

THE SILVER-OXYGEN INTERACTION IN RELATION TO OXIDATIVE DEHYDROGENATION OF METHANOL

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ABSTRACT

The interaction of unsupported silver with oxygen at atmospheric pressure and at temperatures between 100 and 600°C has been studied using temperature programmed reduction and desorption experiments with temperatures ranging up to 900°C. In addition, the interaction of an oxygen-loaded silver surface with methanol has been studied using both these techniques and temperature programmed reaction. It appears that the silver-oxygen chemistry is influenced strongly by hydrogen dissolved in the silver during the pretreatment of the catalyst, the hydrogen giving rise to a new type of sub-surface species, possibly sub-surface OH groups, and also to an increase of the amount of sub-surface oxygen formed. Sub-surface oxygen can be converted into a strongly bound species that is not present to a measurable extent after normal oxidation. Defects, partly generated as a consequence of the interaction between oxygen and hydrogen in the sub-surface region of the silver, probably generate this strongly bound oxygen species. The presence of the sub-surface oxygen species appears to activate the silver for methanol dehydrogenation.

INTRODUCTION

Silver is widely used as a catalyst for the oxidative dehydrogenation of methanol to produce formaldehyde. The process is carried out commercially at temperatures around 600°C and at atmospheric pressure; it is possible with an excess of methanol relative to oxygen to reach a selectivity of 90% towards formaldehyde with almost complete conversion of methanol [1].

From earlier work in our laboratory [2], it appears that the influence of reaction conditions on the conversion of methanol to formaldehyde and to the by-products H₂, H₂O, CO and CO₂ can be explained by assuming that two different oxygen sites exist on the silver surface. This is in agreement with Kaliya et al. [3] and with Robb and Harriott [4] who also suggests that selective reaction and total oxidation to CO₂ take place on different sites; in further support for these conclusions, Benninghoven and coworkers [5,6] have shown with SIMS that only one of two oxygen species is involved in the interaction of silver with methanol.

In order to confirm these ideas, it is important to have improved knowledge of the interaction of silver with oxygen. Reviews of those publications concerned with this interaction have been given by Barteau and Madix [7], Verykios et al. [8] and Sachtler et al. [9]. Oxygen adsorption has till now mostly been studied

at low pressures with both single crystals and silver films using ultra high vacuum (UHV) systems and a number of surface techniques. However, adsorption and desorption measurements using higher oxygen pressures have been performed by Czanderna and coworkers, who used small silver particles, e.g., powders and supported silver [10-12] and also larger silver particles including silver wire [13]; they reported that several different oxygen species, including a strongly-bonded form of oxygen, were present. It has been shown by Backx and coworkers [14] and also by Russian researchers [15,16] that the presence of strongly-held sub-surface oxygen species is essential in the epoxidation of ethylene over silver catalysts. However, the properties and behaviour of sub-surface oxygen during the oxidation of methanol are still poorly understood.

The only study of the interaction of oxidised silver surfaces with methanol has been carried out by Wachs and Madix [17,18] at rather low temperatures and pressures, using single crystals (see also reviews by Madix [19,20] and Hedge [21]). It appears that no such studies have been performed under near-industrial conditions despite the fact that different results might be expected: for example, H_2 is only found as an important byproduct under industrial conditions. There are also large differences in temperature and in surface roughness between the two types of experiment.

The present work was performed to obtain more information on the silver-oxygen interaction at temperatures and pressures comparable to those used commercially in the oxidation of methanol. Temperature programmed desorption (TPD) and temperature programmed reduction (TPR) were therefore performed for temperatures up to 900°C with samples treated with oxygen under different conditions. Furthermore, an elementary form of temperature programmed reaction spectroscopy (TPRS) was performed to study the interaction of such surfaces with methanol. In order to eliminate support effects, the measurements were performed using a pure metallic silver material.

EXPERIMENTAL

Methods

The equipment used for the temperature programmed measurements is shown schematically in Figure 1. All the flows except that of air are regulated with pressure and flow controllers.

The valves in the gas-handling system allow selection of the gases used in the system. In the TPR mode, the flow over the silver sample contains 6% H_2 in Ar (10 ml min^{-1}), whereas N_2 is used for the reference flow (20 ml min^{-1}) and also for the flow added to the gas leaving the reactor (the so-called "diluent flow" (10 ml min^{-1}) which has the function of helping to stabilise the detector response). In the TPD mode, He is used for all streams, the same flow rates being used. In the TPRS mode, He is also used for all flows; methanol is now introduced into the flow which passes the sample by using a saturator [1] held at a tempera-

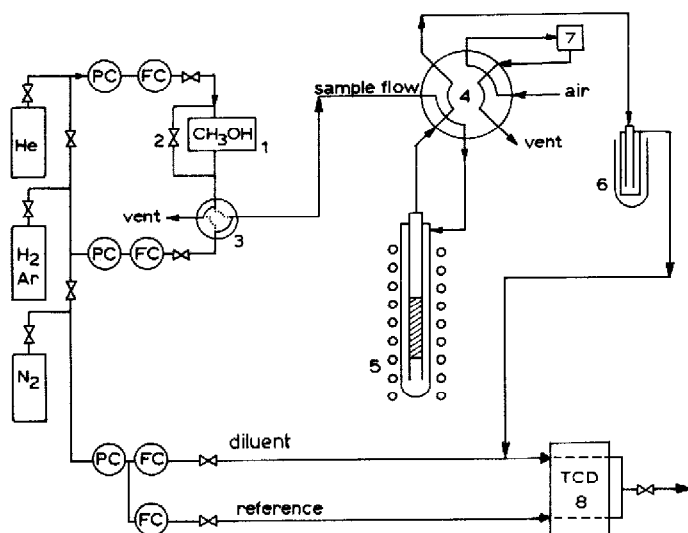


FIGURE 1 Schematic diagram of temperature programmed reaction, desorption and reduction equipment.

ture of 0°C . The methanol can be switched in and out of the flow by use of a bypass loop [2]. The four-port valve [3] allows the flow over the sample to be changed without influencing the other streams.

The flow through the reactor [5] may be selected using the eight port valve [4]. In one position, the sample flow passes through the reactor and the exit stream is directed to the thermal-conductivity detector (Packard 903) via the cold finger [6] and the diluent flow. In the other position of the eight-port valve, air passes through the reactor whereas the sample stream still reaches the detector, now via the dummy reactor [7].

In the TPR mode, the cold finger is maintained at a temperature of about -30°C to condense the water formed by the reaction of hydrogen with oxygen emanating from the surface. In the case of TPRS, measurements made with and without use of the cold finger give different results because only a part of the reaction mixture (i.e., CH_3OH , CH_2O and H_2O) is trapped at -30°C , the other gases being allowed to pass through; analysis of the individual products is not carried out. The cold finger is not used in the TPD mode. In all experiments, the change in thermal conductivity of the mixture leaving the sample is measured; in the TPD mode, this is related to the desorption, in the TPR mode to the amount of hydrogen consumed during the reaction with adsorbed species. The interpretation of thermal conductivity changes during TPRS will be discussed later.

All measurements reported in this paper were performed using a heating rate for the reactor of $17^{\circ}\text{C min}^{-1}$. The temperature was measured with a separate thermocouple situated within the heater but outside the reactor. This setup is able to

reach a temperature of 900°C. Temperature differences over the length of the sample were smaller than 10°C. The total pressure in the reactor during the measurements was about 1.3 bar. Measurements were performed using two different sensitivities of the detector, these being achieved by variation of the wire temperature. Measurements at low detector sensitivity have been corrected for a baseline shift caused by the temperature programme; no attempt has been made to correct for this shift using the high sensitivity of the detector.

The morphology of the silver samples were examined with a JEOL JSM-35CF scanning electron microscope.

Materials

The helium used had a purity of 99.995%; no adsorption was observed on passing pure He or a H₂/Ar mixture over the sample overnight. The air used was cleaned with a molecular sieve. The silver sample used (1.5 g per experiment) was that described earlier [2] as AgIII. Preceding all measurements, the sample was subjected to several oxidation-reduction or oxidation-desorption cycles in order that most of the structural changes caused by high temperature treatment of the type reported by Read and Mykura [22] had already taken place. This pretreatment was used to ensure that no further structural changes occur during the experiments; it is well established that significant structural changes occur in catalysts in the practical situation. Furthermore, a number of experiments were performed on a fresh sample to study the influence of the structural changes brought about during the pretreatment; the detailed results will be presented in a subsequent publication.

RESULTS AND DISCUSSION

Influence of pretreatment before oxidation

It can be seen from the data depicted in Figure 2 that the results of temperature programmed measurements are influenced by the preceding treatment. If a sample is subjected first to TPR and then to oxidation for 18 h at 200°C, three peaks are observed in the subsequent TPR experiment (curve a); these occur at 275°C (Species I), 400°C (Species II) and 850°C (Species III) respectively. When TPD preceded the oxidation, only Species I is clearly present (curve b); Species II is absent and the proportion of Species III remaining is much smaller.

The results of comparable TPD measurements are presented in Figure 3. If TPR was performed before an oxidation step and the TPD experiment was then performed with the cold finger in function (curve a), a spectrum was obtained with a main peak at about 300°C and a shoulder at about 360°C. The first peak almost certainly corresponds to Species I of the curves shown in Figure 2 while the shoulder was probably caused by Species II. No peak corresponding to Species III was observed. The size of the shoulder increased when the cold finger was kept at room temperature (curve b); we therefore conclude that at least a part of the desorption product responsible for this peak consists of water. A TPD treatment before

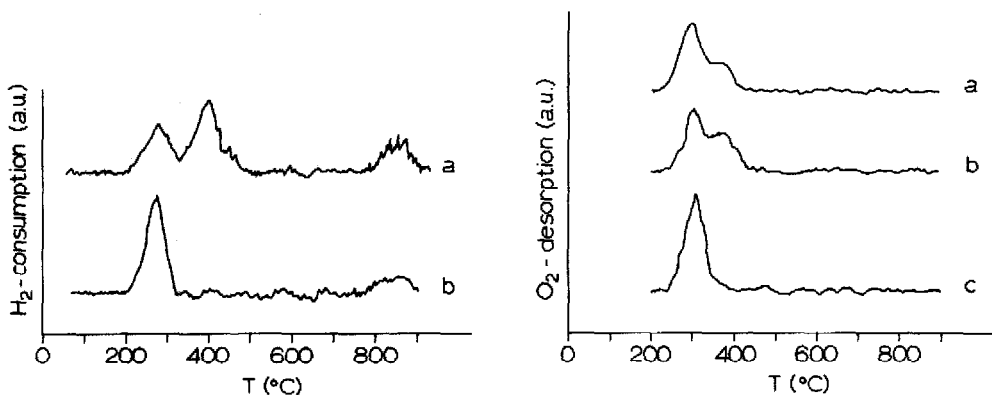


FIGURE 2 TPR after oxidation in air at 200°C during 18 h, preceded by (a) TPR and (b) TPD.

FIGURE 3 TPD after oxidation in air at 200°C during 18 h, preceded by (a) TPR, cold finger in function; (b) TPR, cold finger out of function and (c) TPD.

oxidation (curve c) results in there being only a single peak at 300°C corresponding to Species I in the subsequent TPD experiment. Neither TPR nor TPD experiments carried out with the empty reactor showed any peaks.

A scanning electron microscopic study of the sample after more than 50 TPR and/or TPD measurement cycles showed that holes of about 5 micron diameter had formed in the silver surface, especially at the grain boundaries; no such holes were present in the fresh sample. This phenomenon will be discussed in detail in a subsequent publication.

Before proceeding to give a description of the effect of pretreatment parameters on the behaviour of the different species observed in the TPR and TPD experiments, we shall now offer an explanation for Species I, II and III.

Species I. We believe that the Species I, observed in both TPR and TPD, is due to desorption as molecular oxygen of weakly held atomic surface oxygen; the presence of hydrogen has no effect on this desorption process. The desorption of atomic oxygen from silver surfaces has been studied using UHV techniques and is reported to occur at 300-330°C on both single crystals and polycrystalline materials [7,8,13,28], in good agreement with the results shown in Figure 3.

Species II. The most reasonable explanation of the behaviour of Species II is that dissolution of hydrogen in the silver occurs during the TPR experiment (temperatures rising to 900°C); such dissolution is known to be possible at temperatures above 400°C [23]. During the subsequent oxidation step at 200°C, the dissolved hydrogen then interacts with oxygen to form OH groups; these OH groups can subsequently react with H₂ and be desorbed at around 400°C either as H₂O (which condenses in the cold finger) or O₂. The relative temperatures of

desorption of Species I and II implies that the OH species are more strongly bonded than the oxygen species. It is possible that the OH groups are on the surface, in agreement with the results of Plakidkin and coworkers [24]; however, this is in contrast with the results of Au et al. [25], who show that surface OH groups are only stable on Ag below room temperature. We have carried out additional temperature programmed experiments, to be described in detail in a subsequent publication, which confirm the latter conclusion. We are therefore led to the suggestion that the OH groups responsible for Species II are present in the sub-surface of the silver. It is not clear to what extent the dissolved oxygen and hydrogen making up these groups interact with one another; however, the relative sharpness of the reduction peak at 400°C is consistent with the presence of a real OH entity and not merely of a mixture of absorbed oxygen and hydrogen. Processes involving dissolution of both oxygen and hydrogen are also indicated by the appearance of holes in the surface of the silver after extended series of oxidation-reduction treatments. This is in agreement with observations made by Klueh and Mullins [26] in a study of the hydrogen embrittlement of silver.

Because the rather large silver samples used in the measurements reported here cause significant peak broadening in the TPD and TPR peaks, no attempt has been made to calculate from the data presented for Species I and II the activation energies or the orders of reaction for the desorption and reduction steps.

Species III. This species, giving rise to the reduction peak at 850°C in Figure 2, is not observed in TPD experiments at temperatures up to 900°C (Figure 3), indicating that it is only rapidly removable in the presence of hydrogen. This is in agreement with the results of Czanderna [10], who observed an oxygen species which could only be removed chemically. The suggestion has been made in the literature that such an oxygen species is present in the sub-surface of the silver [9,25,27,28]. It appears from the results of Figure 3 that hydrogen treatment before oxidation increases the amount of sub-surface oxygen. The absorption of hydrogen is thus responsible for an increase in the proportions of both sub-surface oxygen and sub-surface OH groups. It would thus seem that oxygen diffusion is assisted by the presence of dissolved hydrogen; this might be due to an increase in the concentration of defects in the lattice as a result of the interaction of hydrogen and oxygen in the sub-surface of the silver, as also suggested by Meima and coworkers [29].

The following sections describe the results of experiments designed to show more about the sub-surface OH and O species; unless otherwise stated, these were carried out after an oxidation treatment which had been preceded by a TPR measurement. This was done to maximize the amount of oxygen present on the sample. It was also felt that the hydrogen pretreatment was necessary because hydrogen is also present in the product mixture during the oxidative dehydrogenation of methanol [2]; the presence of this hydrogen in the process is likely to have an effect on the oxygen species similar to that caused by the treatment applied here.

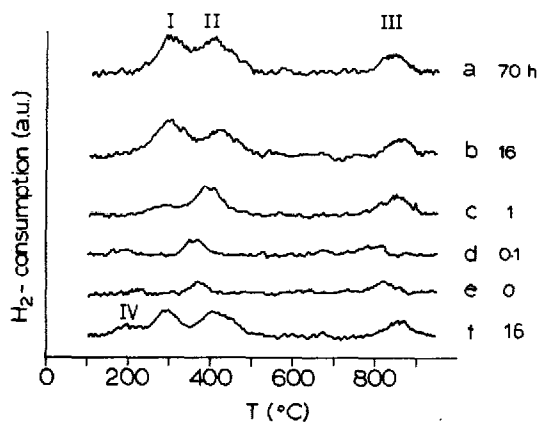


FIGURE 4 Influence of oxidation time on TPR after oxidation in air at 200°C and then cooling in air.

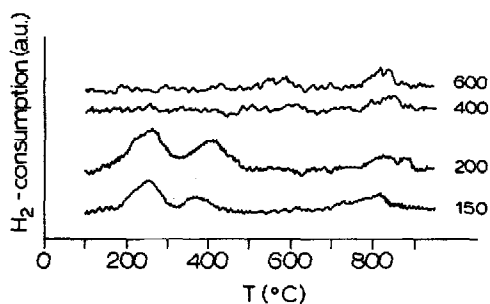


FIGURE 5 Influence of oxidation temperature on TPR after 17 h oxidation in air and cooling in He; oxidation temperature in °C.

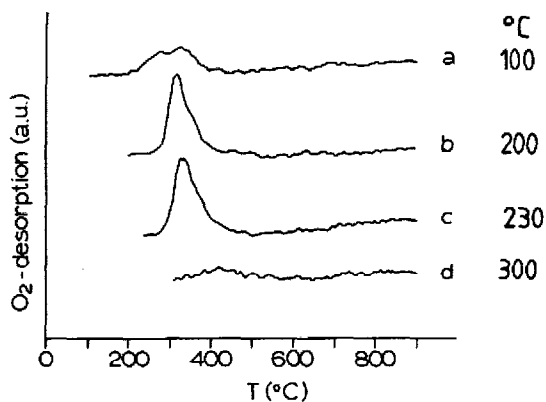


FIGURE 6 Influence of oxidation temperature on TPD after 17 h oxidation in air, preceded by TPD; oxidation temperature in °C.

Influence of oxidation parameters

The uptake of oxygen on the silver during treatment for different times and at different temperatures was studied in TPR and TPD experiments. The influence on the TPR profiles of the time of oxidation in pure oxygen at 200°C is shown in Figure 4; these plots are equivalent to curve a in Figure 2. It appears that Species I starts to develop after Species II and III have reached their maximum values. There was no increase of the oxygen uptake with time after about 16 h and no differences were observed between results after oxidation in pure oxygen and in air; similar results were obtained for TPD measurements. All subsequent oxidation treatments were thus performed for 16-18 h in air.

The influence of the temperature of oxidation in air (for 18 h) is shown in Figures 5 (TPR results) and 6 (TPD results). It can be seen that a maximum occurs in the oxygen uptake (Species I and II) if the pre-oxidation occurs in the range 200-230°C; above this temperature range, both peaks decrease and only Species III is visible in TPR spectra for oxidation at 400°C and above. This is in agreement with the results shown in Figure 3: both Species I and II are observed to desorb at 400°C and higher temperatures. The subsequent measurements were in consequence performed after oxidation in the former temperature region.

It was found that the procedure used for cooling the sample after pretreatment could also influence the results. When the oxidation step was performed at such a high temperature that the oxygen uptake was limited (i.e., for experiments of the type reported in Figures 5 and 6), the sample had to be cooled in an inert atmosphere to prevent adsorption at lower temperatures during cooling; if this was not done, peaks appeared which were characteristic of adsorption at lower temperatures. The start-up procedure used for the TPR measurements after having carried out the oxidation at 200°C was also found to influence the results; this is illustrated by curve f of Figure 4. A small extra peak (Species IV) was observed at 200°C after cooling down in air and starting the measurement within 10 minutes after removal of air from the sample (curve f). This extra peak was not observed when the sample was cooled in He or when it was kept in an atmosphere without oxygen for longer than 15 min before starting the TPR measurement (compare curve b, discussed above).

Species IV is adsorbed very weakly and is desorbed when the air is removed. This observation is in agreement with the results of Czanderna [12] who suggested that a di-oxygen species desorbs slowly at 140°C. Joyner and Roberts [27] showed with XPS that O_2^- is present on silver foil only when the oxidation is performed at higher pressures than those usual in UHV studies. Grant and Lambert [28] also observed adsorbed dioxygen species on Ag(111); these workers reported that the adsorbed concentration was remarkably sensitive to gas pressure and that desorption takes place at 100°C. It therefore appears that adsorbed molecular oxygen is only present after high pressure oxidation and that it can be desorbed very easily.

Because of the weak bonding of this entity to the surface, it is unlikely that this molecularly adsorbed oxygen is an important surface species during oxidative dehydrogenation of methanol at high temperature.

From the results given in Figure 4, it appears that the rate of oxidation of the silver to give maximum coverages by Species I, II and III is extremely low. Czanderna [10], Scholten et al. [30] and Seyedmonir et al. [31] have observed essentially higher rates of oxidation on silver powders and on small supported particles. Single crystal studies, as reviewed by Barteau and Madix [7], also showed markedly higher oxidation rates on the faces [100] and especially [110]; on Ag [111], however, adsorption appears to take place only on surface defects, this causing an extremely low oxidation rate. Facetting on silver crystallites has been shown by Rhead and Mykura [22] and by Sundquist [32] to take place at temperatures between 900 and 1000°C, this giving especially an increase in the proportion of [111] faces. Such facetting might be responsible for the low oxidation rate observed here; facetting would be favoured by the high temperatures used during the measurements. It would also explain the observation that the amount of oxygen that can be adsorbed decreases with the age of the sample. This was observed especially for TPD measurements; during TPR measurements, surface roughening and enlargement maintain the amount of oxygen adsorbed at an approximately constant value. In all cases, the amount of atomic oxygen on the surface (Species I) corresponds to less than that required for a monolayer. The ratio between Species I and III was also found to vary somewhat during experiments and this might have been caused by surface rearrangements. We shall report further on the influence of surface structure on the interaction of silver with oxygen in a subsequent publication [33].

Influence of helium treatment after oxidation

Because the observed peaks reported in the spectra of Figures 2-6 were rather small, the measurements which will now be reported (Figures 7-10) were performed using a higher detector sensitivity. This results in a larger baseline shift during the TPR and TPD experiments. Base-line corrections have not been made; instead, the appropriate approximate base-lines are shown as dotted lines for each spectrum. The peaks occurring in all the spectra at about 100°C arise from instabilities in the system at the beginning of the temperature increase and have no significance; they also appear in blank spectra at this sensitivity setting.

Figure 7 shows the results of a sequence of experiments in which we examined the effect on the TPR behaviour of different TPD treatments after the initial oxidation treatment; in all cases, the sample was first subjected to a standard TPR experiment and then oxidised for 17 h in air at 210°C before the TPD treatment and subsequently cooling in He. The final temperature of the TPD pretreatment as well as the time (min) at this temperature are given beside each curve in Figure 7. The TPD treatment totally removed the surface atomic oxygen (Species I at about

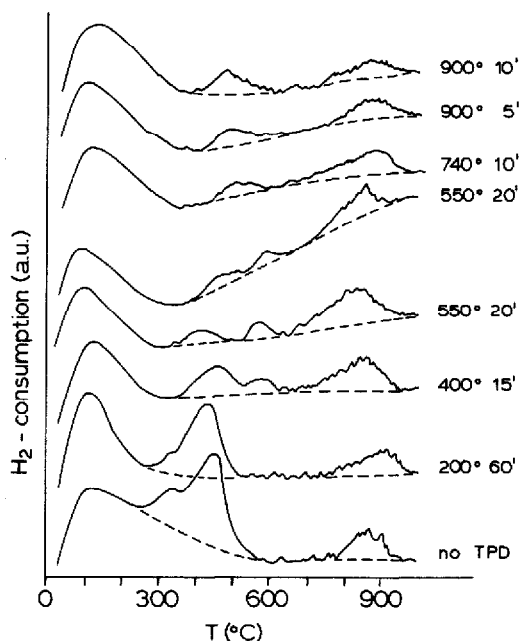


FIGURE 7 Influence of preceding TPD on TPR experiments after 17 h oxidation at 210°C in air; parameters final temperature (°C) and time (min) of the preceding TPD.

300°C, see Figures 2-6) but the sub-surface OH groups (Species II at about 450°C) were only removed totally if desorption was performed with a final temperature of 740°C or above. A new peak was observed at a temperature of around 550°C (Species V) when the desorption pretreatment was carried out at temperatures above about 400°C. This new peak persisted up to a temperature of desorption of 900°C but the peak temperature decreased slightly at higher pretreatment temperatures; its magnitude also increased with increasing pretreatment temperature. Finally, the amount of sub-surface oxygen (Species III, at a temperature of about 850°C) decreased with higher desorption temperatures.

The new reduction peaks (Species V) shown in Figure 7 at a temperature of about 550°C thus arise after the sequence: (i) reduction at temperatures rising to 900°C; (ii) oxidation at 200°C; and (iii) treatment in helium at temperatures up to 400°C or above. In order to explain this peak, we suggest that sub-surface oxygen (Species III) segregates to the surface during the He treatment; it is subsequently reducible at a lower temperature than if it remained in the bulk but at a higher temperature than that required for normal surface oxygen (Species I). This is in agreement with the observation that the amount of Species III decreases as Species V increases (Figure 7). However, the new form of surface oxygen cannot be adsorbed on the same type of sites as is the normal surface oxygen (Species I) as it is reducible at higher temperatures. We therefore suggest that the new

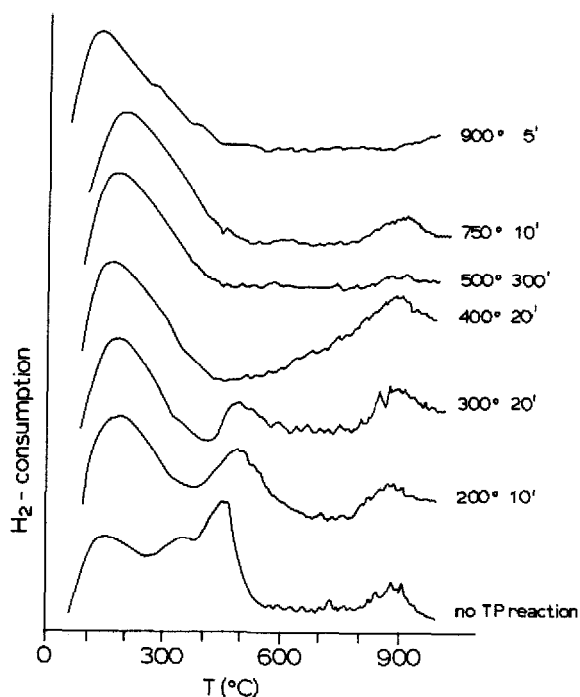


FIGURE 8 Influence of preceding TPRS on TPR after 17 h oxidation at 210°C in air; parameters final temperature (°C) and time (min) of TPRS.

species is associated with surface defects. This suggestion is reasonable as the new species is formed from sub-surface oxygen atoms; the latter (Species III) is probably concentrated around defects in the bulk structure which must be accessible via rapid diffusion paths (e.g., grain boundaries) as it can be formed readily even at low temperatures (as low as 150°C, see Figure 5). During the He treatment, the process is reversed and the oxygen species become concentrated at defects located at or very close to the surface. These surface defects must be associated in some way with the rapid diffusion paths postulated above; i.e., they must occur at the edges of grain boundaries or other faults in the structure. These new oxygen species can only be removed by hydrogen at about 550°C (Figure 7), in contrast with the normal surface Species I, which can also be removed at much lower temperatures. It is possible that the defects at which Species V is adsorbed are formed concurrently with the desorption of sub-surface OH groups during the desorption treatment, as Species V is not formed until the size of the peak corresponding to Species II is reduced; we cannot exclude the possibility that Species II is directly responsible for Species V but, if that were the case, we would expect to find no effect on the concentration of Species III.

Species V was also observed in the TPR spectrum of a fresh sample of oxidised silver free of dissolved hydrogen; after about ten measurements using temperatures

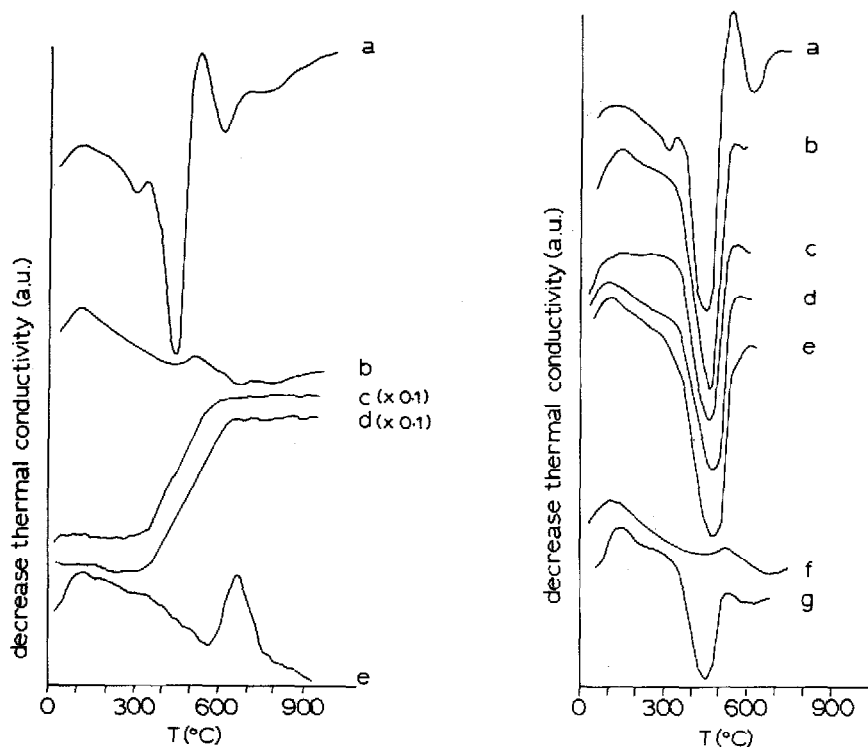


FIGURE 9 TPRS profiles with cold finger out of function (a,b,e) and in function (c,d); pretreatment: 17 h oxidation at 210°C (a,c) or TPR up to 900°C (b,d); curve e is for the empty reactor.

FIGURE 10 Influence of pretreatment after TPR followed by 17 h oxidation at 210°C in air on TPRS (a-f); (a) only oxidation; (b) TPD up to 300°C (10 min); (c) TPD up to 400°C (10 min); (d) TPD up to 550°C (10 min); (e) TPR up to 600°C (10 min); (f) TPR up to 900°C (5 min); (g) oxidation after TPD (hydrogen free), followed by TPD up to 600°C (10 min) and the TPRS measurement.

up to 900°C, this peak was no longer clearly observable and this must be due to the gradual removal of surface defects and to grain growth caused by high temperature annealing during the measurements. More detailed information on these experiments will be given in a subsequent publication. These experiments give evidence for the suggestion that Species V is associated with defects in the surface [33]. A similar argument is used by Meima and coworkers [29] to explain variations in the activity of silver catalysts for CO oxidation.

The size of the reduction peak of Species V (Figure 7) is of the same order as that for atomic surface oxygen (Species I). Thus, it is impossible that only oxygen adsorbed on the defects is involved. We suggest that the oxygen dissolved in the silver in the direct vicinity of those defect planes which inter-

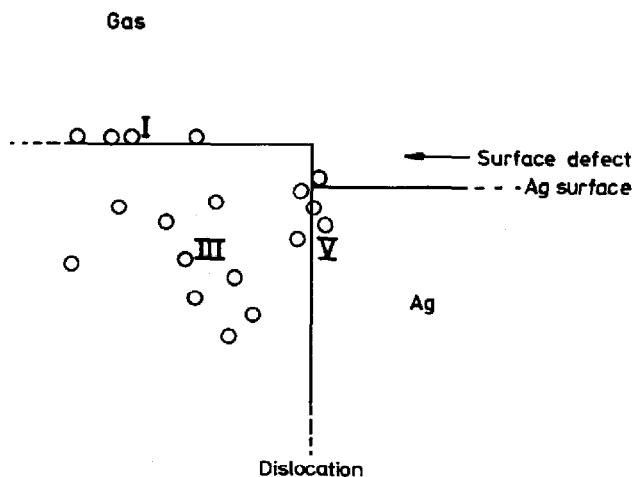


FIGURE 11 Possible location of atomic surface oxygen (Species I), oxygen in the vicinity of surface defects (Species V) and sub-surface oxygen (Species III) on and in silver.

sect the surface contribute to the reduction peak of Species V. The sub-surface oxygen (Species III) is probably located either in the undisturbed silver lattice close to the surface or deeper in the silver sample close to the defect planes; the presence of these defects increases the proportion of the silver lattice accessible for the formation of this sub-surface oxygen (Species III). Figure 11 gives a schematic representation of the possible location of the Species I, III and V in the case of a dislocation intersecting the surface.

It is interesting to note that Haul [34] reported the desorption of sub-surface oxygen from polycrystalline silver at 530°C; Tan et al. [35] observed the same desorption peak on Ag(111). In our case, sub-surface oxygen (Species III) is not desorbed in TPD experiments and can only be removed by TPR at high temperatures (Figure 7). We therefore suggest that the observations of Haul might be explained by the adsorption and absorption of oxygen in the vicinity of the surface defects required for the formation of sub-surface oxygen, as discussed above. The observation of Tan and coworkers [35], that a desorption peak at about 600°C is observed on Ag(111) with a high content of lattice oxygen, seems not to be in agreement with our explanation of the results presented here. However, the desorption peak at 600°C is so small compared with the atomic peak that it is not unreasonable to suggest that defects can occur even on single crystal Ag(111) and that oxygen in the vicinity of these defects (especially on the edges of the sample) may be responsible for the desorption peak. Furthermore, it should be noted that Tan et al. [35] obtained their high concentration of "solved oxygen" by repeated exposure of the sample to chlorine and oxygen; this could also be responsible for increased surface defect concentrations. The fact that we observed no TPD peak attributable to sub-surface oxygen after oxidation at 200 or 400°C.

may be caused by our samples having a low surface-defect concentration as a result of the high temperatures used in pretreatment, as discussed above. The limited sensitivity of the equipment used as compared to that used in desorption studies in UHV systems may be responsible for the fact that no Species V can be observed in this work after normal oxidation.

We have suggested that sub-surface oxygen (Species III) can segregate to form oxygen in the vicinity of surface defects (see above). This is in agreement with the observations of Grant and Lambert [28], Hau et al. [34] and Kagawa and coworkers [36], namely that sub-surface oxygen can exchange with surface oxygen. It is likely that sub-surface oxygen can migrate to the surface, especially along rapid diffusion paths, and this results in the formation of the Species V observed. Further exchange with atomic surface oxygen (Species I) is apparently possible [28,34,36]; however, this migration of species is not observed in the experiments reported here because formation of oxygen in the vicinity of surface defects (Species V) was only observed when the temperature was above that for the desorption of atomic surface oxygen (Figure 3). It can only be concluded that exchange between Species V and I is slow compared with the formation of Species V (from Species III); otherwise Species V would not be observed (Figure 7).

Interaction with methanol

The interaction of methanol with oxidised silver was studied using a combination of TPR experiments and an elementary form of Temperature Programmed Reaction Spectroscopy (TPRS), in which the existence of a reaction of any sort with methanol in He could only be inferred from the changes in thermal conductivity of the gases passing through the detector. Two types of experiment are reported. Firstly, the influence of methanol on the various oxygen species present on the surface was studied by comparing the TPR behaviour of two prerduced silver samples after oxidation for 17 h at 210°C, one with and the other without a TPRS experiment. Secondly, the TPRS technique was used to study effect of various types of pretreatment on the reaction of methanol in order to try to clarify the role of the various types of oxygen species on the reactions of methanol.

Figure 8 shows the effect of TPRS experiments on the subsequent TPR behaviour and compares the results with the TPR spectrum for a sample pretreated in the same way except that no TPRS was carried out; the figures after each curve indicate the uppermost temperature used in the TPRS experiment and the time (min) for which this temperature was maintained. Reaction with methanol even at 200°C removes all sign of the peak due to Species I (weakly bounded surface oxygen) even though this species does not begin to be removed by hydrogen until about 250°C. Species II, due to sub-surface OH groups, is unaffected by reaction at 200°C or 300°C but it is removed by reaction in methanol at 400°C. Species III, sub-surface oxygen, is also much more reactive towards methanol than towards hydrogen; whereas in hydrogen it is removed at about 850°C, it can be removed by

methanol at a temperature as low as 500°C if the time of reaction is sufficient. A striking difference between Figures 7 and 8 is the absence of oxygen in the vicinity of surface defects (Species V at 550°C) in Figure 8. Methanol apparently reacts with this species, resulting in removal of oxygen from the surface defects. This might be the reason that sub-surface oxygen is also removed; however, this process is retarded by the diffusion step involved in the conversion of sub-surface oxygen into oxygen in the vicinity surface defects.

Before discussing the TPRS results of Figures 9 and 10, it is necessary to give a short explanation of the types of response expected. Four types of reaction are possible:



In reaction (1), methanol decomposes to give hydrogen and CO, in (2) it reacts selectively to give formaldehyde and hydrogen, and in (3) and (4) it reacts with oxygen from the catalyst to give formaldehyde and water or CO₂ and water; however, reactions (3) and (4) will not be sustained as there is a limit to the amount of oxygen which can be supplied by the catalyst. Other reactions are also possible: for example, CO₂ can also be formed by reaction of CO with oxygen species and it is also possible that molecular oxygen is formed by desorption. Of these products, formaldehyde will not reach the detector as it forms paraform under these conditions and condenses on the walls of the connecting tubing. Water and the majority of the methanol will condense in the cold finger (-30°C) if it is in place. The thermal conductivities of all the gases other than hydrogen are lower than that of the carrier gas, helium, whereas that of hydrogen is about the same. As a result, when the cold trap is in position, CO and CO₂ (and O₂) will give a decrease in conductivity and H₂ and formaldehyde will have no effect; water production and methanol consumption will have a negligible effect. When the trap is not in position, water will now cause a decrease in conductivity while consumption of methanol will now show up as an increase in conductivity.

Figures 9 and 10 show the TPRS results. Curves (a) and (b) of Figure 9 show the results without a cold trap for experiments carried out after oxidation but without and with subsequent reduction (TPR) at 900°C respectively while Figure 10 gives more detail for similar experiments after other pretreatments. The increase in thermal conductivity with a peak at about 450°C is the most obvious feature of the results. This must indicate that reaction (2) is proceeding in the tempera-

ture range in which the conductivity is increasing. Beyond the peak, the conductivity returns towards the original value; however, when TPRS was performed for not too long a time at 600°C, the negative peak at 450°C was still present when the TPRS measurement was repeated. This indicates that another reaction may be occurring, possibly complete decomposition according to reaction (1), which is thermodynamically possible [37]. To see if this was the case, curves (c) and (d) of Figure 9 were obtained with the cold trap in position: a decrease in conductivity was obtained above about 400°C, confirming that reaction (1) is probably taking place in this temperature region. To confirm that no reaction was occurring on the walls of the reaction vessel, curve (e) was obtained; although a peak was seen at about 650°C (possibly due to reaction 1), few changes of significance occurred, up to that temperature, in the region of interest in relation to curves (a) to (d). We note in passing that the small increase in the thermal conductivity in the experiment of curve (a) of Figure 9 at about 330°C is probably due to reaction of the methanol with surface oxygen according to equation (4); this is a transient phenomenon as this weakly bonded oxygen is rapidly used up; also in Figure 8 it was observed that weakly bonded oxygen is removed easily during TPRS. This is in agreement with our conclusions, drawn from the influence of reaction conditions on the product mixture [2], that weakly bonded oxygen is responsible for the reaction to CO₂ whereas strongly bonded oxygen acts as active site for CH₂O formation.

Curve (a) of Figure 9 is repeated in Figure 10 together with the results of experiments (without the cold trap) with a number of other pretreatments of the silver. Curves (b), (c) and (d) show results obtained after TPD at 300, 400 and 550°C respectively. We conclude from these that these pretreatments have little effect on the ability of the surface to carry out the dehydrogenation of methanol as compared to the pretreatment for curve (a) as discussed above; the only difference is that the small peak at about 300°C is now missing, indicating that the weakly-bonded surface oxygen has been removed. Curve (e) involves prereluction in a TPR experiment up to 600°C; again, this has little effect, apart perhaps from reducing the size of the peak somewhat. However, curve (f), obtained after TPR up to 900°C, is completely different; the catalyst has now effectively no activity and we must conclude that this is because all the strongly-held oxygen species have been removed from the catalyst.

All measurements in Figure 10 were performed after oxidation preceded by exposure to hydrogen at 900°C, so the sample was able to take up hydrogen as discussed above. Only curve g in Figure 10 shows TPRS after oxidation preceded by TPD. We now observe a smaller negative peak at 450°C which is in agreement with the suggested influence of the presence of hydrogen; this creates defects in the surface as a result of the removal of sub-surface OH groups. The amount of strongly bound surface oxygen is thus decreased when no hydrogen was present in the silver during oxidation; this explains the decrease of the TPRS peak at 450°C as observed in Figure 10, curve g.

CONCLUSIONS

The interaction of silver with oxygen has been characterized with TPD and TPR measurements up to 900°C on a relatively high area, pure silver material. The influence of pretreatment before and after oxidation and the interaction with methanol has been studied.

- (1) Four different oxygen species have been detected on the silver surface: (a) molecular oxygen only present for a short time after removing air from the sample; (b) atomic surface oxygen; (c) atomic surface oxygen strongly bound in the vicinity of surface imperfections; and (d) sub-surface oxygen.
- (2) Hydrogen treatment before oxidation, causing the dissolution of hydrogen in the silver, results in a fifth species, probably sub-surface OH groups. Furthermore, the amount of sub-surface oxygen was increased, probably by the introduction of defects.
- (3) A model is proposed in which sub-surface oxygen and gaseous oxygen may be inter-converted via oxygen adsorbed and absorbed in the vicinity of defect surface sites related to rapid diffusion paths. This species is only observable after the introduction of defects due to desorption of sub-surface OH groups.
- (4) Sub-surface oxygen or atomic oxygen strongly bound in the vicinity of surface imperfections appear to be able to catalyse the dehydrogenation of methanol to formaldehyde. This supports the suggestion that formaldehyde production in oxidative dehydrogenation of methanol takes place on strongly bound oxygen, whereas CO₂ is formed on weakly bound oxygen. The active sites for methanol dehydrogenation are removed only slowly during the methanol dehydrogenation reaction.

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