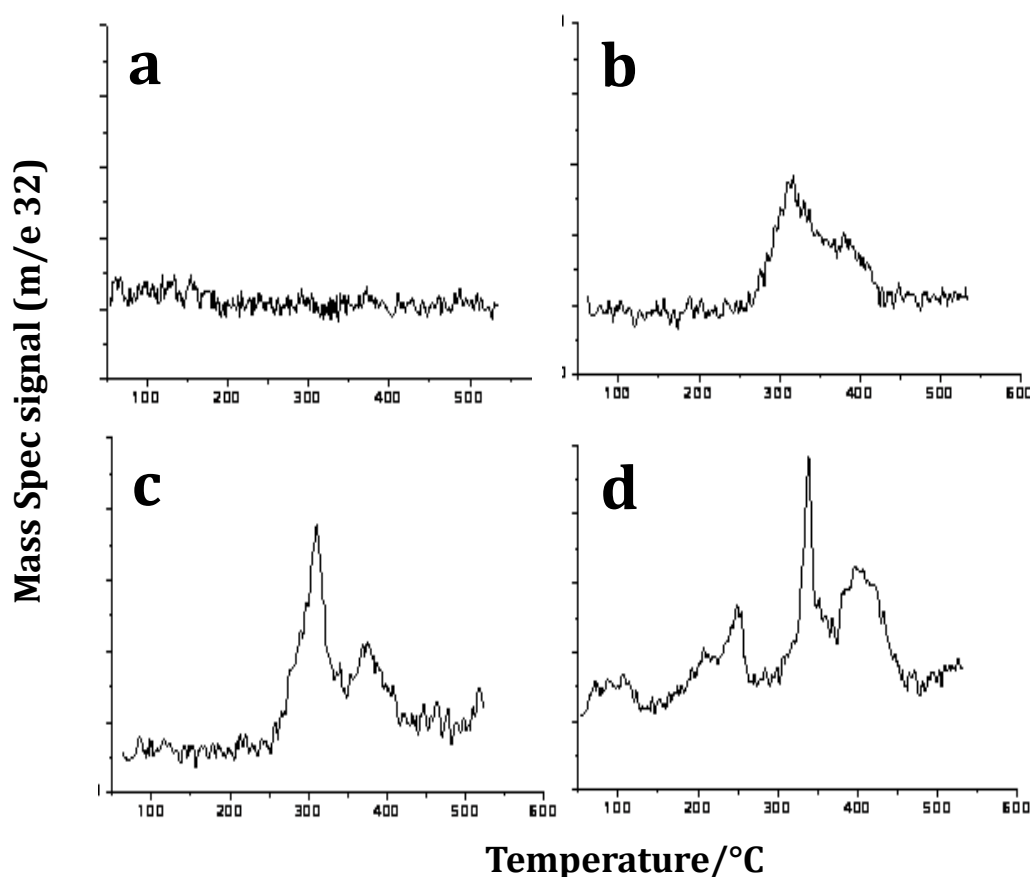


Figure 6. Temperature programmed desorption of O₂ from the K layer following the molecular beam experiments shown in figure 4. The K doses were a) 0s b) 60s c) 120s and d) 360s.

To support these arguments we carried out measurements on similar layers in a separate machine equipped with XPS, as described in the supplementary information. In this case the K and oxygen were co-dosed onto the surface at 573K, followed by cooling, and the binding energies are all ~ 293.5 for the K(2p_{3/2}) state, which corresponds with the oxidised K species. The O(1s) at first seems to exhibit a single, broad state at low potassium coverage at 532 eV, but splits into two states at higher coverage, the main one with a peak at 531.7 eV, together with a lower binding energy shoulder corresponding to a peak at ~ 530 eV. The latter is probably associated with an atomic state and the former with a peroxidic K₂O₂ species (see supplementary table 1), thus largely supporting the chemical reactivity results shown above.

If we combine the reactivity data for CO and oxygen, we can examine the effect of potassium coverage on the adsorption, figure 7. We have assigned coverage as 0.17 at the transition from ionic to metallic K coverage (as defined by others^{14,15,20}) as close to the 120 s dose of K, since that is where there is a clear transition in reactive behaviour, and is also reported as the minimum point in work function measurements. Thus above that K coverage the CO sticking and uptake drop rapidly, and have changed to very low values by 0.33 ML coverage of potassium. Similarly oxygen sticking has increased to its final value of 0.67 by ~0.17 ML. However, it doesn't reach its maximum coverage until ~0.33 ML, and at 0.17 ML of K, the saturation coverage of O₂ is only ~ 1/3 of its maximum value of ~0.5 ML at 0.33 ML K. This is rather more than expected for formation of a layer of K₂O₂, potassium peroxide-like layer, and so is presumably due to the presence of extra dissociated oxygen atoms which adsorb on the Pt surface exposed as the 0.33 ML saturated metallic layer becomes oxidised and contracts. This is supported by the XPS shown in the supplementary section where there is both atomic and molecular oxygen present with the amount of the former being ~ 1/2 that of the latter. Note also that we have simply extrapolated K dose time with coverage, assuming they are linearly related, but it is quite possible that above the 0.5 ML coverage associated by others with K saturation in the metallic state (~200 s dosing time), the sticking may be very low after that point. Note that Garfunkel and Somorjai stated that multilayer potassium formation was not possible at room temperature¹⁰.

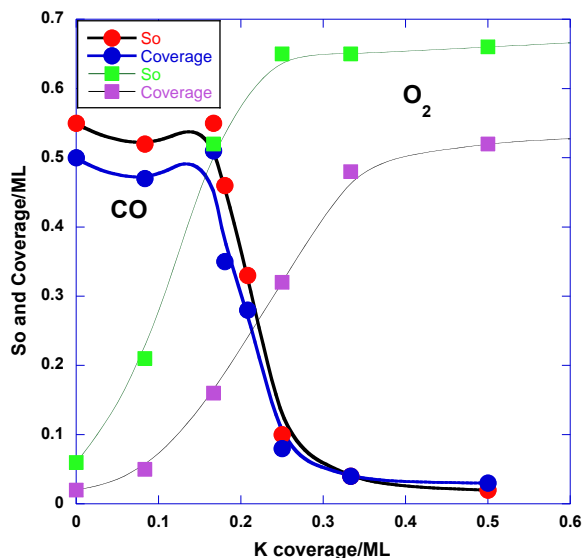


Figure 7. Showing the dependence of initial sticking probability and saturation coverage for O_2 and CO upon the coverage of pre-dosed K. Thick fitted lines and circle data points are for CO, thin lines and squares for O_2 ,

In summary we have shown that K on the Pt(111) surface tends to have opposite effects on the adsorption of CO and O_2 . That is, CO adsorption is poisoned by the presence of K on the surface, whereas O_2 is promoted. At full coverage of K CO is completely blocked, having low adsorption probability and coverage, whereas O_2 has a high adsorption probability and high coverage. This is essentially due to the electron donor characteristics of CO, which are not supported on a metallic K layer, whereas the oxygen acceptor characteristics of oxygen certainly are. Effectively the barrier to dissociation of oxygen is reduced at low K coverage, but also a pathway to peroxide formation opens up at high coverage.

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Supporting Information Available: This includes a description of the K dosing methodology, together with that for the dosed gases, and XP spectra for oxygen

dosed with K on the surface. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

1. Crowell, J.E., Garfunkel, E.L., Somorjai G.A., The coadsorption of potassium and CO on the pt(111) crystal surface: A TDS, HREELS and UPS study *Surf. Sci.*, **1982**, *121*, 303-8.
2. Steininger H., Lehwald, S., Ibach, H., On the adsorption of CO on Pt(111) *Surf. Sci.*, **1982**, *123*, 264-9.
3. Ertl, G., Neumann, M., Streit, K.M., Chemisorption of CO on the Pt(111) surface *Surf. Sci.*, **1977**, *64*, 393-9.
4. Campbell, C.T., Ertl, G., Kuipers, H., Segner, J., A molecular beam investigation of the interactions of CO with a Pt(111) surface, *Surf. Sci.*, **1981**, *107*, 207-215.
5. Yeo, Y.Y., Vattuone, L., King, D.A., Calorimetric heats for CO and oxygen adsorption and for the catalytic CO oxidation reaction on Pt{111}, *J. Chem. Phys.*, **1997**, *106*, 392-403.
6. Gland, J. L., Korchak, V. N., The adsorption of oxygen on a stepped platinum single crystal surface, *Surf. Sci.*, **1978**, *75*, 733-50.
7. Bonzel, H.P., Ku, R., On the kinetics of oxygen adsorption on a Pt(111) surface *Surf. Sci.*, **1973**, *40*, 85-101.
8. Hopster, H., Ibach, H., Comsa, G., Catalytic oxidation of carbon monoxide on stepped platinum(111) surfaces, *J. Cat.*, **1977**, *46*, 37-47.
9. A. C. Luntz, M. D. Williams, and D. S. Bethune, The sticking of O₂ on a Pt(111) surface, *J Chem. Phys.*, **1988**, *89*, 4381-95.
10. Garfunkel, E.L., Somorjai, G.A., Potassium and potassium oxide monolayers on the platinum (111) and stepped (755) crystal surfaces: A LEED, AES, and TDS study, *Surf. Sci.*, **1982**, *115*, 441-54.
11. Gurney, R.W.,_Theory of electrical double layers in adsorbed films_, *Phys. Rev.* **1935**, *47*, 479-82.
12. Windham, R.G., Bartram, M.E., Koel, B.E., Coadsorption of ethylene and potassium on platinum (111),_ *J. Phys. Chem.*, **1988**, *92*, 2862-70.
13. Lehmann, J., Roos, P., Bertel, E., Incorporation of alkali metals on Pt (111), *Phys. Rev. B*, **1996**, *54*, R2347-50.
14. Kiskinova, M., Pirug, G., Bonzel, H.P., Coadsorption of potassium and CO on Pt(111), *Surf. Sci.*, 1983, *133*, 321-43.
15. Lehmann, J., Roos, P., Bertel, E., Incorporation of alkali metals on Pt(111), *Phys. Rev. B*, **1996**, *54*, R2347-50.
16. Pirug, G., Bonzel, H.P., Brodén, G., The adsorption of potassium on Pt(111) and its effect on oxygen adsorption, *Surf. Sci.*, **1982**, *122*, 1-20.
17. Brodén, G., Pirug, G., Bonzel, H.P., Adsorption of oxygen on potassium-covered Pt(111) and Fe(110), *Chem. Phys. Lett.*, **1980**, *73*, 506-9.
18. Pirug, G., Bonzel, H.P., Ordering of potassium overlayers on Pt(111), *Surf. Sci.*, **1988**, *194*, 159-71.
19. Wenter, P., Memmel, N., Anomalous adsorption of potassium on Pt(111), *Surf. Sci. Lett.*, **2002**, *513*, 2002, L419-22.
20. Hannon, J.B., Giesen, M., Klunker, C., Schulze Icking-Konert, G.,

- Stapel, D., Ibach, H., Muller, J.E., Incorporation of potassium at the Pt(111) surface, *Phys. Rev. Lett.*, **1997**, *78*, 1094-7.
21. Ibach, H., The role of surface stress in reconstruction, epitaxial growth and stabilization of mesoscopic structures, *Surf. Sci.Reports*, **1997**, *29*, 193-263.
22. Whitman, L.J., Ho, W., Desorption kinetics on an alkali metal-precovered surface: CO and K on Pt(111), *J. Chem. Phys.*, **1989**, *90*, 6018-27.
23. Jiang, L.Q., Koel, B.E. Falconer, J.L., Effects of K, O, and H adatoms on the adsorption kinetics of CO on Pt(111), *Surf. Sci.*, **1992**, *273*, 273-84.
24. Bonzel, H.P., Alkali-metal-affected adsorption of molecules on metal surfaces *Surf. Sci. Rep.*, **1987**, *8*, 43-96.
25. Garfunkel, E.L., Maj, J.J., Frost, J.C., Farles M.H., Somorjai, G.A., Interaction of potassium with pi electron orbital containing molecules on Pt(111), *J. Phys. Chem.*, **1983**, *87*, 3629-35.
26. Garfunkel, E.L., Crowell, J.E., Somorjai, G.A., The strong influence of potassium on the adsorption of carbon monoxide on platinum surfaces: a TDS and HREELS study, *J. Phys. Chem.*, **1982**, *86*, 310-3.
27. More, S., Berndt, W., Bradshaw, A.M., Ordered phases of potassium on Pt(111), *Phys. Rev. B*, **57**, 1998, 9246-54.
28. Bowker, M., Pudney, P.D.A., Barnes, C., A simple molecular beam system for surface reactivity studies, *J. Vac. Sci. Tech.*, **1990**, *A8*, 816-820.
29. Archard, D., PhD thesis, Cardiff University, 2008.
30. Liu, Z.M., Zhou, Y., Solymosi, F., White, J.M., Vibrational study of carbon dioxide(1-) on potassium-promoted platinum (111), *J. Phys. Chem.*, **1989**, *93*, 4384-9.
31. Pirug, G., Winkler, A., Bonzel, H.P., Multilayer growth of potassium on a Pt(111) surface, *Surf. Sci.*, **1985**, *163*,153-63.
32. Handbook of Chemistry and Physics, 96th edition, CRC Press, Boca Raton, 2015.
33. Hannon, J.B., Giesen, M., Klunker, C., Schulze Icking-Konert, G., Stapel, D., Ibach, H., Muller, J.E., Incorporation of potassium at the Pt(111) surface, *Phys. Rev. Lett.*, **1997**, *78*,1094-7.
34. Luntz, A.C., Williams, M.D., Bethune, D.S., The sticking of O₂ on a Pt(111) surface, *J Chem. Phys.* **1988**, *89*, 4381-95.
35. Brown, J.K., Luntz, A.C., Molecular beam studies of alkali promotion, *J. Chem. Phys.*, **1991**, *186*, 125-9.
36. Rettner, C.T., Mullins, C.B., Dynamics of the chemisorption of O₂ on Pt(111), *J. Chem. Phys.*, **1991**, *94*, 1626-35.
37. Bashlakov, D.L., Juurlink, L., Koper, M., Yanson, A.I., Subsurface Oxygen on Pt(111) and Its Reactivity for CO Oxidation, *Catal. Lett.*, **2011**, *142*, 1-6.
38. Cassuto, A., Schmidt, S., Mane, M., The interaction of potassium submonolayers adsorbed on Pt(111) with oxygen and the adsorption of ethylene on the resulting modified surfaces: a TDS and UPS study, *Surf. Sci.*, **1993**, *284*, 273-80.

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