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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.

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3 **Introduction.** Transition metal catalysts often have sub-monolayer amounts of alkali
4 metals incorporated due to the ability of the alkali metal to alter the adsorption
5 characteristics of the catalyst. This is believed to occur via the low ionisation potential
6 of the alkali metal leading to the transference of a valence electron from the alkali metal
7 to the transition metal, which sets up a localised dipole. This transfer of electronic
8 charge is normally evidenced by a marked decrease in the work function of the
9 transition metal surface. The first demonstration of this effect was the observation of a
10 significant enhancement in electron emission from the transition metal surface upon
11 alkali adsorption¹. The adsorption of the alkali metal onto a metal crystal surface hence
12 normally results in a range of altered properties such as differing adsorption kinetics,
13 differing vibrational frequencies of adsorbed species and different adsorption sites
14 becoming available. This effect is most pronounced in heterogeneous catalysis where
15 alkali metal promotion is used to increase the activity of the catalyst and/or the
16 selectivity towards certain products. For instance, in ammonia synthesis it enhances
17 activity of pure iron surfaces, whereas in ethene epoxidation it enhances selectivity. It
18 must be remembered that in catalytic systems the potassium is present in the K⁺ ionic
19 form, associated with anions such as, O, OH or CO₃, depending on the reaction system.
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34 Clean Pt(111) has been found to adsorb CO with a high initial sticking probability
35 (S_0)²⁻⁵, although the exact value determined varies. The coverage is a strong function of
36 temperature, but at ambient temperature it is reported to be between 0.3 and 0.5. In
37 contrast to this oxygen has great difficulty in dissociating with S_0 , being low (<0.06) and
38 variable^{4,6-9}, perhaps because dissociation occurs mainly at steps on the surface, the
39 density of which vary from one sample to another. This, of course, implies a high
40 activation barrier to dissociation on pure Pt(111) itself, as described by Luntz et al⁹.
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47 Contaminant-free potassium adlayers have been found to be hexagonally
48 ordered on Pt(111) for potassium coverages of $\theta = 0.9-1$ ¹⁰. A complete monolayer of
49 potassium, $\theta = 1$, is reported to be ~36% of the surface density of platinum atoms or 5.4
50 $\times 10^{14}$ atoms cm⁻². The ordering of the surface was only visible at low temperature and
51 at room temperature more than one complete monolayer of potassium was not
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3 attainable. The potassium layer could, however, be thermally stabilised by exposure to
4 oxygen¹⁰.
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7 Early models of potassium adsorption onto the Pt(111) surface assumed the
8 charge transfer model as proposed by Gurney¹¹, in which the adsorbing potassium
9 donates electron density to the surface from an s-orbital. Repulsion between the
10 resulting dipole species formed leads to the adsorbate being spread evenly over the
11 surface rather than clumping into islands. In this model potassium atoms adsorb with a
12 sticking probability that is independent of coverage and at a constant rate¹².
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18 The adsorption of potassium onto Pt(111) has been shown to reduce the work
19 function of the surface greatly, due to the ionic nature of potassium at low
20 coverages^{12,13}. Early work by Kiskinova and colleagues showed that the decrease in
21 work function (~6eV for clean Pt(111)) reaches a minimum of 1.4 eV at 0.5 ML,
22 whereafter it increases to almost that of bulk potassium (~2.2 eV) at 1 ML (as defined by
23 the authors, where 1 ML = 1 complete adlayer).¹⁴ The point at which the minimum
24 occurs in the workfunction curve was disputed in a following paper by Lehmann and
25 colleagues, who placed the minimum work function much closer to the point of
26 monolayer formation.¹⁵ As the coverage of alkali metal increases metallization and the
27 formation of ordered overlayers are observed^{16,17} as the potassium becomes more
28 neutral due to depolarisation effects^{10,13}. Many early studies have claimed that
29 potassium adsorbs on the surface with a sticking coefficient that is independent of
30 coverage^{12,18} however later work has suggested that the rate of potassium adsorption is
31 much more rapid at lower coverages.^{12,13,19}
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43 Lehmann et al¹⁵ and Hannon et al²⁰ have suggested that for low
44 coverages of potassium (less than 0.2 ML) potassium is absorbed into sub-surface sites
45 and migrates to the surface upon adsorbing above a critical amount. While Lehmann
46 states that all potassium is absorbed below 0.22 ML coverage with no measurable
47 activation energy barrier, Muller has observed initial adsorption of potassium up to 0.1
48 ML (where 0.33 ML is equal to a complete adlayer being deposited) on the surface, after
49 which there is a migration to subsurface sites in the second layer on the Pt crystal. The
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3 fact that there have been LEED observations of a (3x3) pattern at low coverages and
4 that there is no evidence of potassium incorporation below the surface at 100 K would
5 seem to argue against the proposals by Lehmann and co-workers.
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9 This incorporation of potassium has been confirmed by scanning tunnelling
10 microscopy experiments that show a potassium-induced reconstruction of surface steps
11 with some buckling outwards of localised surface regions²⁰. This is supported by
12 cantilever bending measurements in AFM. Room temperature adsorption of potassium
13 onto Pt(111) causes a compressive surface stress, whereas at lower temperatures the
14 tensile stress of the surface was found to increase, the compressive and tensile stresses
15 created being due to incorporated K atoms and surface-bonded atoms respectively²¹
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21 If we consider CO adsorption on the K dosed surface, some authors have
22 reported a marked decrease in the sticking coefficient of CO as potassium coverage
23 increases past a certain limit^{14, 24}. Whether this is due to an increase in potassium radius
24 with an associated increase in site blocking of platinum CO adsorption sites, or to a
25 change in the lifetime of a precursor state¹⁴ remains to be seen. Below this limit ($\theta_K =$
26 0.19) the initial sticking coefficient is independent of K coverage. It is worth noting that
27 although the initial sticking coefficient changes from almost 1 to less than 0.25 as this
28 threshold is passed the saturation coverage of CO still remains high and in fact appears
29 to increase with increasing potassium coverage¹⁴.
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38 It has been shown that the co-adsorption of potassium and carbon monoxide
39 increases the heat of adsorption of CO and causes a decrease in the strength of the C-O
40 double bond^{22,23}. This is in agreement with observations that the increased
41 temperature of desorption observed in temperature programmed desorption
42 experiments with potassium was due to an increased C-Pt bond strength²⁴. This C-O
43 bond weakening has been shown to be caused by the potassium which enhances
44 electron back-donation from the platinum surface into $2\pi^*$ antibonding orbitals on the
45 CO with simultaneous strengthening of the C-Pt bond^{14,25}. The decrease in the strength
46 of the C=O bond results in an increased dissociation probability²⁶. In apparent
47 contradiction to this, dissociative adsorption of CO on K covered Pt(111) is reported not
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3 to occur at ambient temperature and that CO adsorption on the potassium adatoms
4 does not occur¹⁴.
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7 It has frequently been found that the presence of oxygen, either bonded as an
8 oxide or coadsorbed with the alkali metal, is able to accentuate the catalytic effect of
9 the catalyst¹⁶. Oxygen adsorbs very readily on this potassium monolayer and induces a
10 contraction, making the potassium coverage higher in the local vicinity when co-dosing.
11 Exposure to oxygen makes a layer of adsorbed potassium (provided coverage > 0.2 ML)
12 more thermally stable, reflected in an increase in the heat of desorption¹⁰ (105 kJ mol⁻¹
13 for a monolayer of pure potassium to 209 kJ mol⁻¹ for the same coverage after exposure
14 to oxygen).
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21 Two adsorbed oxygen states are commonly observed, a potassium-oxygen
22 bonded state and a more loosely held platinum-oxygen state. Temperature
23 programmed desorption studies have shown a simultaneous desorption of molecular
24 oxygen and potassium with low potassium coverages also producing some weakly
25 bound oxygen¹⁰. The Pt-O state is similar to that obtained for chemisorbed O₂ on
26 Pt(111) and it has been claimed that that the K-O state is not K₂O¹⁶. However
27 adsorption stoichiometries of 2:1 are observed and other groups suggest the existence
28 of K₂O species for potassium coverages of less than a monolayer¹⁰. The work of Brodén
29 *et al*¹⁶ shows that potassium oxide does not exist at monolayer coverages. They
30 theorize that oxygen is chemisorbed to the substrate and incorporated into the
31 substrate lattice or present as a substrate-metal oxide.
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41 In addition to this, the work of More *et al* shows that substitutional or
42 subsurface incorporations do not occur at reduced temperatures²⁷. Pirug *et al*¹⁶ also
43 noted that exposure to oxygen caused the ($\sqrt{3} \times \sqrt{3}$)R30° LEED pattern to disappear, with
44 greater exposures also causing a weakening of the Pt(111) substrate spots and an
45 increase in background, indicating a loss of surface order. However annealing this layer
46 brought an ordering of the surface with a (4 x 4) LEED pattern being observed. It has
47 been suggested that in addition to potassium-bonded species being formed the
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3 potassium is able to reduce the dissociation barrier of O₂ resulting in atomic oxygen
4 being created and spilling over to free platinum binding sites¹⁶.
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7 Oxygen monolayers form much more readily on potassium-dosed platinum than
8 on platinum alone. Pirug et al report an increase from very low values of S₀ on the clean
9 surface to near unity with a monolayer of K¹⁶.
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12 It was our aim to study the interaction of the K layer on Pt(111) with CO and
13 oxygen more completely by examining the adsorption characteristics in more detail
14 using molecular beam methods, and to clear up some of the inconsistencies described
15 above.
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21 **Experimental.** The experiments were carried out in an instrument described in more
22 detail previously^{28,29}. Briefly it consists of a UHV system equipped with a thermal
23 molecular beam system²⁸, facilities for TPD, both of these using a Hiden Hal200
24 quadrupole mass spectrometer for background molecular detection. Also present was a
25 VG retarding field analyser used for Auger analysis. Background pressures in the
26 machine were ~ 1x 10⁻¹⁰ mbar. The sample was cleaned by Ar ion bombardment, and
27 gases were 99.99% pure. The K was evaporated from an SAES getter source, and
28 deposition of the K was followed by Auger electron spectroscopy, as reported in the
29 supplementary material.
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40 **Results and Discussion**

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

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

43 CO adsorbs with high initial sticking probability S₀ = 0.55 ± 0.03 on clean Pt(111)
44 at 25 °C, figure 1. Others have reported values of 0.4-0.9²⁻⁵ However, we have found
45 that that S₀ on high doses of potassium is negligibly small.
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51 Figure 1 indicates that surface doses of potassium up to 120 s appear to adsorb
52 roughly the same amount of CO as the clean surface, have similarly shaped uptake
53 curves, and saturate at about the same coverage. As the potassium surface dose is
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3 increased further there is a large decrease in the saturation coverage and sticking
4 coefficient until no CO adsorption is visible at 360 s of potassium surface dose. This
5 decrease in CO sticking with increased potassium surface dosage has been reported in
6 the literature, with a reduction in measured sticking coefficient but with a relatively
7 stable total saturation CO coverage. However, the authors note that much greater CO
8 exposures are required to reach these coverage than at lower θ_K^{14} . All the sticking
9 profiles have an initial plateau followed by a steep decrease indicating that precursor
10 kinetics are important. To aid analysis of the growth of the potassium on the surface
11 the initial sticking coefficient, S_0 , was plotted against time of dose and figure 2 clearly
12 shows a transition in behaviour after 120 s, when S_0 and coverage diminish rapidly with
13 increasing K dose. The decrease continues until both properties are near zero.

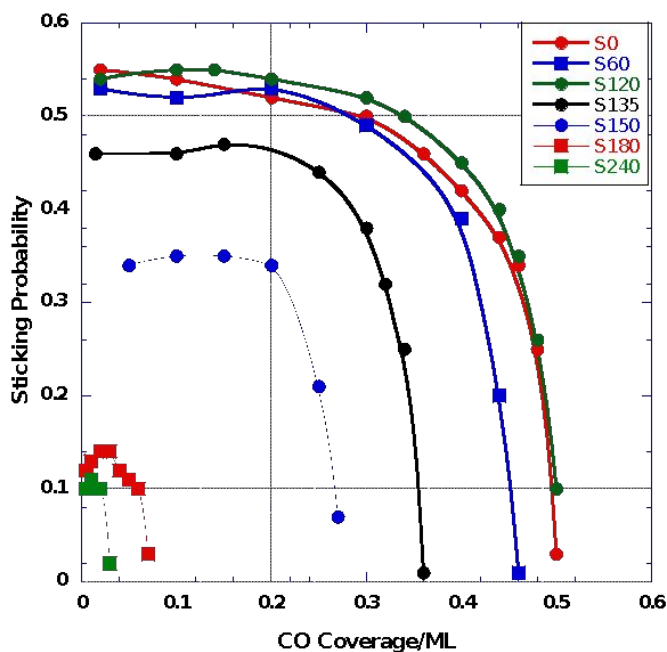


Figure 1 – The variation in the sticking probability of CO with CO coverage for increasing K doses on the Pt(111) crystal surface.

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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.

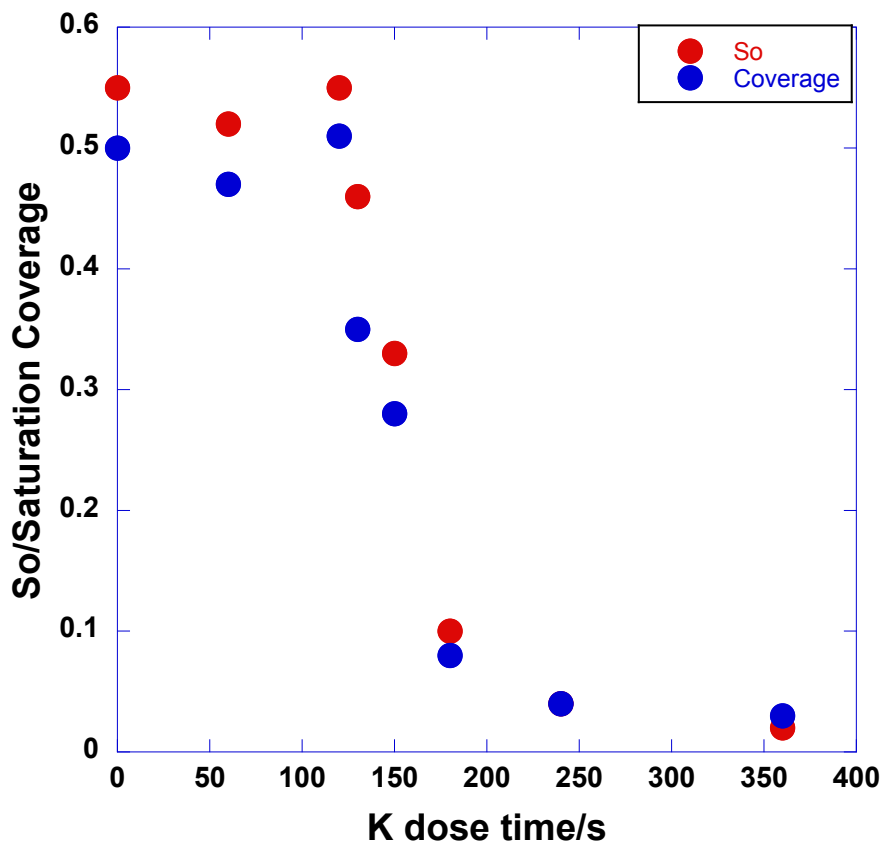


Figure 2 – The initial sticking probability of molecular beams of CO plotted against time of potassium dose of Pt(111) crystal surface.

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

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3 coverage increases and these are necessary for strong CO chemisorption. It has been
4 observed in the literature that no CO dissociation occurs on K-promoted Pt(111)¹⁴. The
5 shape of figure 2 appears to be related to the changes in work function observed when
6 dosing potassium onto the Pt(111) surface. Both Windham¹² and Pirug³¹ have observed
7 a decrease in workfunction with increasing potassium up to half a complete monolayer
8 of potassium, after which the workfunction increases to resemble that of bulk
9 potassium. The rise from the minimum in the workfunction curve reported by Kiskinova
10 and colleagues¹⁴, at which point metallic potassium begins to form, is likely to be at
11 a point co-incident with the fall in sticking probability in figure 2. It therefore appears that
12 the decrease in sticking probability of CO is caused by the beginning of the formation of
13 metallic potassium. The fall then is most likely due to the blocking of CO adsorption sites
14 on the Pt(111) both because of the increasing coverage and the increased size of
15 metallic K atoms (~0.2 nm covalent radius³²) compared with K ions (~ 0.14 nm radius³²).
16 K seems to be inert to CO, as might be expected since there are no room temperature-
17 stable K-CO compounds, because CO is a both sigma donor and a pi acceptor, but K has
18 no orbitals of appropriate symmetry for bonding and is not an electron acceptor. No
19 doubt there is a physisorbed state which can adsorb on this K layer, but it is not stable at
20 ambient temperature.
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36 It is a little surprising that there is so little effect of K dosing on the CO curves at
37 low coverage of K up to 120s dosing. The minor change in adsorption profiles and
38 sticking probabilities of CO could perhaps be explained by invoking the sub-surface
39 adsorption model of K as described by Hannon³³ and Lehmann¹³ in which the initial
40 adsorbed potassium migrates to sub-surface sites, leaving CO adsorption sites un-
41 obstructed for adsorption. At these low coverages K is in the ionic state and, at least in
42 Madelung terms, the radius of this species is reduced, but K ions in crystals are actually
43 relatively large, at ~ 0.14 nm ionic radii. It certainly appears that K⁺ does not block Pt
44 adsorption sites at these coverages, and that the adsorption profile is not affected, even
45 though surface electronic structure is, as evidenced by the large work function changes
46 at low coverage^{13,14}. This is probably because the precursor adsorption kinetics
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3 dominate and the barriers between precursor and chemisorbed CO, and the heat of
4 adsorption of physisorbed CO are not significantly affected by the K. Nevertheless, the
5 binding of chemisorbed CO to the surface certainly is affected, as shown below.
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9 The temperature programmed desorption spectra recorded after the molecular
10 beam experiments (figure 3) show several interesting features that help to clarify the
11 adsorption processes that are occurring in this system. With no potassium surface
12 coverage there is just a single CO desorption environment at relatively low temperature
13 (~ 120 °C), characteristic of CO desorbing from clean Pt(111)²³. Already at 60 s K dosing
14 there is a clear change in CO desorption with several states apparent including new CO
15 desorption peaks at 180 °C and 220 °C. The magnitude of the desorption peak
16 associated with clean Pt(111) has decreased and when potassium is dosed onto the
17 surface for 120 s this peak has essentially disappeared and the CO desorption has
18 shifted to one main higher temperature peak at 300 °C. This then shifts slightly higher in
19 temperature and with decreased integral up to the maximum dose. Note that the TPD
20 after molecular beam dosing shows some desorption, whereas the sticking curves show
21 a very low sticking probability. TPD from the molecular beam patch is not ideal, since it
22 is only a small part of the surface (~ 7 mm² vs ~ 110 mm² for the whole crystal), and so
23 the high K dose TPD may represent a low coverage of CO over the whole crystal surface,
24 rather than from just the beam patch. This feature has been observed by Somorjai and
25 co-workers, however they have interpreted it as being a gradual shift of the potassium-
26 influenced CO-Pt rather than as a K-CO species²⁶. Crowell *et al.*¹ observed that no CO
27 adsorption took place on multilayer potassium.
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45 Kiskinova and co-workers have observed, using ultraviolet photoelectron
46 spectroscopy and x-ray photoelectron spectroscopy, two separate CO environments
47 when adsorbing CO on potassium pre-covered Pt(111). They state that the initial CO
48 adsorption takes place into a potassium-influenced site on the platinum, followed by
49 adsorption on the clean platinum. The potassium-influenced adsorption sites have a
50 greater adsorption energy than the platinum sites alone (~ 200 kJ mol⁻¹ compared to 138
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3 kJ mol⁻¹ for CO on clean Pt(111)). They also observe exchange in the relative
4 populations of clean and potassium-influenced sites as the surface potassium coverage
5 increases¹⁴. These conclusions aid rationalization of figure 3. At 60 s dose two separate
6 CO environments are visible, a lower temperature desorption peak at 125 °C resulting
7 from CO adsorption on Pt(111), and a higher temperature CO desorption peak at 183 °C
8 that is therefore due to the adsorption of CO on the electronically perturbed platinum
9 immediately adjacent to potassium. As the surface dose is increased to 120 s both of
10 these environments are drastically reduced in size and a new desorption peak at 290 °C,
11 that is obviously due to CO adsorption affected by K, has appeared. All potassium doses
12 greater than this lack the lower temperature desorption peaks associated with CO on
13 clean Pt(111) and only show the single higher temperature desorption peak associated
14 with potassium. It is likely that these various high temperature states are due to CO
15 interactions with different ensembles of K⁺, perhaps isolated K ions (180 °C peak),
16 multiple K⁺ ions (210 °C peak), and perhaps isolated Pt sites in a sea of K ions (300 °C
17 peak). Note that peak appears rather large compared with what would be expected
18 from the molecular beam data, but it is likely to be due to a small coverage of CO all
19 over the catalyst surface, as described above. Note that this model would then explain
20 the apparent contradiction of high CO binding induced by K, yet low coverages being
21 reported^{1, 14}.
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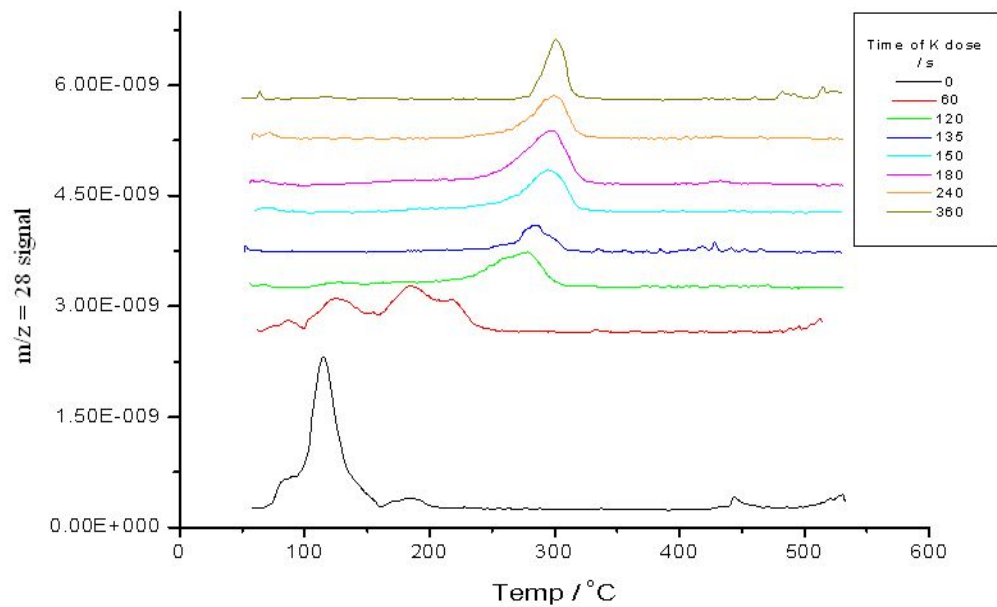


Figure 3 – Temperature programmed desorption of the crystal surface following the molecular beam experiments shown in figure 1.

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.

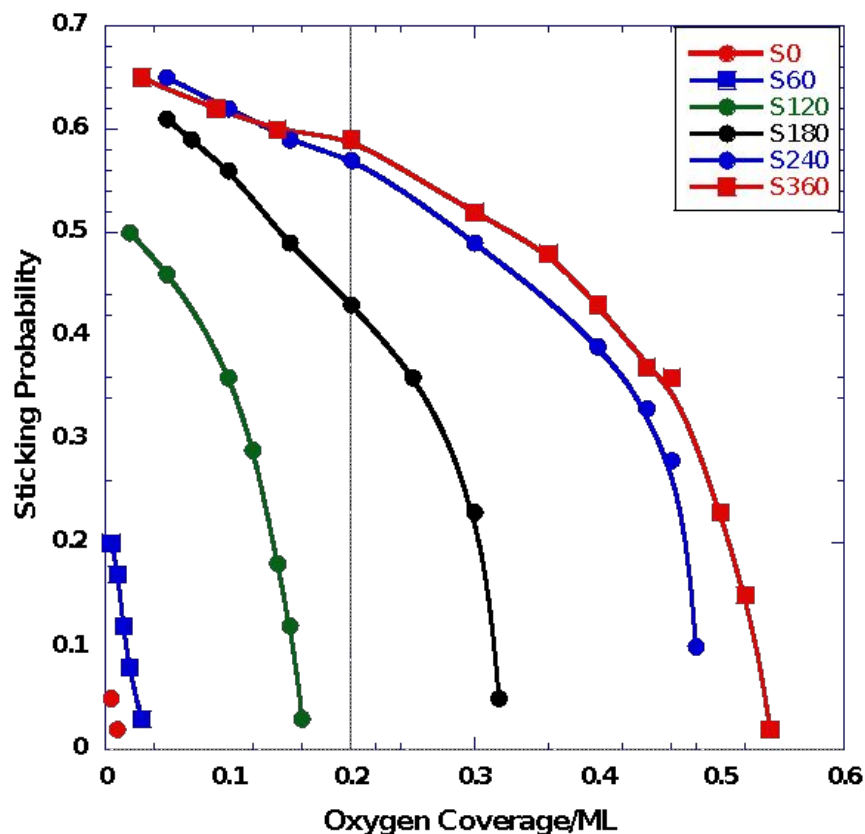


Figure 4 – The sticking probability of a molecular beam of O_2 and its dependence on O_2 coverage for increasing time of K surface dose.

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

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3 structure of the Pt adjacent to it, which reduces the activation barrier to dissociation on
4 the surface³⁵. Effectively polarisation of the incoming molecule by the presence of K
5 enables easier electron transfer into the incoming molecule, which is much more
6 difficult on the clean surface.
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10 This increase in sticking is clearly near complete by 120 s in fig. 5, close to the
11 point at which CO sticking starts to diminish, which we have proposed above is due to a
12 change in the nature of the K layer, from ionic to metallic-like. However, unlike for CO,
13 coverage of oxygen is high on these surfaces, even on the metallic-like layer, which
14 implies that there is intrinsic reactivity of the K layer itself. That the coverage in fig. 5
15 increases beyond the sticking maximum is probably due to two processes occurring with
16 increasing coverage; i) enhanced adsorption onto Pt at low K coverage, increasing as K
17 coverage increases in the K⁺ state, followed by ii) direct adsorption onto the K metallic
18 layer. Note that although there is a transition from ionic to metallic K, the latter still has
19 a very low work function (2eV^{13,14}) thus enabling easy electron transfer into the
20 incoming O₂ molecule. It is, of course, very likely to be the case that, even after the
21 metallic K layer has been formed, it returns to the ionic state when oxygen is adsorbed,
22 and can create extra 'room' for incoming oxygen. The XPS described below and in the
23 supplementary section, figure S2, confirms this.
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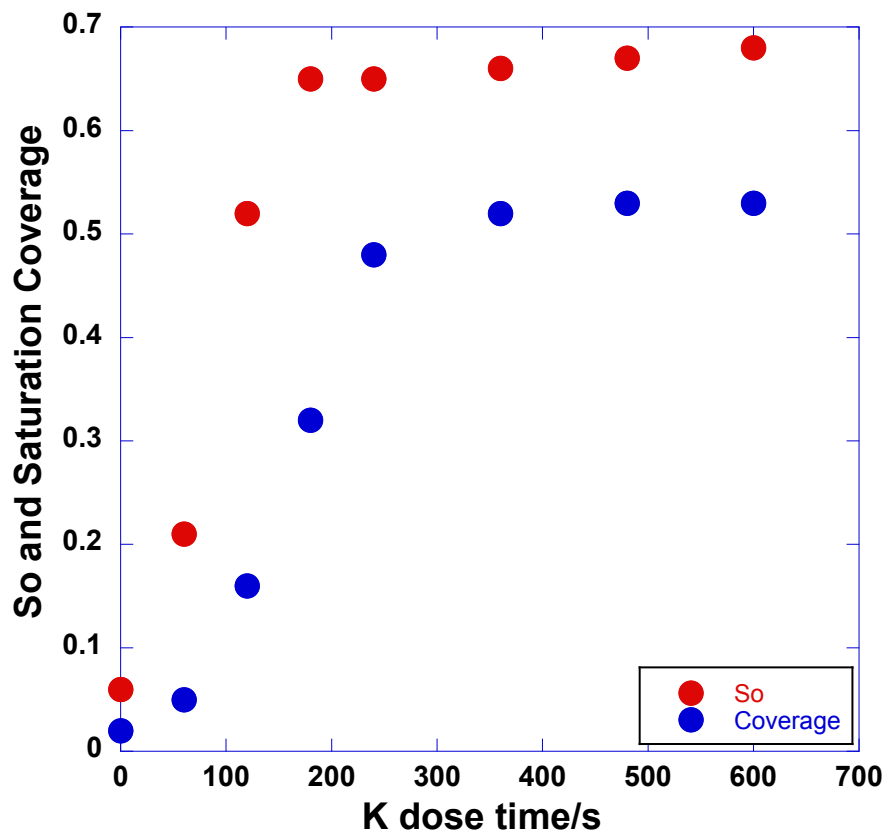


Figure 5 – A plot of initial sticking probability and saturation coverage of O_2 against the time of potassium dose of the Pt(111) crystal surface.

The work of Pirug¹⁶ has shown that potassium adatoms induce O_2 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 O_2 on K/Pt(111) is not simple, with multiple adsorption mechanisms being responsible for the oxygen adsorption.

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3 To complement the molecular beam work, temperature programmed desorption
4 experiments were carried out following the experiments in figure 4 (figure 6). With no
5 potassium present on the surface, due to the very low initial sticking coefficient of O₂ on
6 Pt(111), no O₂ desorption is evident. As O₂ has a finite adsorption coefficient on Pt(111)
7 ($S_0 < 0.06$) it seems likely that the lack of a desorption peak, which should appear for
8 Pt(111) at ~ 420 °C is due to a clean-off reaction with the low level of background CO³⁶.
9 However, with 60 s potassium dosed onto the surface there is a desorption peak at 310
10 °C with a higher temperature shoulder. Increasing the potassium surface coverage
11 resolves this shoulder and shifts it to higher temperatures. With three minutes of
12 potassium dose another oxygen desorption peak at 480 °C becomes visible. It is likely
13 that the initial m/z = 32 desorption peak at 325 °C is a result of the desorption of atomic
14 oxygen created by a potassium-induced reduction in the barrier to O₂ dissociative
15 adsorption (this peak is noted in temperature programmed desorption spectra of
16 potassium oxide by Somorjai *et al.*¹⁰, who also note that it disappears for potassium
17 coverages of greater than a monolayer). The fact that this peak does not disappear in
18 the temperature programmed desorption experiments shown in figure 6 is due to a
19 difference in experimental procedure – in our experiments the potassium layer was
20 deposited before oxidation by the molecular beam. This peak is therefore evidence of
21 the contraction that occurs when oxidising a layer of potassium (a contraction in a
22 complete monolayer of potassium of the magnitude described by Brodén and co-
23 workers would leave 25% of the underlying platinum surface exposed)¹⁷ This
24 chemisorbed oxygen-platinum species has also been noted by Bonzel *et al.*¹⁶ when
25 examining oxygen adsorption on potassium-covered Pt(111). The smaller size of the
26 oxide allows atomic oxygen adsorption on the exposed Pt(111). Garfunkel and Somorjai
27 also note that potassium desorption occurs at the same temperature as the highest
28 temperature oxygen desorption peak, making it likely that the peak at ~ 480 °C is due to
29 a potassium oxide species decomposition, and we see some K desorption too²⁵. If so, it
30 is worth noting that this species only occurs after a complete monolayer of potassium
31 has been deposited, indicating that the potassium oxidation does not occur if the
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3 potassium is ionic in character. However, Brodén and co-workers have provided
4 evidence that potassium oxide does not form on Pt(111). They theorise that this state is
5 due to oxygen incorporation into the platinum surface¹⁷. It seems likely that, as they
6 deposited the potassium at 600 K, only sub-monolayer coverages of potassium were
7 formed; these were shown to be reluctant to oxidise (making the sticking observed in
8 the early parts of figures 4 and 5 to be likely to be due to K-induced O₂ dissociation and
9 spillover of atomic oxygen to nearby K-affected platinum adsorption sites). The mid-
10 temperature peak is likely to be due to a substrate-metal-oxide species as theorised by
11 Brodén *et al*¹⁷. The formation of potassium oxide at half-monolayer coverages has been
12 proven by Cassuto and co workers. Using UPS they proved that molecular oxygen
13 adsorbs via dissociative adsorption on a potassium-promoted Pt(111) surface and that
14 the atomic oxygen produced either chemisorbs on the potassium/platinum or forms
15 potassium oxide³⁸. They also formed potassium peroxide and superoxide species at 95
16 K. O₂ molecularly adsorbs in the form of O₂⁻ on Pt(111) as a precursor to dissociative
17 adsorption. The adsorption is facilitated by partial transfer of electronic charge into a
18 π^* antibonding orbital on the oxygen molecule. It is therefore to be expected that the
19 enhanced back-donation from the platinum as a result of increased local electron
20 density provided by adsorbed potassium would reduce the barrier to sticking by
21 stabilising the precursor state as a species and reducing the barrier to dissociation. This
22 is evidenced by the increased sticking of O₂ that is visible with low coverages of surface
23 potassium and the temperature programmed desorption experiment.
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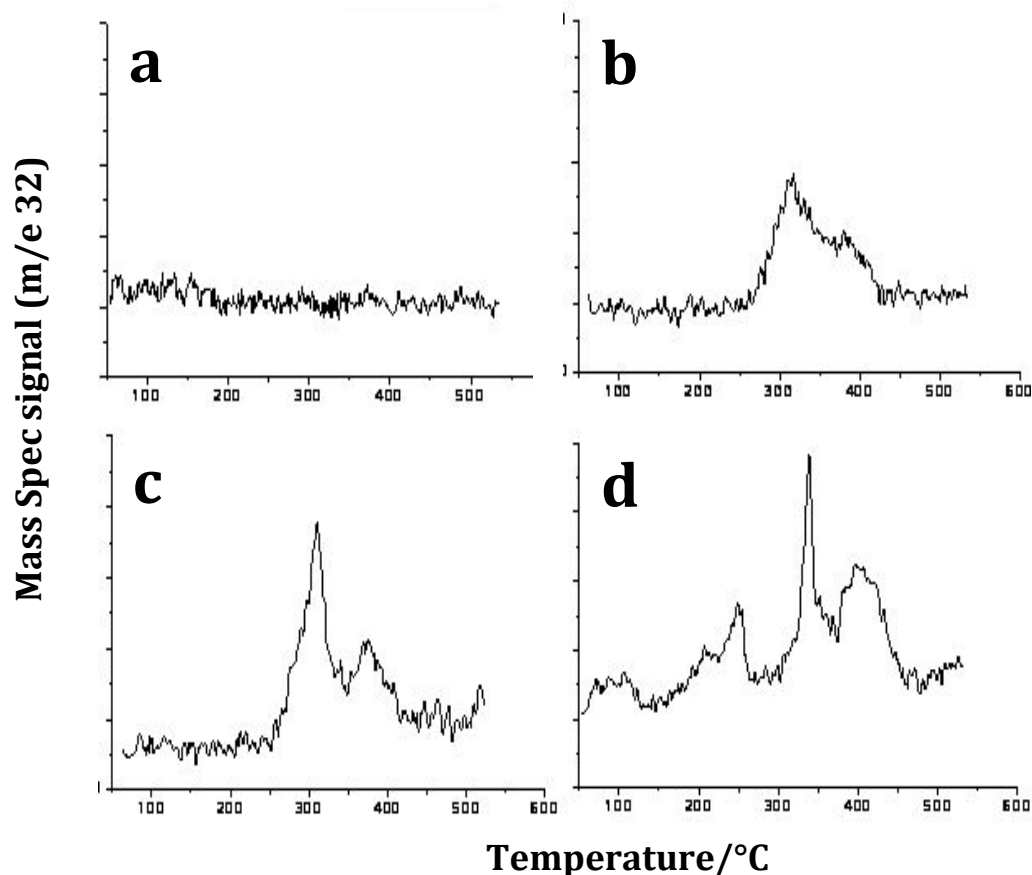


Figure 6. Temperature programmed desorption of O_2 from the K layer following the molecular beam experiments shown in figure 4. The K doses were a) 0s b) 60s c) 120s and d) 360s.

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 eV 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

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3 state and the former with a peroxidic K_2O_2 species (see supplementary table 1), thus
4 largely supporting the chemical reactivity results shown above.
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7 If we combine the reactivity data for CO and oxygen, we can examine the effect
8 of potassium coverage on the adsorption, figure 7. We have assigned coverage as 0.17
9 at the transition from ionic to metallic K coverage (as defined by others^{14,15,20}) as close
10 to the 120 s dose of K, since that is where there is a clear transition in reactive
11 behaviour, and is also reported as the minimum point in work function measurements.
12 Thus above that K coverage the CO sticking and uptake drop rapidly, and have changed
13 to very low values by 0.33 ML coverage of potassium. Similarly oxygen sticking has
14 increased to its final value of 0.67 by ~ 0.17 ML. However, it doesn't reach its maximum
15 coverage until ~ 0.33 ML, and at 0.17 ML of K, the saturation coverage of O_2 is only $\sim 1/3$
16 of its maximum value of ~ 0.5 ML at 0.33 ML K. This is rather more than expected for
17 formation of a layer of K_2O_2 , potassium peroxide-like layer, and so is presumably due to
18 the presence of extra dissociated oxygen atoms which adsorb on the Pt surface exposed
19 as the 0.33 ML saturated metallic layer becomes oxidised and contracts. This is
20 supported by the XPS shown in the supplementary section where there is both atomic
21 and molecular oxygen present with the amount of the former being $\sim 1/2$ that of the
22 latter. Note also that we have simply extrapolated K dose time with coverage, assuming
23 they are linearly related, but it is quite possible that above the 0.5 ML coverage
24 associated by others with K saturation in the metallic state (~ 200 s dosing time), the
25 sticking may be very low after that point. Note that Garfunkel and Somorjai stated that
26 multilayer potassium formation was not possible at room temperature¹⁰.
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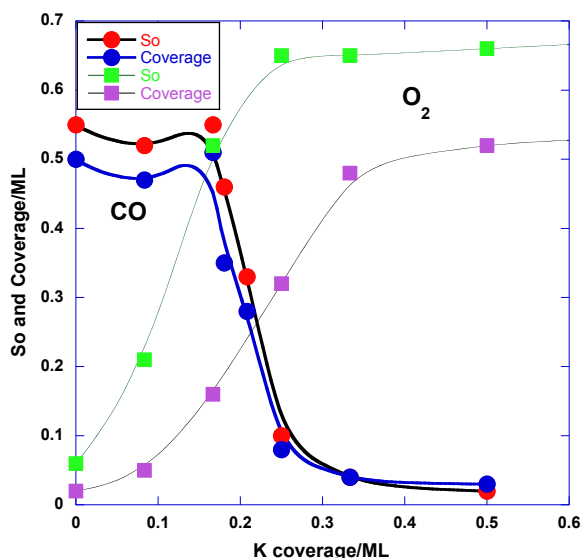


Figure 7. Showing the dependence of initial sticking probability and saturation coverage for O_2 and CO upon the coverage of pre-dosed K. Thick fitted lines and circle data points are for CO, thin lines and squares for O_2 ,

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>.

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TOC Graphic

