Oxygen Adsorption on a Potassium-Promoted Ag Catalyst

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The effects of the addition of a K surface promoter upon the adsorption of oxygen on a Ag/α-Al$_2$O$_3$ catalyst has been investigated under low-pressure conditions using temperature-programmed desorption as the probe technique. The effect is to increase the initial sticking probability 300-fold at 300 K, compared with the unpromoted sample. This is achieved by a combination of a decreased barrier to adsorption (from 16 to 8 kJ mol^{-1}) and an increased prefactor. The barrier (associated with electron pickup by O$_2$ to form O$_2^-$ relatively far out from the surface) is reduced by the effect of the alkali ion on the work function of the metal surface. The prefactor is increased by the presence of the K (which acts in a way similar to that of preadsorbed O atoms) which increases the corrugation of the mainly (111) orientated Ag particles and so enhances energy transfer from, or electron transfer to, the incoming O$_2^-$ ion. The desorption shows all adsorbed states to be affected. The clean surface dissociated state is least affected, being shifted 20 K higher in peak temperature, but otherwise showing similar desorption kinetics. A second dissociated state is seen as a broadening of this peak to higher temperatures (representing a peak $\approx$70 K higher than the unpromoted surface desorption) and we associate this with a state adjacent to the promoter. Since both adsorption states are affected by the alkali and are present in similar amounts we infer that the promoter is fairly homogeneously spread on the catalyst. A third desorption state is present on these catalysts, a relatively weakly held species desorbing in a broad peak at $\approx$420 K. This is considered to be a molecularly held state by analogy with other workers' results on alkali-doped single crystals. The amount of this state which is desorbed is sensitively dependent on the nature of the promoted surface and this effect is discussed in more detail in the text. © 1989 Academic Press, Inc.

INTRODUCTION

The effect of poisons and promoters on catalytic activity has been the subject of some controversy since the earliest days of catalysis (*1*), and still remains so today (*2*). The phenomenon has been the subject of intense activity in recent years, particularly in the disciplines of experimental and theoretical surface science, and it seems that a clearer understanding of the effect at the atomic level is emerging (*3, 14*). It must nevertheless be remembered that it is really a very complex effect which depends upon many factors; these include the electronic effect of the promoter on the catalyst, the geometrical effect, the chemical stability of the compound form of the promoter (the atom itself usually has a short residence time on the surface under catalytic reaction

conditions (*4*)), and the tendency of the promoter to migrate (spread over the surface, dissolve in the host lattice, aggregate to form microcrystals) under varying conditions of temperature and gas-phase composition. In general only the first two of these factors have been studied in detail in well-defined experiments.

In this work we present experimental data obtained from a supported catalyst of Ag to illustrate the effects of a surface promoter compound (doped as KNO$_3$) on the adsorption and desorption properties of oxygen. In the previous paper (*5*) we discussed the nature of oxygen adsorption on the undoped catalyst and this can be briefly summarised as follows. The sticking probability for oxygen at room temperature is very low, 10^{-6}, indicating that the catalyst is composed almost exclusively of (111)

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planes. The adsorption is strongly activated increasing from 16 kJ mol^{-1} at zero coverage to 50 kJ mol^{-1} at one-half of saturation. However, this increasing activation barrier was compensated for by a strongly increasing prefactor with coverage. It was concluded that, as found previously by Campbell on a (111) single crystal (6), the activation barrier is situated relatively far out from the surface and represents the formation of O_2^-. On the atomically flat (111) planes the probability of subsequent dissociation is low, but as the oxygen adatom coverage increases so does the surface corrugation and this seems crucial to dissociation in this case, perhaps by enhancing energy exchange with or electron tunnelling to the incoming ion.

The most detailed studies of K promotion effects on adsorption on Ag have been carried out by Kitson and Lambert (7) on single-crystal surfaces. Essentially they found a much enhanced sticking on Ag(100), although absolute values were not reported. They also found a multiplicity of states in the desorption spectra, especially when there was greater than a monolayer of K. In relation to the present work (less than a monolayer of promoter) the states they identified have desorption peaks at 350 (very small amount adsorbed), 650, and 780 K. The middle peak they associate with desorption from the clean Ag surface. The higher temperature state is ascribed to dissolved oxygen and/or to potassium oxide decomposition. The low-temperature state Kitson and Lambert ascribe to a molecularly adsorbed form of oxygen since it shows no mixing of oxygen isotopes in O_2^{16}/O_2^{18} codosing experiments (7); they also propose that it is associated with a "subsurface" form of K. Presumably this subsurface state must be in the selvedge to be having any influence on the adsorption at all. The molecular state, however, has also been seen by Grant and Lambert (8) on undoped Ag surfaces after dosing at high pressures.

In what follows we describe the results for oxygen adsorption on the promoted, supported Ag catalyst and compare this with our previous work on umpromoted Ag and with the reported effects of promotion on well-defined Ag surfaces.

EXPERIMENTAL

The apparatus and methodology have been described previously (5). The equipment consisted of a UHV machine (but operated without bakeout, at base pressures of $\approx 5 \times 10^{-9}$ Torr) equipped with a Vacuum Generators QX200 mass spectrometer. The latter was used for the temperature-programmed desorption (TPD) measurements and could follow four masses simultaneously. Oxygen (BDH, Poole, Dorset, UK, 99.6%) was dosed through a fine leak valve and the sample was heated by radiation from a W filament situated ≈ 1 mm away from it. The sample (0.094 g) was pressed on a steel mesh with a thermocouple spot-welded to it and embedded in the catalyst powder. The heating rate in all cases was 1.5 K s^{-1}.

The catalyst was made by the impregnation of α-alumina (1 m^2 g^{-1}) with $AgNO_3$ (BDH, 99.9% pure) in an aqueous solution of 1.8 M using the "incipient wetness" method. The sample was dried by heating to 423 K in an oven. The sample was subsequently also impregnated with KNO_3 (BDH, 99.5%) in aqueous solution (0.005 M) by the same method. The Ag loading of the dry catalyst was 13% of the total catalyst weight. The aim of the promoter doping was to get a coverage of approximately 0.5 of the surface, assuming that it covered it homogeneously. The actual coverage achieved is outlined below.

It was found that this catalyst treatment results in a catalyst which was very difficult to clean up in the vacuum system. By "clean up" we mean a process of oxygen treatment (mostly at ≈ 620 K, 2×10^{-4} Torr, but including some temperature programming) which results in gradually increasing amounts of oxygen desorption after a fixed dose. After several treatments

this results in a reproducible desorption spectrum and integral. The main function of this kind of treatment is to remove carbonaceous contamination from the surface. However, it was found impossible to clean up the K-promoted catalyst prepared as described above, without heating above ≈800 K, and this resulted in loss of promotion effect, the catalyst then behaving in the same way as described previously for the undoped catalyst (5). This also seems to correlate well with Kitson and Lambert's observation that K (in submonolayer amounts) begins to evaporate from a single-crystal surface at ≈870 K (7). To get around this problem the same sample was prepared as described above and was heated *ex situ* in air to 620 K for 4 h, with the hope of removing the contamination layer in this way. This proved successful since the catalyst was subsequently very easy to clean up in the vacuum system and quickly gave a reproducible amount of desorption without heating above 760 K; the sample was then never heated above this temperature during the subsequent TPD experiments in order to avoid gradual loss of the promoting layer.

RESULTS

1. Promoter Coverage

From the saturation uptake of the oxygen layer at 475 K we can estimate the promoter coverage. As mentioned above we loaded the catalyst with a promoter level to give approximately one-half monolayer coverage assuming (i) one promoter species per surface site and (ii) homogeneous coverage of the surface. The loading was 142 ppm of K by weight of the final dried catalyst (K added as KNO_3). The subsequent desorption (detailed in the next section) showed a saturation uptake of 1.4×10^{16} molecules g^{-1} of catalyst which compares with 5.6×10^{16} molecules g^{-1} for the unpromoted catalyst (5). This then indicates a total blockage of surface sites of 0.75 by the promoter species. This assumes that Ag

particle size (specific metal area) has not been altered by either the modified treatment (heating to 620 K in air) or the presence of the small amount of the potassium salt; the specific metal area was estimated to be 0.18 m^2 g^{-1} Ag (5).

2. Temperature-Programmed Desorption

Some of the TPD data are presented in Fig. 1 to show the effect of varying adsorption temperature (spectra a) and varying dose (spectra b) on the desorption profile. Figure 2 compares spectra obtained for a dose of 6×10^4 L on the catalyst at 300 and 473 K with and without promoter. No CO_2 or H_2O desorption was observed during the TPD. It is immediately obvious that the promotion, in addition to blocking sites and thus reducing saturation uptake, has had a substantial effect on the desorption. First, the clean surface desorption state appears to have shifted by ≈40 K to higher temperature and has broadened to the high-temperature side. Second, there is evidence of a more weakly held state of oxygen, desorbing over a broad range of temperature between 300 and ≈550 K. This looks similar to that state reported by Lambert *et al.* as a molecularly bound oxygen species (7–9). It must be noted that in the data reported in this section and that following, these spectra were reproducible over a long period of time (involving ≈100 desorptions). However, considerable changes were observed in the size of the low-temperature state desorption after a period of system shut down. This is described more fully in Section 4.

The low-temperature state was very small compared with the rest for the sets of data analysed to determine detailed dissociation kinetics, amounting to only ≈25% of the total amount adsorbed at 300 K for the highest dose used in these experiments at 300 K. This, in turn, amounted to only ≈40% of saturation at 473 K and so the maximum molecular state coverage was ≈10% of saturation. It is so broad that it
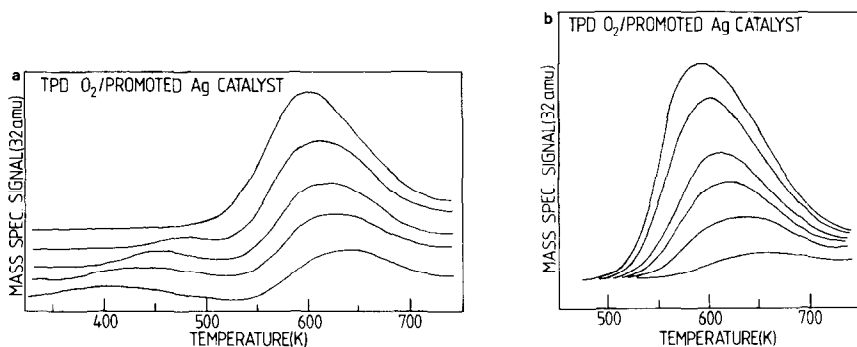
FIG. 1. TPD spectra after oxygen adsorption on the promoted Ag catalyst. Spectra (a) show the effects of increasing adsorption temperature on the desorption after a fixed dose of 6×10^4 L; from bottom to top the adsorption temperatures were 300, 333, 376, 424, and 473 K. Spectra (b) show the effect of increasing exposure to gas of a constant dosing temperature of 473 K; from bottom to top the doses were 560, 1800, 3000, 6×10^4, and 18×10^4 L.

may represent two or more overlapping states.

The high-temperature desorption states appear similar to those of the undoped catalyst desorption and are likely to be due to desorption from the atomic states adsorbed on the Ag metal. However, the broadening indicates the presence of more than a single state and the shape change of the desorption at low coverages supports this. Nevertheless the components of this desorption all fill at a similar rate. It is likely that the curve is composed of two main components—one characteristic of Ag *relatively* unaffected by promotion and one which is strongly affected. An Arrhenius plot of ln

(desorption rate) vs reciprocal temperature for the leading edge of the desorption curves (where the coverage is changing very little) gives a desorption activation energy of ≈ 140 kJ mol^{-1}, similar to that for the umpromoted catalyst (5). An approximate deconvolution can then be made using a desorption curve from the clean surface by aligning the leading edges; this is shown in Fig. 3. Note that the leading edge of this curve is almost identical to that for the promoted curve, but only if the unpromoted curve is shifted by 20 K to higher temperatures, thus showing that none of the desorp-
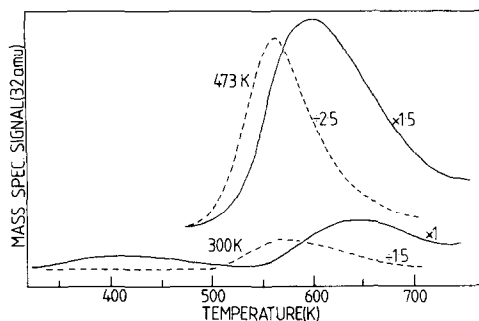

FIG. 2. A comparison of desorption spectra from the clean catalyst (---) and the promoted sample (—) after dosing 6×10^4 L at 300 and 473 K.
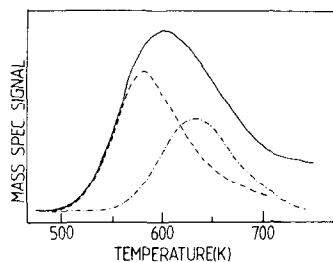

FIG. 3. Deconvolution of the promoted surface desorption spectrum into low-temperature and high-temperature components. The low-temperature desorption curve is a clean surface desorption spectrum (5) shifted 20 K to higher temperatures. A background rise in O_2 pressure has been subtracted from the experimental curve.
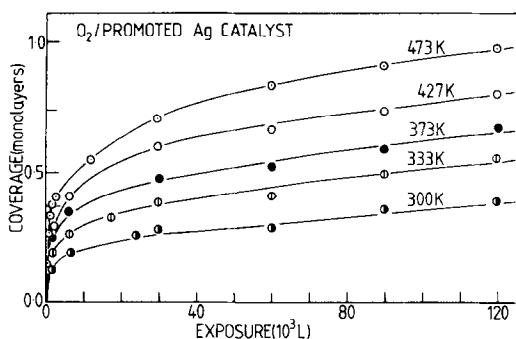
FIG. 4. Isotherms of oxygen uptake on the promoted Ag catalyst derived from the desorption spectra integrals. Saturation coverage corresponds with 1.35×10^{15} molecules desorbed from the sample.

tion is unaffected by the presence of the promoter. The deconvolution then reveals a peak at ≈ 640 K, approximately 60 K higher in temperature than the lower peak. The ratio of coverage in the two peaks is an approximate value, due to the approximate nature of the deconvolution. It is to be noted that there is a high-temperature rising background on the spectrum which may be associated with a further higher temperature state of oxygen, perhaps that seen by Kitson and Lambert with a desorption peak at 780 K (7). They associate this with bulk oxygen or alkali oxide decomposition or both. Whatever it may be, this desorption did not apparently affect the reproducibility of the lower temperature desorption, since heating a layer with the same dose to either 700 or 760 K made no significant difference to the desorption spectrum.

3. Adsorption Rates

From several sets of desorption spectra obtained by varying the gas dose at a series of temperatures a set of isotherms was obtained and these are shown in Fig. 4. They show a very rapid initial uptake of gas followed by a slower region. Saturation uptake was reached only at the highest temperature (highest adsorption rate) and was 1.35×10^{15} molecules, or 1.4×10^{16} molecules g^{-1} catalyst (1.1×10^{17} g^{-1} Ag). Figure 5 shows the sticking probability, S, for

oxygen as a function of oxygen coverage determined from the slopes of the isotherms, and they reveal a dramatic increase for the promoted catalyst over the values for the clean surface. At 473 K the initial sticking probability is increased by 100, whereas at 300 K it is ≈ 300 times higher. Furthermore the overall coverage-dependent shape is opposite for the two catalysts, the undoped catalyst showing the opposite curvature of most of those of Fig. 5; S/S_0 remains much higher for the undoped catalyst as coverage increases (S_0 being the zero coverage sticking probability). Both catalysts show a very much reduced sticking probability value at one-half monolayer coverage. The high-temperature curve for the promoted catalyst shows an initial plateau of constant sticking over a short range of coverage, but S then drops sharply. Although the sticking probability shows a severe decline with increasing coverage, even at 0.8 monlayer coverage the promoted catalyst still shows a higher adsorption rate at 473 K than the unpromoted catalyst does at
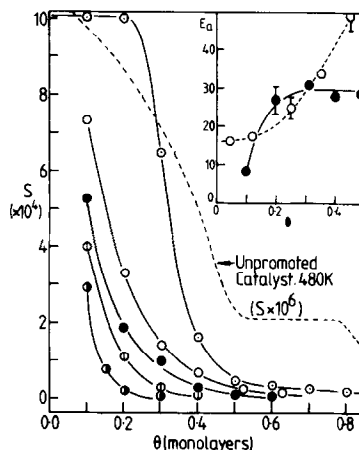

FIG. 5. Sticking probability profiles derived from the slopes of the isotherms in Fig. 4 for the promoted catalyst. The inset shows variation of the adsorption activation energy as a function of surface coverage for both the clean surface (---) and the promoted surface (—). Note that in both cases θ is referred to the saturation coverage of oxygen; in absolute terms the saturation coverage for the unpromoted catalyst was four times that for the promoted sample.

zero coverage ($\approx$1.5 $\times$ 10^{-5} vs 10^{-5} (5)). Similarly, at 300 K, the sticking probability has dropped to 5 $\times$ 10^{-6} by 0.3 monolayer coverage, still 5 times the value for the unpromoted case at zero coverage.

Arrhenius plots of ln $S(\theta)$ at constant coverage versus reciprocal temperature yield the activation energy values shown in Fig. 5 and are compared with results for the unpromoted surface. The main difference is that the presence of the promoter has lowered the activation energy for adsorption— being 16 kJ mol^{-1} for the latter at zero coverage and 8 kJ mol^{-1} for the promoted catalyst. Otherwise Fig. 5 shows that the activation barrier increases quickly with coverage to a value of $\approx$30 kJ mol^{-1}.

From the values of the activation energy the prefactor to adsorption at zero coverage can be estimated and is 5 $\times$ 10^{-4} for the clean surface and 10^{-2} for the promoted case. This indicates activation entropies for adsorption in the two cases of -62 and -37 J K^{-1} mol^{-1}, respectively. These numbers are similar to that estimated for desorption from the clean Ag(110) surface ($+44$ J K^{-1} mol^{-1}) and indicate, as expected, a transition state to adsorption which is restricted in its translational motion and appears to be more restricted on the clean surface than on the oxygen-covered (5) or promoted metal.

4. Variability of the Molecular State Desorption

As mentioned above the desorption spectra were reproducible over a series of many experiments but after a system shutdown for a period of 12 days (during which the pressure in the isolated chamber rose to $\approx$10^{-4} Torr) the catalyst needed further oxygen cleaning before reproducible desorption was obtained. This involved heating the sample in oxygen at 2 $\times$ 10^{-4} Torr and 650 K for a period of approximately 30 min (in several cycles, including TPD under vacuum) after which the desorption features were found to be fairly reproducible, but modified compared with the previous data described above. In particular, al-
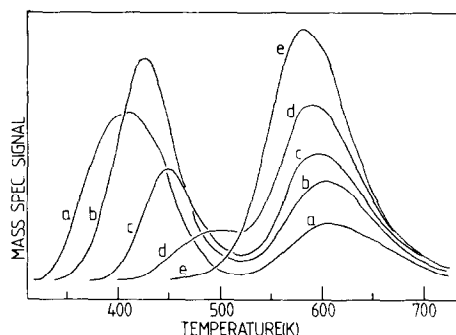

FIG. 6. A series of desorption spectra showing the enhanced adsorption into the molecular state. The spectra were obtained for a dose of 6 $\times$ 10^4 L at adsorption temperatures of (a) 305 K, (b) 343 K, (c) 385 K, (d) 427 K, (e) 473 K.

though the high-temperature states were apparently altered only a little by this, the molecular state was found to have increased significantly in its adsorption. This is illustrated in Fig. 6 and can be compared with the spectra of Fig. 1. The sticking probability into the higher temperature states appears to be little affected by the change in the uptake of the molecular state. The shape of the high-temperature states is slightly different, being a little narrower, indicating less adsorption into the highest temperature state (that shown with a peak at 640 K in Fig. 3).

A limited number of experiments were carried out in order to determine whether the molecular state was blocked in its adsorption by atomic oxygen. The result proved positive in that a large molecular state was obtained for adsorption at 300 K (Fig. 6), whereas preadsorption of the atomic layer to $\approx$0.8 monolayer coverage at 473 K resulted in very little molecular state desorption for a subsequent similar dose after cooling to 300 K.

DISCUSSION

1. Dissociation

The results obtained above for dissociation on the promoted surface fit in broadly with the findings for the unpromoted cata-

lyst (5). The first step involves electron pickup by an incoming O_2 molecule and so the activation barrier is sensitive to the work function of the surface. Thus, on the umpromoted surface, this barrier increases significantly with increasing O atom coverage (see Fig. 5). In the data above, the barrier is reduced at zero coverage due to the lower work function of the promoted metal surface. As the oxygen coverage increases the work function will rise also and so E_a again increases (Fig. 5). However, it is the local electronic structure which is important and not only the global work function value which determines E_a. In particular, it is likely that ϕ for the promoted catalyst is lower than for the Ag(110) plane, yet the latter has a near zero activation barrier (10) whereas the former has a value of ≈ 8 kJ mol^{-1}. This activation barrier is situated relatively far from the surface and selects out molecules of high normal velocity. It was proposed that this was responsible for the low efficiency of dissociation of those molecules which have passed over the barrier ($\approx 5 \times 10^{-4}$, temperature independent) (5), because either momentum transfer is inefficient on the smooth (111) planes or electron tunnelling is limiting dissociation (the high perpendicular velocity results in short sojourn time near the tunnelling barrier). Thus any agent which increases the

corrugation of the surface increases this process—increasing oxygen coverage does it, both in previous work (5) and in this (see Table 1) and so does the presence of the promoter species. Table 1 shows that at zero coverage on the clean surface S_0' is 5×10^{-4} whereas with the promoter present it has increased to 8×10^{-3}. Thus both the decreased activation barrier and increased prefactor support the conclusion of the earlier paper. However, it is clear that factors such as the *local* electronic structure and the surface morphology (long-range and short-range order) are the sources of the details of these differences.

The results clearly show a much enhanced probability for oxygen dissociation. This is a feature which has been observed previously on crystal surfaces (7, 9), but our result is of more significance to catalytic processes for the following reason. In general workers studying promotion on single crystals have concentrated on the alkali metal alone. At low coverages it is ionic, but due to mutual depolarisation it becomes metal-like at high coverages (11, 12). This alkali species is likely to be (i) relatively thermally unstable on its own (4) and (ii) highly reactive. Thus the presence of alkali on silver has been found to enhance the sticking probability to close to unity (7, 9, 13), but it is likely that this is initially due to

TABLE 1

Adsorption Parameters at 473 K

θ	Unpromoted			Promoted		
	$S(\theta)$	$E_a(\theta)^a$	$S_0' \cdot f(\theta)^b$	$S(\theta)$	$E_a(\theta)^a$	$S_0' \cdot f(\theta)^b$
0.0	1.5×10^{-5}	≈ 16	$\approx 5 \times 10^{-4}$	10^{-3}	?	?
0.1	1.0×10^{-5}	16	5×10^{-4}	10^{-3}	8	8×10^{-3}
0.2	8.5×10^{-6}	20	1.2×10^{-3}	10^{-3}	28	1
0.3	7.5×10^{-6}	28	8×10^{-3}	6.5×10^{-4}	30	1
0.4	5.5×10^{-6}	40	0.12	1.6×10^{-4}	28	0.2
0.5	2.5×10^{-6}	≈ 53	≈ 1	5×10^{-5}	29	0.1

^{a} In kilojoules per mole.

^{b} Where S_0' is the zero coverage preexponential factor and $f(\theta)$ is the coverage dependence of the adsorption: $S(\theta) = S_0' \cdot f(\theta) \exp(-E_a(\theta)/RT)$.

direct adsorption at and reaction with the alkali (13) to form a surface compound. Usually, once the process is complete the sticking drops considerably. In the present work the promoter is present in a form more likely to be found in a working catalyst (and the sample has been prepared in a similar manner). Nevertheless it is clear that there is still a remarkable increase in adsorption rates. Holloway et al. (14) recently showed that the promotion effect of an alkali metal atom in terms of its induced electronic structure is still substantial even when an oxygen atom is adsorbed next to it and this is apparently supported here.

Of course, without the benefit of surface analysis or surface structural information we are somewhat handicapped in our further interpretation of the results; the TPD data themselves however contain a wealth of information which can give some general insight into these surface properties. First, it seems that the promoter species has been evenly distributed over the catalyst at the macroscopic level. The evidence for this is that there is little further uptake of gas at 473 K after a dose of $\approx 1 \times 10^5$ L, whereas for unpromoted particles the uptake by that stage has been only ≈ 0.5 of saturation. Thus, if there were a significant number of the latter there would be considerable extra uptake above this exposure, which is not the case.

If we now consider the microscopic promoter coverage, the first thing to note is that we are not sure of the coverage by promoter. The loading, if it were spread homogeneously with respect to coverage between the support and the metal phase, would give an approximate surface coverage of 0.22 by K atoms (assuming 1 site coverage, 10^{15} sites cm^{-2} of catalyst surface, total area of catalyst 1 m^2 g^{-1}). The blockage of oxygen adsorption is 75%, the saturation coverage on the undoped surface was 4.3×10^{17} molecules g^{-1} of Ag, whereas for the same catalyst loaded with the promoter it was 1.1×10^{17} g^{-1}. We can consider two extreme situations for the pro-

moter coverage above—(i) homogeneous coverage of the Ag particles at the atomic level and (ii) promoter in the form of large islands. From the data above it is clear that the real situation is more akin to the former. For (i) it is to be expected that the oxygen adsorption will be largely blocked by such a coverage, since oxygen adsorption requires at least two adjacent sites (saturation monolayer coverage on Ag(111) being $\theta = 0.38$, a $p(4 \times 4)$ surface structure (6)). This is found to be the case. Furthermore all the adsorption would be expected to be modified, which it is (S higher for both states, shifting of states to higher temperatures than those for the unpromoted system). Case (ii) above would be expected to show (a) largely unaffected desorption and (b) rapid saturation of those sites of high S adjacent to the promoter islands, S then being close to that for the undoped catalyst. Neither of these is the case. From our data we suspect that the promoter actually exists as very small islands containing several alkali ions in compound form, since if the promoter were at atomic dispersion it is likely that at such a high promoter coverage the little oxygen that can adsorb would be strongly affected and affected similarly. However, as shown in Fig. 3 there is more than one state in the desorption, the lower temperature state desorbing at 580 K being relatively little affected (in its desorption kinetics). Thus there seem to be two or possibly more types of atomic oxygen, the state desorbing at higher temperatures presumably being adsorbed closest to the promoter. Thus we are associating the two states with nearest neighbour and next nearest neighbour configurations indicating that the alkali compound is indeed present as small islands (it is important to note that the alkali compound unit itself may well occupy more than one site). Although there is this discrimination between sites in the TPD, both have a very similar uptake rate since the shape of the desorption profile varies relatively little with exposure (see Fig. 1), indicating a difference of possibly

only a factor of 2 in favour of the high-temperature state. Thus the effect of promotion is greater than first nearest neighbours and has a significant effect on the uptake rate at more remote sites. Whether a precursor molecular state is now playing a role in the adsorption process, in contrast to the unpromoted catalyst, is uncertain but possible.

2. Molecular Adsorption

Although we have not carried out isotopic labelling experiments to confirm the molecular integrity of the state desorbing at 420 K, we rely here on the data of Lambert *et al.* (*7, 8*) who have identified it as such on single crystals. The desorption shape and temperature look very similar to those of Lambert *et al.* It is clear from the data above that this state is very mutable. It seems to be very sensitive to the state, and probably the morphology of the promoter layer. The latter apparently changed during the system shutdown mentioned above resulting in much enhanced uptake into the molecular state while the high-temperature desorption showed a decrease. Since we have associated the latter with adjacence to the promoter, then the molecular state seems to have now been stabilised close to the alkali. It was found that the atomic state can block adsorption of the molecular species. It seems unlikely that the reverse, molecular state blockage of the atomic state occurs since the temperature dependence of the uptake into the atomic states is little changed when the catalyst changed its properties. Since the saturation uptake of $O_{(a)}$ on the catalyst has changed (approximately two-thirds of the previous uptake) it seems likely that there has been a morphology change in the promoter structure at the surface. This is presumably induced by chemical change of the promoter layer— perhaps due to conversion to a carbonate (the major gas-phase contaminant being CO during the shutdown), although other forms are possible. This has resulted in the creation of the sites for $O_{2(a)}$ which were not

there previously, perhaps by interaction with the new anion associated with K. These sites can be blocked by $O_{(a)}$ which is relatively unaffected in its adsorption/desorption properties. A possible cause of this is location of the new anion directly above the K species with the $O_{2(a)}$ situated upright at the surface. For this to be the case the outward end of the $O_{2(a)}$ dipole would have to have an induced +ve charge, even though the molecule, as a whole, appears to be an $O_{2(a)}^-$ entity (*16*). The nature of this adsorption cannot be resolved here, but requires more detailed investigation. A study with a much lower promoter coverage could give us more information regarding the range of the promoter effects. This would be greatly aided by an *in situ* surface analysis capability. Second, the surface morphology and coverages need to be accurately defined; single-crystal studies of the type initiated by Lambert *et al.* (*7–9*) and by Campbell *et al.* (*6, 16, 17*) need to be extended to gain more detail regarding the sites for these various species. It is our intention to head in these directions in the future.

It can rightly be said that a study of a catalyst under the conditions of this work leaves many questions unanswered, questions which are best considered by careful single-crystal studies. Nevertheless, several questions have been answered regarding the nature of such catalysts in this work and in the previous one (*5*). First, the Ag particles in such catalysts are polycrystalline, but mainly (111) orientated at the surface. The dissociative sticking probability is low—10^{-6} at 300 K, a number which is very difficult to measure on single crystals (*6, 18*). The adsorption is inefficient due to (i) a higher activation barrier to dissociation and (ii) inefficient dissociation of even those molecules which surmount the barrier. Promotion has a huge effect on the dissociation probability, increasing it by 300 at 300 K and results in the appearance of two new adsorption states at the surface—a more strongly held atomic state proposed to be

adjacent to promoter sites and a relatively weakly held molecular state. The latter appears to be very sensitive to the state of the promoter, varying from very low coverages to high coverages at different phases of the experiment. During these changes the sticking probability into the dissociated states remains high.

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