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THE INFLUENCE OF HYDROGEN TREATMENT AND CATALYST MORPHOLOGY ON THE INTERACTION OF OXYGEN WITH A SILVER CATALYST

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ABSTRACT

The interaction of an unsupported silver catalyst which had been pretreated by hydrogen at various temperatures with oxygen at 210°C has been studied using Temperature Programmed Reduction (TPR) over a temperature range up to 900°C. Hydrogen treatment at 500°C or above before the oxidation step causes the formation of extra species, thought to be OH groups in the sub-surface of the sample. A peak in the spectra attributable to oxygen strongly bound in the vicinity of surface defects is found to be dependent on the surface roughness and grain size of the silver sample used; hydrogen pretreatment causes the strongly bound oxygen in the vicinity of surface defects to be converted to sub-surface OH. It is also shown that the TPR measurements themselves influence the morphology of the sample and that these changes are comparable with structural changes which occur during the use of the catalysts for oxidative dehydrogenation of methanol. It is suggested that these structural changes are caused by the interaction of the sub-surface of the silver with both oxygen and hydrogen.

INTRODUCTION

Silver is widely used as catalyst for the production of formaldehyde by oxidative dehydrogenation of methanol. Under industrial conditions, 600°C and atmospheric pressure, almost total conversion of methanol is achieved with a selectivity of 90% towards formaldehyde, as reported by Sperber [1].

We have recently shown that interaction of oxygen with the silver is also of importance in methanol oxidation; the influences of temperature and reactant concentrations on the conversion to the different products (H_2, CO, CO_2, CH_2O, H_2O) can be explained with the suggestion that total oxidation takes place at sites associated with weakly bound atomic surface oxygen whereas the selective reaction involves surface oxygen which is more strongly bound in the vicinity of surface defects [2]. Evidence for the existence of these species was obtained with help of temperature programmed reduction (TPR) and temperature programmed desorption (TPD); the activity of the strongly bound oxygen species for the dehydrogenation of methanol was shown by using temperature programmed reaction spectroscopy (TPRS) with methanol vapour [3]. It was also shown [3] that hydrogen treatment at 900°C strongly influences the interaction with oxygen: a new

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species, thought to be sub-surface OH, is formed and there is also an increase in the amount of sub-surface oxygen. XPS results have been obtained [4] which are in agreement with these conclusions.

In work reported in the literature, hydrogen pretreatment is often used for silver samples for catalytic or adsorption studies. For example, treatment in hydrogen at temperatures between 150 and 350°C was used by Harriott [5] and Verykios et al. [6] in the preparation of catalysts for ethylene expoxidation, and also by Vannice et al. [7-9], Scholten et al. [10] and Kagawa et al. [11,12], all of whom performed studies on oxygen adsorption. Even higher temperatures were used by Bazillo and coworkers [13], who studied methanol oxidation with IR spectroscopy, and by Haul and Neubauer [14,15] who studied oxygen adsorption and desorption and ethylene epoxidation.

To establish to what extent the silver-oxygen interaction is influenced by this sort of hydrogen pretreatment, we have performed TPR measurements after oxidation treatments which had been preceded by pretreatment in hydrogen at different temperatures. Furthermore, in order to understand differences found in the TPR results which were apparently dependent on the history of the sample under investigation, we have investigated the influence on the morphology of the silver of sequences of oxidation-reduction cycles. In our previous publication on this subject [3], the results were restricted to pre-reduction in a TPR experiment at temperatures up to 900°C and transient structural effects were eliminated by obtaining results only after a number of oxidation reduction cycles had been performed.

EXPERIMENTAL

The equipment used for the TPR measurements has been described in detail elsewhere [3]. All the measurements were performed using 6% hydrogen in argon with a heating rate of 17°C min^{-1}. After a TPR measurement, normally up to a maximum temperature of 900°C, the sample was flushed with helium (99.995% purity) and cooled to the temperature of the next hydrogen treatment, again using the mixture of 6% hydrogen in argon. It was then cooled further in hydrogen to 210°C, at which temperature it was oxidized in purified air.

The silver material used for this work has been described earlier [2] and is given the name, AgIII; a sample of weight 1.5 g was used in all experiments. The morphology of the samples was studied with a JEOL JSM-35CF scanning electron microscope.

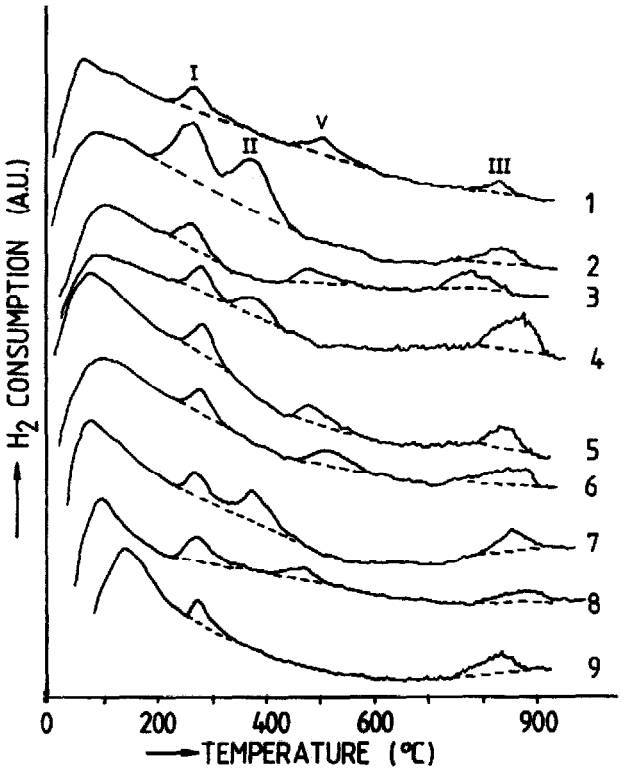

FIGURE 1 Effect of structural changes on TPR results after oxidation at 210°C; measurements in chronological order; measurement (9) after ten further oxidation-reduction cycles.

	1	2	3	4	5	6	7	8	9
Hydrogen treatment T/°C	250	900	-	500	250	-	900	315	-
t/h	17	0.5	-	17	44	-	0.2	17	-
Oxidation time/h	3	17	3	3	17	17	3	3	3

RESULTS AND DISCUSSION

Catalyst ageing effects

Figure 1 shows a sequence of TPR measurements made on one sample, the first eight of these curves representing results obtained in chronological order and curve 9 after ten further oxidation-reduction cycles; the pretreatment for each experiment (temperature and time of hydrogen pretreatment and time of subsequent treatment in air at 210°C) is given in the legend to the figure. Peaks corresponding to four different types of reducible oxygen species can be seen in the various curves, these being at 270, 400, 520 and 850°C. In a previous

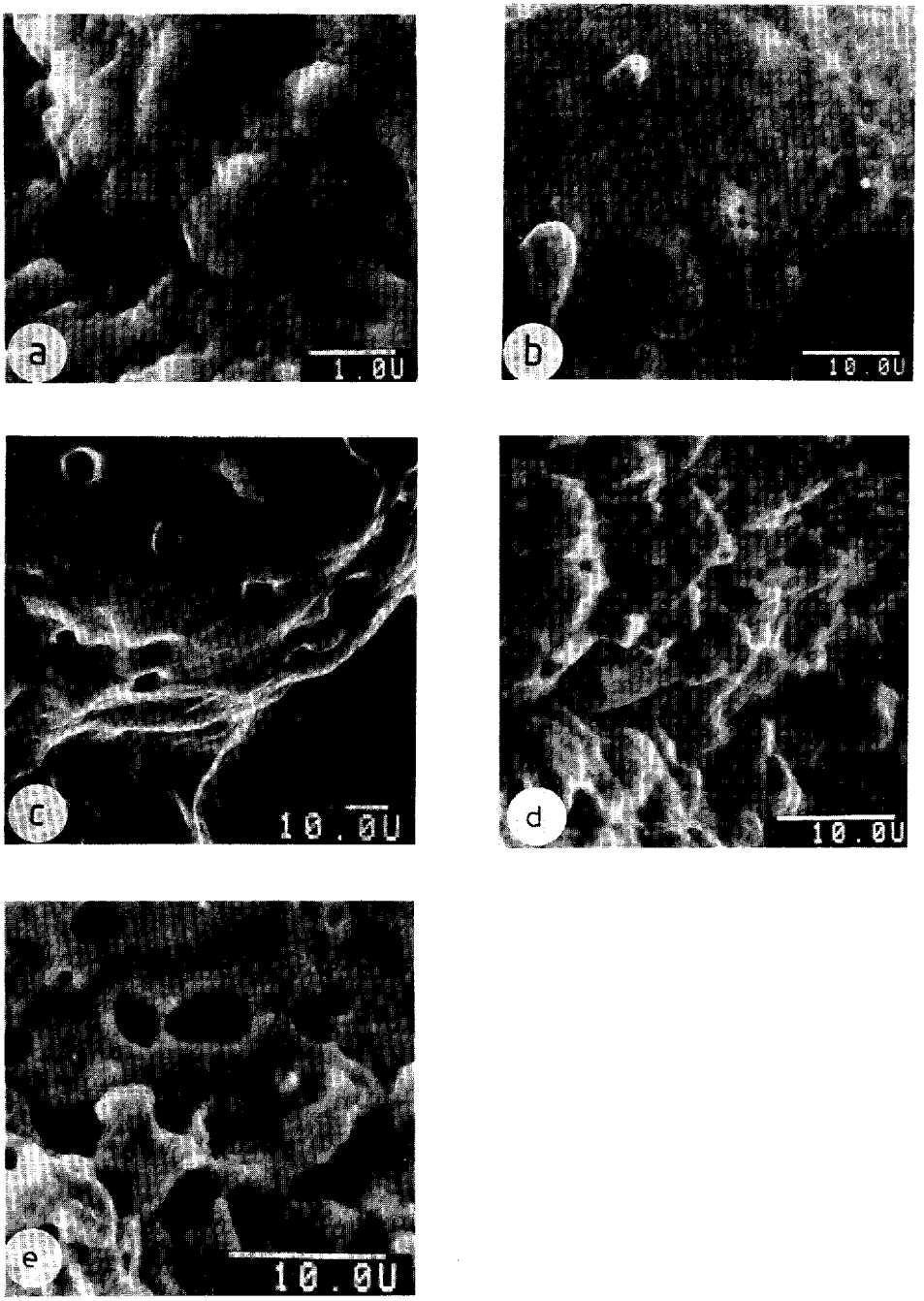

FIGURE 2 SEM photographs of the silver surface; a: fresh sample, b: after three TPR measurements, c: after twenty TPR measurements, d: after methanol oxidation for two days at 500°C, e: after methanol oxidation for 14 days between 150 and 650°C.

publication [3], these peaks were assigned to atomic surface oxygen (Species I), sub-surface OH (Species II), atomic oxygen adsorbed in the vicinity of surface defects (Species V) and sub-surface oxygen (Species III), respectively. The same nomenclature will be used here.

Concentrating first on the measurements in which there was no hydrogen uptake during the pretreatment (i.e., curves 1,3,5,6,8,9, all of which will be discussed in greater detail later), we observe a decrease in the amount of oxygen present in the vicinity of surface defects (Species V) in successive experiments. This is most probably due to a decrease in the concentration of surface defects brought about by the high temperatures encountered by the silver during the measurements. The scanning-electron micrographs of Figure 2(a), (b) and (c) show the surface morphologies of the silver at various stages in this sequence: (a) shows the surface of a fresh sample while (b) and (c) show samples after three and twenty oxidation-reduction cycles respectively. The fresh sample has a rough surface with grains smaller than 1 μm but, after three TPR cycles, the surface appears to have become flattened without there being an observable increase in grain size; after 20 cycles, the surface is relatively very flat and the grain size has increased to about 10 μm. It is also significant that holes have formed in the surface after cycling; this phenomenon will be discussed later.

When pretreatment had been given in hydrogen at relatively high temperatures before the oxygen treatment between the TPR measurements, no desorption peaks characteristic of oxygen adsorbed in the vicinity of surface defects (Species V) were observed; see Figure 1, curves 2, 4 and 7. However, this species was again observed after further pretreatments in which no cycle with hydrogen was carried out (curve 3) and also in experiments in which the hydrogen treatment was at relatively low temperature (curves 1,5 and 8). We therefore suggest that oxygen which would normally be adsorbed in the vicinity of surface defects (Species V) is converted relatively rapidly into sub-surface OH (Species II) if sub-surface hydrogen is present; there must therefore exist some relatively favourable route for the oxygen to diffuse into the sub-surface to combine with the dissolved hydrogen introduced during the pretreatment in hydrogen. Without direct proof for the suggestion, we are inclined to the view that the surface defects are probably mainly associated with grain boundaries and that these boundaries provide an energetically favourable route for the diffusion of the oxygen into the sub-surface. Both suggestions are supported by the general accepted theories on defects and dislocations in metals [16]. We cannot rule out that the presence of hydrogen simply inhibits the formation of Species V; however, the surpression of the formation of Species V and the formation of Species II are observed simultaneously and this observation suggests that Species V is converted into Species II. The amount of sub-surface oxygen (Species III) also changes during the course of the experiments; as suggested earlier [3], changes in the

morphology of the sample are probably responsible for the variations in the amount of such species. We shall return below to a discussion of the effect on the sub-surface OH species of the temperature used for the pretreatment in hydrogen.

As stated in a previous publication [3], the reduction-oxidation cycles result in the formation of holes in the surface of the silver. This is now illustrated in Figure 2c: formation of holes takes place especially at grain boundaries. This has also been observed by Klueh and Mullins [17] who studied the hydrogen embrittlement of silver; they suggested that hole formation probably takes place via the reaction of hydrogen and oxygen in the sub-surface region of the metal, the access also being thought to occur along grain boundaries. This phenomenon gives an increase in the total surface area of the samples, but more important is the introduction of disturbed surfaces during the hole formation. Meima et al. [18] suggest that the same effect is responsible for the increase in the activity of silver for CO oxidation which they observed when their supported catalyst was pre-treated with hydrogen.

Morphology changes during methanol oxidation

Similar changes in morphology to those described above were found when the catalysts were used for methanol oxidation for relatively short times under the conditions described previously [2]. Micrograph (d) of Figure 2 was obtained after carrying out the oxidation of methanol for two days at a temperature of 500°C while micrograph (e) was obtained after reaction for 14 days at temperatures ranging from 150 to 650°C. The formation of holes only occurs in the upper active part of the bed in which the oxygen is used up and hydrogen is also produced by dehydrogenation of the methanol. It is therefore probable that a process which involves solution and reaction of hydrogen and oxygen in the silver is responsible for the hole formation in the silver.

Similar changes in the structure of silver during methanol oxidation have been reported extensively by Benninghoven et al. [19]. These workers suggest that volatile organo-silver compounds are involved in the process of surface roughening. Our explanation would seem to be a reasonable alternative.

Hydrogen treatment

Figure 3 shows the influence on the resultant TPR measurements of pretreatment in hydrogen for 17 h at different temperatures prior to oxidation at 210°C for 3 h; these results can be compared with the result when the sample is cooled in hydrogen from 900°C (curve 5; see also curves 2 and 7 of Figure 1). The peak due to surface oxygen (Species I, at about 300°C) is relatively unchanged through the whole series of experiments. However, sub-surface OH groups (Species II at 400°C) only appear after pretreatment in hydrogen at 500°C and the amount of sub-surface oxygen (Species III at 850°C) also increases under these circumstances.

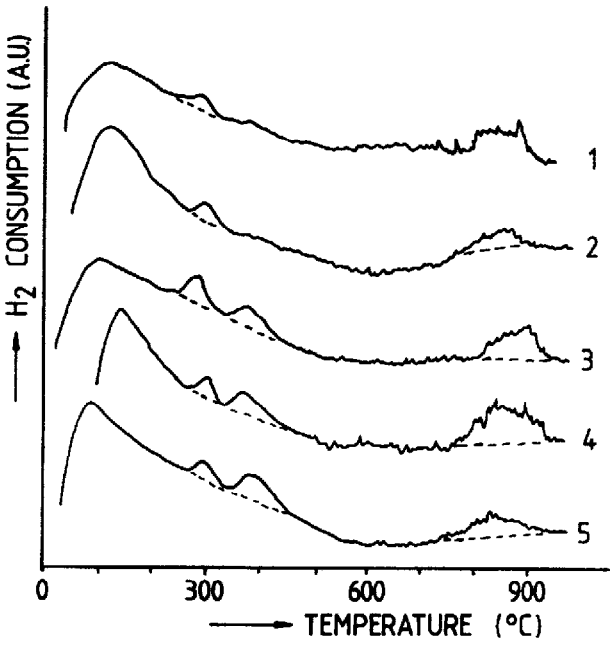

FIGURE 3 Influence on TPR results of hydrogen pretreatment at different temperatrues for 17 h prior to oxidation for 3 h at 210°C in air; temperature of hydrogen pretreatment (°C): 1) 415, 2) 460, 3) 500, 4) 555, 5) 0.3 h at 900°C.

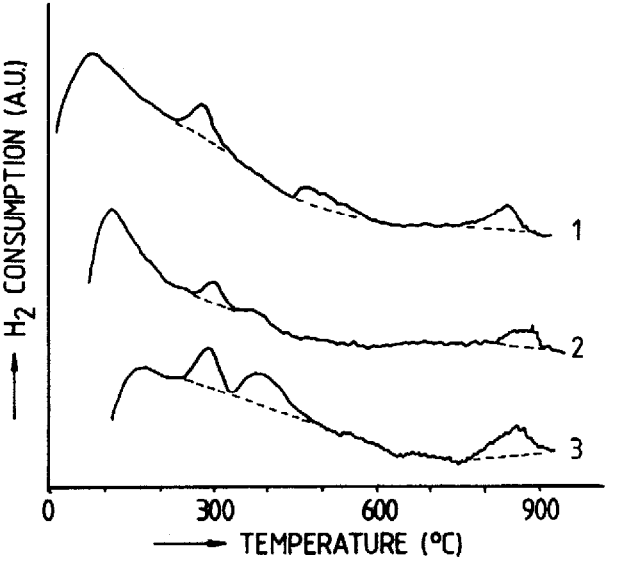

FIGURE 4 Influence on TPR results of hydrogen treatment for 44 h prior to oxidation for 17 h at 210°C; temperature of hydrogen pretreatment (°C): 1) 250, 2) 395, 3) 0.5 h at 900°C.

Figure 4 gives results equivalent to those of Figure 3 but with pretreatment in hydrogen for 44 hours at the different temperatures shown, followed by oxidation for 17 h; the measurements were carried out after a small number of oxidation-reduction cycles had been carried out with the sample. It is clear that sub-surface OH (Species II) does not form to a significant extent even after these longer hydrogen exposures at 250 or 395°C and the subsequent oxidation treatment. Curve 1 does show the presence of oxygen species adsorbed in the vicinity of surface defects (Species V, peak at 500°C).

We shall now discuss the significance of the conclusions reached here in relation to results given in the literature. From the results given in Figures 3 and 4, it appears that hydrogen treatment at temperatures of 500°C and above influences the silver oxygen interaction. Thus, we can conclude that of those investigations mentioned in the introduction in which a hydrogen pretreatment has been applied, only the results of Bazilio et al. [13] and of Haul and co-workers [14,15] are likely to have been influenced by the hydrogen pretreatments applied.

Basilio and his coworkers [13], who studied the surface species on silver catalysts during the oxidation of methanol at 150-200°C using IR spectroscopy suggest that adsorbed OH groups exist on the silver surface during methanol oxidation. Our work shows that the hydrogen pretreatment, which was applied for 24 h at 500°C, may cause the formation of sub-surface OH groups, represented by a TPR peak at 400°C as discussed earlier [3]. This suggestion is in agreement with the observations of Au et al. [20], who observed with XPS that OH groups on the silver surface are only stable beneath 50°C. We have observed, again using TPR measurements, that OH species are not present after exposure to oxygen and water at 200°C; these results will be reported in a subsequent publication [21]. Furthermore, in an IR study of the oxidation of methanol reported by Morozov et al. [22], only carbonate species were observed; no hydrogen pretreatment was performed in that work. As the mechanism of the oxidative dehydrogenation of methanol proposed by Bazilio et al. [13] is based on the supposition that surface OH species are present, its validity must be doubtful; furthermore, the mechanism cannot explain the formation of hydrogen as a reaction product, as observed in our work [2]. We conclude that if surface OH groups are involved in the mechanism, their concentration must be low due to their low stability.

Haul and coworkers [14,15], who studied the TPD of oxygen and the epoxidation of ethylene over silver foils, also used hydrogen pretreatment at temperatures in the range 500-600°C; however, this was followed by oxidation for 6 hours at 350°C. In our earlier work [3], we found with TPD measurements that sub-surface OH desorbs slowly at such a temperature. We therefore believe that little sub-surface OH will remain in the samples of silver in the experiments of Haul et al. [14,15] and so little or no influence of the presence of such sub-surface

OH species is to be expected; however, it is possible that changes in the surface structure similar to those occuring with reduction-oxidation cycles, as discussed above, may have influenced their results.

The influence of hydrogen treatment at 500°C on the silver-oxygen interaction has also been reported by Sandler and coworkers [23,24]; the activation energy for the desorption of oxygen species between 160 and 200°C was reported to decrease after hydrogen treatment. The desorption of weakly-bound oxygen is apparently influenced by the presence of sub-surface OH species. ESR experiments [24] showed the presence of paramagnetic species after hydrogen treatment; the presence of an OH species was put forward as a suggestion to explain this observation and this is in agreement with our conclusions.

Both Meima et al. [18] and Sandler et al. [23] have argued that hydrogen adsorption is possible only at strongly-bound oxygen species, i.e., at what we term sub-surface oxygen. Neither of these groups of workers used hydrogen treatment up to 900°C prior to the adsorption of hydrogen at lower temperature; the sub-surface oxygen present in the samples was therefore not removed in their work and was still present during their hydrogen treatment. We believe that sub-surface oxygen is not a prerequisite for the absorption of hydrogen; it can be seen from the results of Figure 3 that sub-surface OH groups are also formed in an experiment in which hydrogen treatment and subsequent exposure to oxygen were carried out after reduction in hydrogen at 900°C had been carried out to remove sub-surface oxygen. Thus hydrogen can be absorbed in the bulk or sub-surface of the silver without the necessity of the presence of strongly-held (sub-surface) oxygen. We shall now discuss our results further in the light of this possible explanation.

From the results of Siegekelin and coworkers [25], a quantity of 1.7×10^{-8} mol of H_2 can be expected to be soluble in 1.5 g silver at a hydrogen pressure of 0.06 atm, at 500°C, the corresponding figure is 3.2×10^{-7} mol at 900°C for the same pressure. Up to double these amounts of OH species could subsequently be formed by reaction with oxygen. The areas of the reduction peaks at 400°C are equivalent to amounts of 5×10^{-7} and 2×10^{-6} mol after hydrogen treatment at 500 and 900°C (followed by oxidation) respectively, these being significantly higher values. However, a similar discrepancy exists in the amount of sub-surface oxygen resulting after oxidation at 210°C, as calculated from the area of the reduction peak at 850°C: based on the data of Steacie and Johnson [26], only 1.4×10^{-9} mol of oxygen will be soluble in 1.5 g silver at that temperature; however, the amount measured thereis of the order of 10^{-7} mol. It would thus appear that our results may be best explained in terms of an enlarged solubility of hydrogen and oxygen in the sub-surface layer of the silver material used here rather than in terms of a bulk solubility of these species. We suggest that not only the geometric surface is involved in giving rise to the enhanced uptakes

but that dislocations and grain bounderies in the material are also involved and this depends on the history of the sample. It is thus to be expected that the morphology of the silver material is an important factor in determining the extent of the phenomena described. Differences in morphologies of various different types of polycrystalline materials might be responsible for discrepancies in the results given in the literature for the interaction of oxygen with polycrystalline silver materials, as reviewed by Barteau and Madix [27].

CONCLUSIONS

Hydrogen treatment at temperatures above 500°C causes the formation of sub-surface OH groups during oxidation; this is probably caused by hydrogen dissolved in the sub-surface of the silver.

The silver-oxygen interaction is closely related to the micro-structure of the silver sample. Oxygen bonded in the vicinity of surface imperfections is only observable on a rough surface with small grains. Oxygen in the vicinity of surface defects is converted relatively rapidly to sub-surface OH only when hydrogen is present in the silver.

The interaction of silver with successively oxygen and hydrogen results in hole formation in the surface, especially at grain boundaries. Structural changes occurring during oxidative dehydrogenation of methanol are possibly due to interaction of oxygen and hydrogen in the sub-surface of the silver.

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