JOURNAL OF CATALYSIS **114**, 303–312 (1988)

The Interaction between Silver and N_2O in Relation to the Oxidative Dehydrogenation of Methanol

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Received April 22, 1987; revised June 14, 1988

The interaction of N_2O with pure silver at temperatures up to 900°C has been studied using temperature-programmed reduction and desorption; the interaction is compared with that of oxygen with silver. The effect of addition of N_2O, as well as of the complete replacement of oxygen by N_2O, on the oxidative dehydrogenation of methanol on a silver catalyst has also been studied. It was found that the interaction of silver with N_2O was much slower than that of O_2; no atomic surface oxygen species were observed, probably because the formation of subsurface species was not complete; selective adsorption appears to take place on the surface defects and grain boundaries involved in the formation of the subsurface species. Addition of small amounts of N_2O to the reaction mixture (CH_3OH + O_2) for the oxidative dehydrogenation of methanol had almost no influence on the conversion or on the product distribution measured. However, the conversions were considerably lower when oxygen was totally replaced by N_2O; only above 600°C was the N_2O exhausted. At the same level of conversion of the methanol, the amount of CO_2 produced was lowered compared to the case of O_2. This is in agreement with the suggestion that CO_2 is formed via weakly bound surface oxygen.

INTRODUCTION

Silver is widely used as a catalyst for the oxidative dehydrogenation of methanol to produce formaldehyde. Using excess methanol in relation to oxygen at temperatures above 600°C, it is possible to reach a selectivity of 90% at almost complete conversion of methanol, as discussed by Sperber (*1*) and Walker (*2*). A more recently developed process, also used commercially for the production of formaldehyde, uses iron–molybdate oxide catalysts (*3*). Silver is also used as catalyst for the production of ethylene oxide by the partial oxidation of ethylene, as reviewed by Sachtler *et al.* (*4*) and by Verykios and co-workers (*5*). The effect on the latter reaction of using N_2O in place of O_2 has been examined by Neubauer (*6*), Herzog (*7*), and Charman and co-workers (*8*). This was done to examine the suggestion that not atomic oxygen but molecularly adsorbed oxygen is the active species in the production of ethylene oxide; however, the interpretations of the influence of the N_2O put forward in these papers are in contradiction. The main argument against the suggestion that adsorbed molecular oxygen is the active species in ethylene oxidation is that its concentration must be very low due to its low stability. The adsorption of N_2O on silver has been studied by Shimizu and co-workers (*9*), who found that no molecular oxygen was formed after exposure of the catalyst to N_2O at room temperature. The adsorption of N_2O has also been studied by Seyedmonir *et al.* (*10*) and by Scholten and co-workers (*11*) in an attempt to develop a method for the determination of the free metal surface area of silver.

As far as we know, no research has yet been performed on the influence of N_2O on

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0021-9517/88 $3.00

the oxidative dehydrogenation of methanol. Because of the high temperature used commercially for methanol oxidation over silver (500–700°C), molecular oxygen is unlikely to be involved in the process; we have reported previously (*12*) that this species is bound very weakly. We have in addition reported evidence for the presence of other species on the silver surface: atomic surface oxygen, subsurface oxygen, subsurface OH groups, and oxygen adsorbed in the vicinity of surface defects; these species were suggested on the basis of temperature-programmed reduction (TPR) and temperature-programmed desorption (TPD) results obtained in a study of the adsorption of oxygen on silver. This investigation of the influence of N_2O on the catalytic conversion of methanol has been carried out to provide further information on the nature of the surface oxygen species that are involved: the rate of oxidation of the surface will be influenced markedly by total or partial replacement of the oxygen by N_2O. The results provide additional information in relation to the reaction scheme proposed in a previous publication (*13*); this was based on observations of the influence of reaction conditions on the conversions, on the adsorptive behavior of oxygen on the silver, and on the interaction of methanol with adsorbed oxygen (*12*). The reaction scheme (*13*) included the formation of formaldehyde at sites associated with oxygen strongly bonded at imperfections on the surface and CO_2 formation at sites where oxygen was more weakly bonded. To provide further support for the model, we have also performed measurements on the interaction of N_2O with silver using TPR and TPD. In earlier work, we found using TPR and TPD (*12*) as well as XPS (*14*) that hydrogen dissolved in the silver had a marked influence on the adsorbed species present after oxidation in air. We have thus also studied with TPR and TPD the influence on the interaction with N_2O of hydrogen pretreatment of the silver sample at elevated temperatures.

EXPERIMENTAL

Methods

The influence of N_2O on the catalytic reaction was measured in a fixed bed flow apparatus, using gas chromatographic analysis, which was described earlier (*13*). To introduce N_2O into the reaction mixture, an extra controlled flow of pure N_2O was added to the He–oxygen mixture before the methanol saturation section; the methanol concentration was thus kept constant. The temperature program of the GC was modified slightly to give an improved separation of water and CO_2. As a consequence of the better resolution, the areas of the CO_2 peaks could be determined more accurately than was previously possible; this has the consequence that the conversions to CO_2 reported in this work are slightly higher than those reported earlier (*13*). The analysis of the water was still not quantitative but a semiquantitative comparison of the behavior in different experiments was possible. The conditions of the measurements were as follows: reactor temperature (T), between 150 and 600°C; inlet concentration of methanol ($[CH_3OH]_{in}$), 8.8%; oxygen inlet concentration ($[O_2]_{in}$), between 0 and 3.0%; N_2O inlet concentration ($[N_2O]_{in}$), between 0 and 4.2%; total pressure, 1.1 bar; bed height, 6 mm; linear gas velocity (vg), 9.3 cm/s; and space velocity (SV), 5.6×10^4 h^{-1}.

The conversion to various carbon-containing products, water and hydrogen (y_i), and the selectivity to formaldehyde (s) are defined as

$$y_i = [i]_{out}/[CH_3OH]_{in} \times 100\%$$

$$s = [CH_2O]_{out}/([CH_3OH]_{in} - [CH_3OH]_{out}) \times 100\%.$$

The conversion of N_2O to N_2 is defined by

$$y_{N_2} = [N_2]_{out}/[N_2O]_{in} \times 100\%.$$

Consequently, the percentage of unreacted N_2O is $(100\% - y_{N_2})$.

The interaction between silver and N_2O

was studied using the TPR–TPD equipment described earlier (*12*), the only modification being the replacement of air by N_2O in several experiments. A flow of N_2O or O_2 (in the form of pure air, see below) was passed over the catalyst at temperatures between 200 and 500°C for up to 18 h; the sample was then purged by He and cooled in flowing He. TPD measurements were always performed with the cold finger out of function (i.e., at room temperature) and without hydrogen treatment before oxidation. TPR measurements were carried out with and without hydrogen treatment before oxidation. All measurements were performed using a heating rate of 17°C min^{-1}. The temperature program causes a shift of the baseline, especially during the start of the TPR measurements; the estimated actual baselines are represented in the figures by dotted lines.

Materials

The catalytic measurements were performed with a sample of 0.5 g of a commercial catalyst consisting of pure silver particles with an average size of 0.2 mm (Ag 0.2) which had been prepared by an electrolytic method. The TPR and TPD measurements were performed with 1.5 g of a pure silver material with somewhat higher surface area, previously described as Ag III (*13*), which was in the form of hollow spheres. Both samples were checked for purity using XRF and XPS; while the former showed no impurities, the latter revealed the presence of O and C together with traces of Cl and Si on the surface. Each sample was oxidized and reduced many times at temperatures up to 900°C before the measurements were performed; no structural changes are thus to be expected in the sample during the measurements. In a previous publication (*13*), it was shown that Ag III and Ag 0.2 give comparable results as catalysts for methanol oxidation.

The N_2O used, supplied by Matheson, was 99.99% pure. The air used was cleaned with a molecular sieve. It was shown previously (*12*) that no difference was observed in the TPR or TPD results when the air was replaced by pure O_2; we thus conclude that none of the effects observed can be attributed to impurities in the air.

RESULTS

Catalytic Measurements

The influence of temperature on the conversion of a methanol–N_2O mixture in the absence of oxygen is shown in Fig. 1. The yield of all the products increases with increasing temperature. Comparable results for a methanol–oxygen mixture, reported earlier (*13*), are shown for comparison in Fig. 2. It should be noted that the amounts of CO_2 shown in Fig. 2 are about 20% too low as a result of incomplete resolution of the GC peaks of water and CO_2, as was noted under Experimental. However, this is not important in the discussion as long as only measurements with the same water–CO_2 separation are compared in an absolute sense. It appears that N_2O exhaustion is only observed above 600°C; this is in contrast to the results for oxygen, for which the conversion of oxygen is complete above an unstable temperature region occurring around 250°C (Fig. 2). The maximum in the

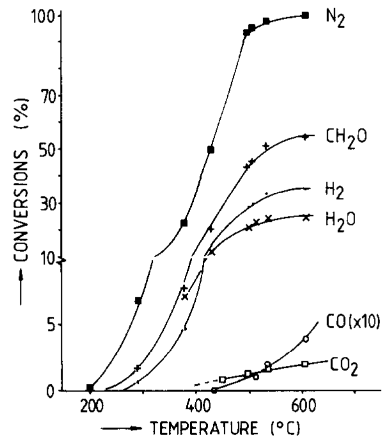


FIG. 1. The influence of temperature on the conversions during methanol oxidation with N_2O on 0.5 g of Ag 0.2; reaction conditions, $[CH_3OH]_{in}$ = 8.8%, $[N_2O]_{in}$ = 4.7%.

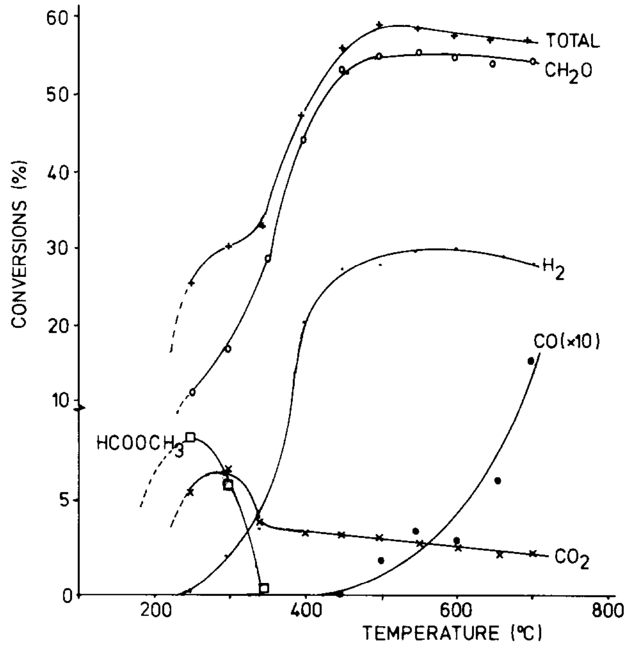


FIG. 2. The influence of temperature on the conversions during methanol oxidation with O_2 on 0.5 g of Ag 0.2; reaction conditions, $[CH_3OH]_{in} = 8.8\%$, $[O_2]_{in} = 2.0\%$, SV = $5 \times 10^4\ h^{-1}$, vg = 8.2 cm/s (from (13)).

conversion to CO_2 at low temperature is not observed in the case of N_2O. Furthermore, the amount of hydrogen produced is higher in the case of N_2O.

Figure 3 shows the effect on the conversions when varying small amounts of N_2O were added to a methanol–oxygen mixture. As with the results shown in Fig. 1, the N_2O was not totally converted to N_2 at 500°C. The added N_2O appears to act as an extra source of oxygen with the consequence that the conversion to formaldehyde was increased slightly. Figure 4 shows the selectivity to formaldehyde as a function of the total conversion of methanol for the reaction of methanol with O_2 and N_2O and for mixtures of the two. The conversion of methanol obtained was controlled by the ratio of the partial pressures of methanol to O_2 and/or N_2O. It can be seen that the selectivity at a given conversion was hardly influenced by the addition of N_2O to the reaction mixture. However, when N_2O was used in the absence of oxygen, the selectivity was higher than that with oxygen over the whole range of conversion at 500°C; the improvement in the selectivity appears to be due to a decrease in the conversion to CO_2.

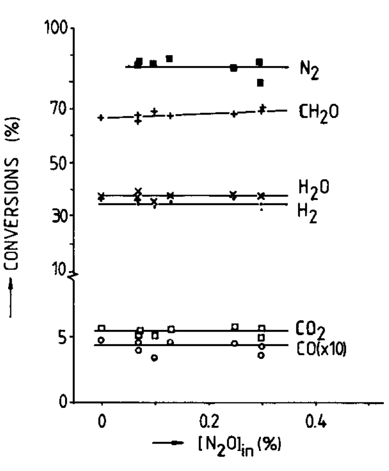


FIG. 3. The influence of N_2O admixture on the conversions during methanol oxidation with oxygen on Ag 0.2; reaction conditions, $[CH_3OH]_{in} = 8.8\%$, $[N_2O]_{in} = 2.9\%$, $T = 500°C$.

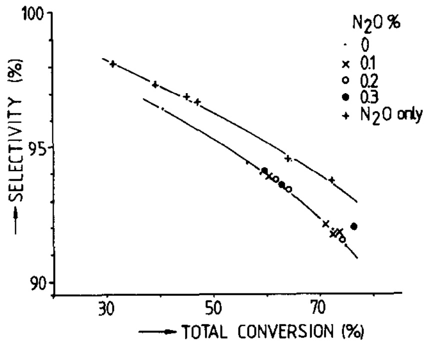


FIG. 4. Selectivity to formaldehyde versus total conversion of methanol for oxidation of methanol with pure oxygen, oxygen with N_2O admixture, and pure N_2O on Ag 0.2; $[CH_3OH]_{in}$ = 8.8%, T = 500°C; +, $[N_2O]$ between 3 and 7%; other symbols, $[O_2]$ between 1 and 3%.

Temperature-Programmed Measurements

The results of TPD measurements after exposure to N_2O at temperatures between 210 and 500°C are shown in Fig. 5. No TPR measurement had been performed prior to exposure of the silver to N_2O; it can thus be concluded that no dissolved hydrogen was present in the silver sample. No significant desorption peaks were observed (curves a, b, and c); this is in clear contrast to measurements obtained after oxidation in air (curve d) which have been presented and discussed previously (*12*). Figure 6 shows equivalent TPR results for experiments in which different pretreatments were given (see legend to the figure). Only a single peak at 850°C was observed when no hydrogen was dissolved in the sample before exposure to the N_2O curve (curve a). When dissolved hydrogen (introduced during the preceding TPR measurement) was present, a reduction peak was also observed at 400°C (curves b, c, and d). However, no reduction peak was present at 280°C, an observation which is in contrast to results (curve e) obtained (*12*) after oxidation in air.

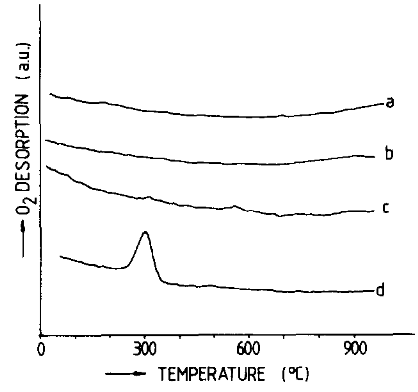


FIG. 5. TPD result on 1.5 g of Ag III; pretreatment in the absence of hydrogen followed by oxidation in pure N_2O (a, b, c) or in air (d); oxidation times and temperatures: (a) 18 h, 210°C; (b) 65 h, 280°C; (c) 2 h, 500°C; (d) 17 h, 210°C.

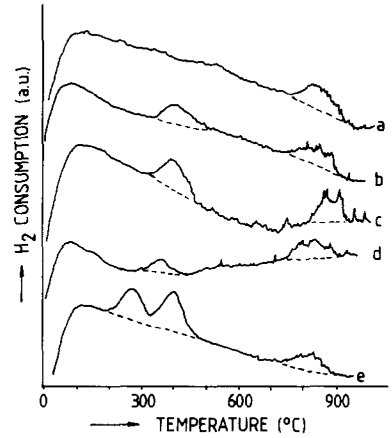


FIG. 6. TPR results on 1.5 g of Ag III: pretreatment in the absence of hydrogen (curve a) or TPR up to 900°C as pretreatment (curves b, c, and d), followed by oxidation in pure N_2O (a, b, c, d) or in air (e); oxidation times and temperatures: (a) 18 h, 500°C; (b) 1.5 h, 500°C; (c) 18 h, 210°C; (d) 2 h, 210°C; (e) 17 h, 210°C.

DISCUSSION

The Silver–Nitrous Oxide Interaction

From Fig. 5, curves (a) to (c), it appears that long exposures of silver to N_2O at varying temperatures do not give rise to the formation of the oxygen species which desorbs at 300°C after oxidation in air (curve d). In a previous publication (*12*), we concluded that this peak at 300°C is due to weakly bound atomic oxygen adsorbed on the silver surface (Species I). (The same nomenclature as that adopted there for the oxygen species will be used hereafter in the present work.) Although it is difficult to distinguish them from the background noise, it is possible that there is in curve (c) of Fig. 5 a small peak at 300°C and a slightly larger one at about 550°C; this indicates that a low concentration of some sort of surface oxygen species may be formed from N_2O at 500°C. That N_2O interacts with the surface of silver at this temperature is in agreement with the results of Hayes (*15*) who reported that N_2O decomposition may be catalyzed by silver at 520°C. The results of Fig. 1, which show that N_2 is formed at temperatures above about 250°C during the reaction of methanol with N_2O, also indicate that N_2O reacts with a silver surface.

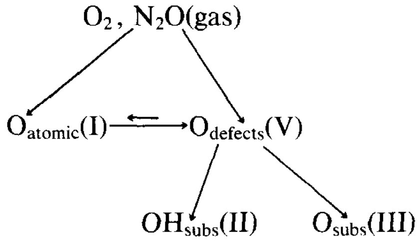
The TPR results of Fig. 6 also demonstrate that exposure to N_2O causes no atomic surface oxygen (Species I) reducible at 280°C of the type observed after oxidation in air. However, independent of the treatment before oxidation, N_2O appears to be able to form subsurface oxygen species, reduced at 850°C (Species III). In earlier work (*12*), we showed that treatment with hydrogen at high temperatures before oxidation caused the appearance of a reduction peak at 400°C (Species II) and we suggested that this was due to an OH species in the subsurface of the sample; this peak was not observed if the sample was not reduced at high temperature before oxidation (*12*). Figure 6 shows that the same effect also occurs when the sample is oxidized with N_2O.

There is thus clearly an interaction between N_2O and silver, but the interaction is apparently much less extensive than that with O_2. The fact that only subsurface oxygen (Species III) and subsurface OH (Species II) are formed during the reaction with N_2O is in agreement with the observation made in earlier work (*12*) that Species II and III are formed first during a short exposure to O_2 and that atomic surface oxygen (Species I) is formed only after the silver has become saturated with Species II and III.

The observation that no atomic surface oxygen (Species I, formed after reaction with O_2 and stable up to 300°C; Fig. 5) is formed is in contradiction with the adsorption studies of Seyedmonir and co-workers (*10*) and of Scholten *et al.* (*11*); the latter, using supported silver particles, suggested that N_2O adsorption can be used to measure silver surface areas. Shimizu and co-workers (*9*) also state that atomically adsorbed oxygen can be formed from N_2O on small silver particles. However, in agreement with our results, all three sets of workers observed a far slower interaction of silver with N_2O than that with oxygen. This difference was also found by Kobayashi and Takegami (*16*) who reported from transient studies of the oxidation of CO with O_2 and N_2O on a silver catalyst that the formation of atomic oxygen from O_2 is 75 times faster than that from N_2O. They suggested that only a proportion of the surface sites was able to decompose N_2O. We reported previously (*12*) that atomic surface oxygen (Species I) starts to form after 1 h during oxidation in air around 200°C; thus, the formation of atomic oxygen might be expected to start after exposure to N_2O for about 75 h. As the maximum time of exposure in this study was shorter than 75 h, this might explain the fact that no weakly bonded atomic oxygen was observed in the present work.

As discussed in a previous publication (*12*), the interaction of Ag III with oxygen is also slow in comparison with the interaction with a supported silver material (*9–11*) or with that with a silver powder (*17, 18*). Furthermore, the (110) face of Ag adsorbs oxygen faster than does Ag III (*18*) and the same is true for the (111) face, despite the fact that adsorption of oxygen on the Ag (111) face is considerably slower than that on the Ag (110) face (*20–23*). The exposures used in all these studies were small compared to those of the present study, in which oxidation overnight in air is equivalent to an exposure of 10^{13} L.

We explain the slow adsorption of oxygen atoms on Ag III from both O_2 and N_2O as follows. Due to the high temperatures



SCHEME 1. Formation of oxygen species.

during the TPR measurements, many low-index planes will be present on the surface of the sample. According to Rhead and Mykura (*24*), the proportion of (111) faces, in particular, increases in oxygen-containing atmospheres. Czanderna (*25*) has suggested that microfacetting occurs and that this increases the proportion of (111) faces during the oxidation–desorption cycles; these microfacets were of the order of 3 nm in magnitude. Effects similar to these may have caused the relatively slow adsorption on Ag III. However, the adsorption of oxygen on Ag III is even slower than that on Ag(111), as was discussed above. We therefore suggest that the formation of subsurface oxygen (which is thought also to take place along paths for rapid diffusion such as grain boundaries) is much more pronounced than that of single crystals and supported silver particles because of the presence of many grain boundaries. (After high-temperature treatment, Ag III consists of particles of about 1 mm, these containing grains of about 10 μm (*26*).) The formation of subsurface oxygen (and of subsurface OH, if the sample is pretreated with hydrogen) must be completed before atomic surface oxygen is formed in measurable concentrations. It is to be expected that the concentration of the possible paths for the rapid diffusion process determines the extent of formation of subsurface species. We thus suggest a model (Scheme 1) for the formation of oxygen species. We suggest that oxygen adsorption takes place preferentially on surface defects and that these are related with the paths for rapid diffusion important for the formation of (subsurface) Species II and III. Enhanced adsorption of oxygen on surface defects has been reported by Albers and co-workers (*22, 23*) to take place on Ag(111). In the temperature region around 200°C, the formation of subsurface oxygen and subsurface OH (if dissolved hydrogen is present) is much faster than the formation of atomic surface oxygen (Species I). Therefore, atomic surface oxygen is formed only after saturation of Species II and III. It cannot be ruled out that atomic surface oxygen (Species I) is formed directly from the gas phase; however, surface diffusion would most probably cause disappearance of these species via interaction with defects and subsequent formation of subsurface species. As long as no saturation of the subsurface species is achieved, this process might also give rise to a small concentration of atomic surface oxygen. During desorption experiments, the subsurface species can be converted into oxygen adsorbed on surface defects, as reported earlier (*12*).

Oxidative Dehydrogenation of Methanol

The gas-phase decomposition of N_2O during the extremely small contact time used in the catalytic experiments is not likely to be significant in the temperature range used (*27*). Oxidation of the methanol with the oxygen formed by homogeneous decomposition of N_2O is thus not likely to contribute to the conversions reported in Fig. 1.

The reactions of O_2 and N_2O with methanol result in comparable product mixtures, as can be seen in Figs. 1 and 2. This indicates that there are probably no differences in the reaction mechanism for the two reactions. The most significant difference is the fact that O_2 is converted totally above 300°C whereas N_2O is not. The reaction rate in the case of N_2O is thus considerably smaller than that with the oxidation of methanol with O_2. This observation is in agreement with the fact that oxygen adsorption from N_2O is considerably slower than with O_2, as discussed above. It may thus be concluded that the formation of oxygen species on the silver surface from the N_2O is the rate-determining step. The same may also be true for methanol oxidation with O_2. The slow formation of adsorbed oxygen species from N_2O also explains the low conversion to CO_2 during the oxidation of methanol at low temperatures compared with that observed (Fig. 2) during the oxidation of methanol with O_2. Neubauer (*6*) has reported that the epoxidation reaction of ethylene on silver also proceeds much more slowly with N_2O than with O_2.

It appears from the TPR measurements that because of the slow interaction, the rate of formation of weakly bound atomic surface oxygen (Species I) is decreased to a greater extent than is the rate of formation of subsurface oxygen after long exposures at 210°C. The TPR measurements suggest that the oxygen species form selectively at surface sites which are related to subsurface Species II and III, e.g., at grain boundaries and defects. The slow formation of adsorbed oxygen species from N_2O thus causes in particular a decrease in the concentration of the weakly bonded atomic surface oxygen which we suggest is responsible for the formation of CO_2 (*12, 13*) during the oxidation of methanol. In this way, our reaction model explains the increase in selectivity when N_2O is used (Fig. 4) as being due to a decrease in the conversion to CO_2. A similar argument, involving weakly bonded atomic oxygen on the surface, was previously used to explain the increase in selectivity when the oxygen concentration is decreased (*13*). The formation of subsurface oxygen will have no effect on the formation of oxygen-containing molecules (Scheme 1) once a steady state is reached; however, the amount of subsurface oxygen present in that steady state might influence the properties of the oxygen species on the surface.

Ethylene Epoxidation

The observed differences in the adsorption behavior of O_2 and N_2O and the related development of subsurface species may also be important in relation to the mechanism of ethylene epoxidation on silver catalysts. Herzog (*7*) suggested that molecular oxygen is the active species for epoxidation because far smaller selectivities were obtained with N_2O than with O_2. The presence of molecular oxygen in the form of O_2^- on silver oxide has been demonstrated with ESR and the reactivity of this species to ethylene was shown by Tanaka and Yamashina (*28*) using TPD.

However, the present study shows a strong difference between N_2O and O_2 in the rate of formation of atomic oxygen on silver. The silver materials commonly used for ethylene epoxidation, such as small supported particles, contain only a few grain boundaries in the silver; the proportion of the paths for rapid diffusion (which enhance the formation of subsurface species) is thus considerably lower. Furthermore, the temperatures used in ethylene epoxidation are lower than those for methanol oxidation which will also decrease the rate of formation of subsurface oxygen. Furthermore, the reactions in which CO_2 and the epoxide are formed both remove oxygen from the surface, in contrast to the dehydrogenation of methanol. This indicates that the substitution of O_2 by N_2O might decrease the proportion of subsurface oxygen present during the catalytic reaction.

According to van Santen and co-workers (*29, 30*), who studied ethylene epoxidation with labeled reactants, atomic surface oxygen can react with ethylene to give ethylene oxide provided that subsurface oxygen is also present. Such surface oxygen was shown to react more rapidly than gas-phase oxygen. We suggest that the decrease in the proportion of subsurface oxygen may be the reason for the loss in selectivity when N_2O is used for ethylene epoxidation. Comparable conclusions were obtained using IR measurements by Force and Bell (*31, 32*) and using the temperature-programmed reaction of ethylene with O_2 and N_2O by Neubauer (*6*). Neubauer interpreted the importance of the presence of subsurface oxygen in terms of the semiconductor properties of a silver oxide surface layer. Verykios and co-workers (*33*) studied the influence of the microstructure of supported silver on its selectivity toward ethylene epoxidation; they reported that the morphology as well as the particle size influenced the rates of reaction to CO_2 and the epoxide. It could well be that the rate of formation of subsurface oxygen is influenced by the particle size and morphology and this may affect the selectivity of the catalyst as discussed above.

CONCLUSIONS

The rate of formation of oxygen species is much smaller for N_2O than for O_2. Only subsurface species are created by N_2O on Ag III; however, when the sample is treated with H_2 at high temperatures prior to the oxidation, both subsurface oxygen and subsurface OH are formed. Selective adsorption probably takes place on surface defects.

A comparison of the results with literature data shows that the formation of subsurface species is strongly influenced by the microstructure of the silver; this is valid for adsorption of both N_2O and O_2. The rate of conversion of atomic surface oxygen to subsurface species (subsurface oxygen and OH) determines the proportion of weakly bonded atomic surface oxygen present after adsorption.

In the oxidative dehydrogenation of methanol, N_2O decreases the conversion to CO_2 compared to that with O_2, supporting the suggestion that atomic surface oxygen, which is weakly bound, is responsible for the formation of CO_2 and that strongly bound oxygen in the vicinity of surface defects is the active site for formaldehyde production.

The adsorption of oxygen is the rate-determining step, at least with N_2O as the reactant.

ACKNOWLEDGMENTS

The authors thank Messrs. C. A. M. van Reissen and S. Doorn for valuable discussions on the results and Mr. G. H. Altena for technical assistance. The financial support of Methanol Chemie Nederland is gratefully acknowledged.

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