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The Influence of Water on the Oxygen–Silver Interaction and on the Oxidative Dehydrogenation of Methanol

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Experiments carried out using temperature-programmed desorption and reduction could detect no interaction between water and silver at 200 °C. However, separate experiments on the effect of water on the oxidative dehydrogenation of methanol over a silver catalyst showed that water affected the selectivity of the reaction, reducing the production of CO_2. It is suggested that this change in selectivity arises from the adsorption of water on the weakly bound oxygen surface species which are responsible for the non-selective reaction to CO_2. The interaction is apparently too weak to give rise to observable species in the t.p.d. and t.p.r. experiments.

Silver is widely used as a catalyst for the oxidative dehydrogenation of methanol to produce formaldehyde. The process is performed at temperatures above 600 °C, using an excess of methanol relative to oxygen. It is possible to reach a selectivity of 90% at almost complete conversion.

It is generally accepted that the admixture of water to the reaction mixture can increase the selectivity under industrial conditions: the addition of water allows the use of higher partial pressures of oxygen; see, for example, reviews of the subject by Walker[1] and by Sperber.[2] This effect was first reported by Trillat,[3,4] and Uhl and Cooper[5] patented the idea in 1949. Yalitov and Lakiza[6] reported that the addition of water reduces the rate of dehydration of s-butyl alcohol during its oxidative dehydrogenation over a silver catalyst. Kurina *et al.*[7,8] suggested that water prevents the decomposition of formaldehyde. However, all these studies[6-8] were performed on supported catalysts; a support effect may thus also have been involved.

In previous publications, we showed that two different types of oxygen species are involved in dehydrogenation and total oxidation, respectively.[9,10] It is possible that water will interact with one or other of these sites, thus affecting the selectivity. Furthermore, it appears fom our temperature-programmed reduction (t.p.r.) and temperature-programmed desorption (t.p.d.) measurements[10] that hydrogen dissolved in the silver creates OH species on either the surface or in the sub-surface of the silver; these OH groups may desorb or be reduced at *ca.* 400 °C. We also confirmed using X.p.s. measurements[11] that there was some sort of interaction between the oxygen species and the dissolved hydrogen.

The literature data on the interaction of water with silver are in contradiction. Kurina and coworkers,[12,13] using adsorption and t.p.d. measurements, found that water interacted with both oxidized and bare polycrystalline silver at temperatures between 20 and 300 °C; absorbed species stable up to 600 °C were observed. Furthermore Bazilio[14] *et al.* observed OH species on polycrystalline silver at 100–150 °C using i.r. spectroscopic measurements.

In contrast to these observations, Bowker *et al.*[15] and Au *et al.*[16] found surface OH

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groups on oxidized Ag(110) exposed to water vapour only at temperatures below 50 °C; Bowker *et al.*[15] performed t.p.d. and isotopic exchange experiments and Au *et al.*[16] used X.p.s. and u.p.s. measurements. Finally, no water adsorption on bare polycrystalline silver at room temperature was observed with SIMS by Wiedmann and coworkers.[17]

The present work was carried out to find out whether or not water interacts with pure or oxidized silver and whether or not the OH species observed in earlier work[10] can be formed from water; further, we wished to find out whether these OH species were present on the surface or in the sub-surface region. Thus, we studied with t.p.r. and t.p.d. the influence of water treatment after long oxygen exposure as well as adsorption from an air–water mixture. Experiments were performed with and without the presence of dissolved hydrogen in the silver before oxidation.[10] Furthermore, we measured the influence of water on the selectivity in the oxidative dehydrogenation of methanol over a pure silver material. We shall attempt to correlate these results with the results on the interaction of water with silver.

Experimental

Methods

The catalytic measurements were performed in fixed-bed flow reactor with g.c. analysis, as described elsewhere.[9] To allow addition of water to the reaction mixture, an extra He stream (20 cm^3 min^{-1}) passing through a saturator filled with water was included and this stream was mixed with the helium–methanol–oxygen mixture (100 cm^3 min^{-1}) at a position immediately before the reactor. The water concentration was varied by changing the temperature of the saturator. The experimental conditions chosen for the measurements were: temperature (T), 500 °C; inlet concentration of methanol ($[CH_3OH]_{in}$), 4.5 %; inlet concentration of oxygen ($[O_2]_{in}$), 1.4 %; inlet concentration of water ($[H_2O]_{in}$), 0–1.6 %; amount of catalyst, 0.5 g; linear gas velocity (v_g), 10.3 cm s^{-1}; and space velocity (v_s), 6.1×10^4 h^{-1}. The total pressure was *ca.* 1.1 bar. v_s is defined as the ratio of total volume flow rate and volume of the catalyst bed and v_g is defined as the ratio between total volume flow rate and the area of cross-section of the reactor. The conversion (y_i) is product i is defined by

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

and the selectivity (s) to formaldehyde is defined by

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

The t.p.d. and t.p.r. equipment used has been described elsewhere[10] with the addition that saturators were included to allow the introduction of water to the silver sample. Apart from the use of these saturators, the experimental conditions were unchanged from those used in earlier work:[10] a heating rate of 17 °C min^{-1} was used throughout, t.p.d. was performed using He while t.p.r. was performed with 6 % H_2 in Ar. T.p.d. measurements were performed with the cold finger both in and out of function; any difference between measurements in the latter experiments must be caused by the occurrence of water. After exposure to water–air or water–He, the sample was cooled in He or air in the absence of water before the t.p.d. or t.p.r. experiment was started. As in previous work,[10] the sample was treated many times using oxidation–reduction cycles (at temperatures up to 900 °C) to prevent the occurrence of morphology changes during the experiments described here.

Materials

The catalytic measurements were performed with 0.5 g of a commercial catalyst consisting of pure silver particles with an average size of 0.5 mm, prepared by an

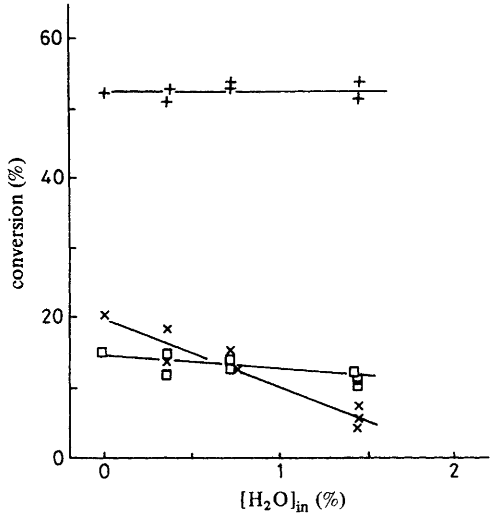

Fig. 1. Influence of water on the conversion of methanol, +, CH_2O; □, H_2; ×, CO_2 (× 10) at 500 °C on 0.5 g sample of Ag 0.5.

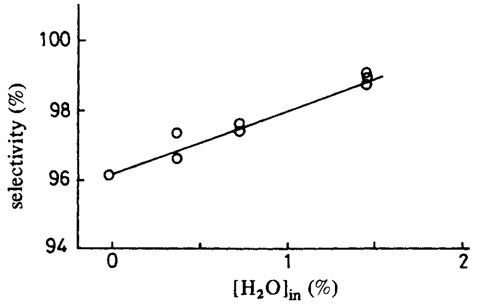

Fig. 2. Influence of water on the selectivity to formaldehyde in methanol oxidation at 500 °C on a 0.5 g sample of Ag 0.5 at a conversion of methanol of 54%.

electrolytic method. The t.p.r. and t.p.d. measurements were performed with 1.5 g of a pure silver material previously described as Ag^{III}.[9] It has been shown elsewhere[9] that these samples have similar properties in methanol oxidation; X.p.s. measurements have shown that only small amounts of impurities (Cl and Si) and larger amounts of O and C were present on both samples.[9, 11]

Results

Catalytic Measurements

Fig. 1 shows the effect on the production of CH_2O, H_2 and CO_2 of adding water to the reaction mixture. The conversion to CO_2 is lowered and there is also a slight decrease in the conversion to H_2; there is no significant influence on the conversion to formaldehyde. No conversion to CO is detected at 500 °C; at this temperature CO is only formed at higher conversions achieved at higher oxygen pressures.[9] The changes in conversion to CO_2 results in an increase of the selectivity to formaldehyde, as shown in fig. 2.

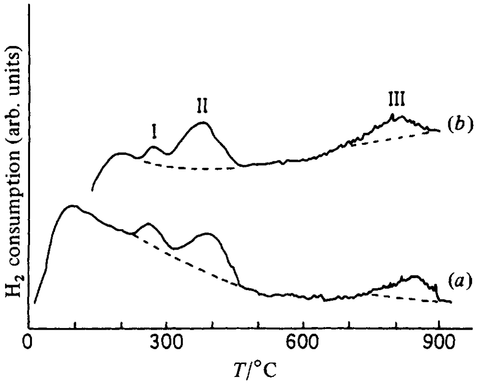

Fig. 3. Influence of water treatment on t.p.r. results after reduction at 900 °C (which causes dissolution of hydrogen) followed by 18 h oxidation in air at 210 °C: (*a*) no subsequent water treatment, (*b*) after a subsequent treatment in He–water at 210 °C for 1 h.

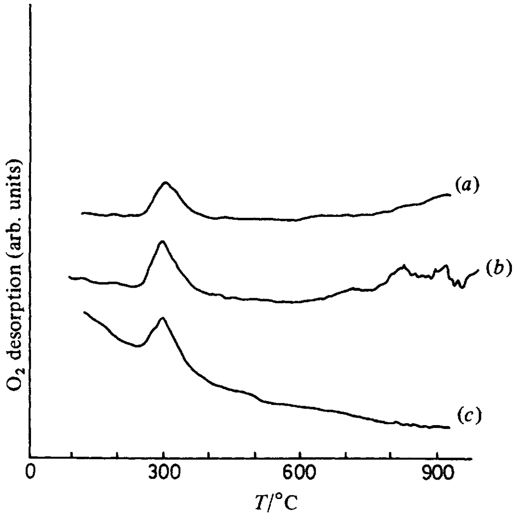

Fig. 4. Influence on t.p.d. measurements of water treatment after a previous desorption experiment (which causes a hydrogen-free sample) and then oxidation in air at 210 °C for 18 h followed by (*a*) treatment for 2.5 h in He at 210 °C, cold finger out of function; (*b*) treatment for 50 min in He–water at 210 °C, cold finger out of function; (*c*) treatment for 1 h in He–water at 210 °C, cold finger in function.

T.P.R. and T.P.D. Measurements

We first have to emphasize that the peak sizes of reduction and desorption are dependent of the previous history of the sample. We showed previously that t.p.d. measurements cause a decrease in the surface area and surface roughness of the silver by sintering, whereas t.p.r. can cause an increase in the surface area and roughness due to the formation of holes in the surface during the reaction of dissolved hydrogen and oxygen.[10,19]

The effects of treatment with He–water of silver oxidized for 18 h in air at 210 °C are shown in fig. 3 and 4. The t.p.r. results shown in fig. 3 were obtained with t.p.r. when hydrogen has been dissolved in the silver before oxidation by the previous t.p.r.

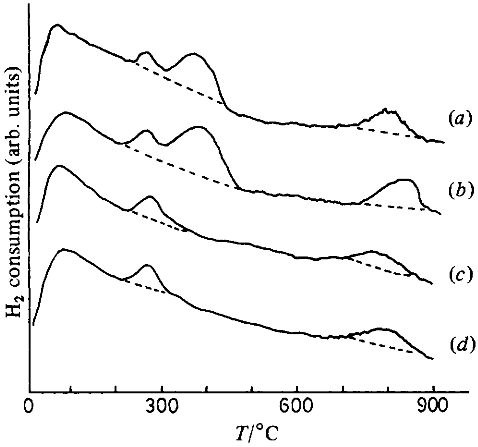

Fig. 5. Influence on t.p.r. measurements of the presence of water during oxidation at 210 °C for 18 h preceded either by a t.p.r. measurement [causing the presence of dissolved hydrogen, curves (*a*) and (*b*)] or a t.p.d. measurement [causing a hydrogen-free sample, curves (*c*) and (*d*)]; (*a*) and (*c*): oxidation in dry air; (*b*) and (*d*): oxidation in an air–water mixture.

measurement. Curve (*a*) was measured when no water treatment was given after the oxidation and curve (*b*) was obtained as a result of treatment with water at 210 °C after the oxidation. No significant influence of the water treatment is observable. T.p.d. results as shown in fig. 4 were obtained on the same sample. The performance of a sequence of t.p.d. measurements implies that no hydrogen treatment at high temperature was given prior to the oxidation; thus no pre-dissolved hydrogen was present. Curve (*a*) was obtained as a result of treatment with He only after oxidation; curves (*b*) and (*c*) were obtained after treatment with He–water of the oxidized sample with the cold finger out of function and in function, respectively. The irregularities seen in curve (*b*) above 700 °C were also observed after water treatment of the empty reactor and are therefore probably due to desorption from surfaces of the tubing near the hot reactor. No influence of the water treatment on the desorption of oxygen from silver is observed in fig. 4.

The influence of the presence of water during oxidation in air at 210 °C for 18 h is shown in fig. 5 and 6. Fig. 5 shows t.p.r. measurements after oxidation in, respectively, dry air and air which contained 2.4% water, in the presence [curves (*a*) and (*b*)] and in the absence [curves (*c*) and (*d*)] of dissolved hydrogen. Fig. 6 gives similar information from t.p.d. experiments after oxidation without the presence of dissolved hydrogen, measured again with and without the cold finger in function. Curves (*a*) and (*b*) resulted from oxidation with dry air; curves (*c*) and (*d*) were obtained after oxidation in air which contained 2.4% water. As in fig. 4, the irregularities in the curves (*c*) and (*d*) are probably due to desorption from surfaces near the hot reactor. It appears from the fig. 5 and 6 that no clear differences exist between oxidation in the presence and absence of water.

Finally, it appears from t.p.d. experiments (not shown in the figures) that no adsorption at all is observed when water is in contact with oxygen-free silver at temperatures between 50 and 300 °C; the oxygen was removed by reduction up to 900 °C. Also when the oxygen was removed from the surface by desorption up to 600 °C after oxidation, no interaction with water was observed.

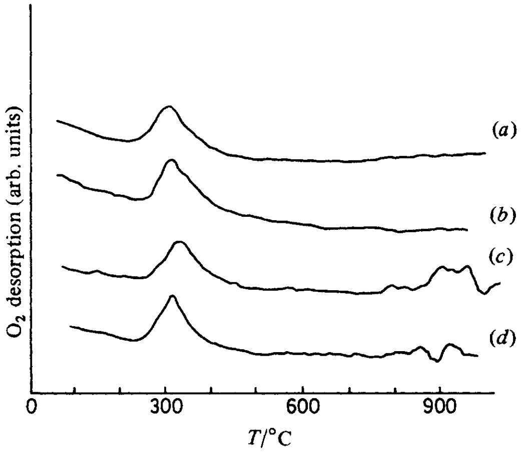

Fig. 6. Results of t.p.d. experiments carried out to examine the influence of the presence of water during oxidation at 210 °C for 18 h preceded by desorption (causing a hydrogen-free sample); (*a*) oxidation in dry air, cold finger out of function; (*b*) oxidation in dry air, cold finger in function; (*c*) oxidation in air–water, cold finger out of function; and (*d*) oxidation in air–water, cold finger in function.

Discussion

We discuss first the results of the t.p.d. and t.p.r. measurements on the interaction of water with silver, and then the results of the catalytic measurements in relation to the former measurements.

T.P.D. and T.P.R. Measurements

The assignment of the different reduction and desorption peaks of spectra such as those in fig. 3–6 has been discussed in a previous publication;[10] the same nomenclatures will be used here. The reduction peak at 275 °C and the desorption peak at 300 °C represent atomic surface oxygen (species I), the reduction peak at 400 °C represents the OH species (species II) that may be present on the surface or in the sub-surface of the silver, and the reduction peak at 850 °C is due to sub-surface oxygen (species III). The peak in the reduction measurements at *ca.* 100 °C has no significance and is due to change in the flow through the silver sample caused by starting up the temperature programme. From our results it appears that water is not able to adsorb on either oxygen-free or strongly oxidized silver at temperatures around 200 °C. Further, no water adsorption is observed on silver containing sub-surface oxygen; according to our earlier work,[10] this is the only species present after oxidation followed by desorption up to 600 °C. If hydrogen is dissolved in the silver [see fig. 3 and 5(*a*) and (*b*)], the formation of OH groups (species II), represented by the reduction peak at 400 °C, is not influenced by the presence of water during the oxidation (fig. 5) or after the oxidation treatment (fig. 3). The small differences observed in fig. 3 are not significant.

If no hydrogen is present in the silver [see fig. 4, 5(*c*) and (*d*) and 6], the presence of water during (fig. 5 and 6) or after oxidation (fig. 4) does not give rise to the formation of OH species (species II) or any other species; this conclusion is reached from both t.p.r. and t.p.d. measurements. Because no adsorption of water takes place, the presence of the cold trap has no effect on the t.p.d. spectra of fig. 4 and 6.

Because the peak at 400 °C (species II) in the various spectra, which we have previously assigned to OH species, is not influenced by water treatment and cannot be observed after water treatment of surfaces not previously treated in hydrogen, we must conclude that the OH groups responsible for this species cannot be present on the surface. We must therefore conclude that species II is due to sub-surface OH groups[10] which are formed *via* interaction of oxygen with hydrogen previously dissolved in the sub-surface of the silver.

The fact that in this work no interaction with water is observed is in contradiction with the results of Plakidkin and Kurina;[13] these workers have reported that water adsorbs on silver at temperatures between 50 and 300 °C and that adsorbed species are present that can be desorbed around 600 °C in t.p.d. experiments. Impurities or adsorption on the equipment may have influenced the results of Plakidkin and Kurina. Several workers have reported that water interacts with oxygen on silver in the temperature range from 50 to 200 °C. Kurina *et al.*[12] observed adsorption of water on both bare and oxidized silver between 50 and 100 °C. Bao *et al.*[18] have also observed interaction of water with oxygen-loaded polycrystalline silver at temperatures below 180 °C with temperature-programmed desorption spectroscopy. Bazilio *et al.*[14] observed, using i.r. measurements, that OH species are present on the surface; this observation was possibly caused by the pretreatment of their sample with hydrogen at 500 °C. In a previous publication[19] we have shown that hydrogen treatment at 500 °C may cause the presence of hydrogen dissolved in the silver which can then interact with oxygen to give sub-surface OH groups as discussed above. Some of those groups may be very near the surface, explaining the i.r. observation. However, the OH species observed by Bazilio and coworkers[14] was unstable above 220 °C. It is possible that the interaction of silver with water reported by these groups of workers[12,14,18] are not observed in this study because of the temperature of 200 °C used during the experiments and because the sample was treated with dry air or dry helium before the t.p.d. or t.p.r. measurements were performed.

Our results are in agreement with the work of Wiedmann *et al.*,[17] who reported that there was no water adsorption on bare silver, and also with the results of Au *et al.*[16] and of Bowker *et al.*,[15] both of which groups observed stable OH groups on the silver surface only below 50 °C. However, it is important to realize that these measurements were performed after mild oxidation treatments. It might be that surface OH groups are far more stable in the presence of sub-surface oxygen, especially on polycrystalline silver. We can state from the present results that such a species can only be present at the surface at 200 °C at significantly smaller concentrations compared with those of surface oxygen.

Influence of Water on the Methanol Oxidation Reaction

From fig. 1 it appears that the improvement of selectivity in the oxidative dehydrogenation of methanol which has been previously reported[1-8] is due to suppression of total oxidation to CO_2. It has not previously been reported that the formation of CO_2 is inhibited by the addition of water when relatively low reactant concentrations are used. Because of these low concentrations, the effect cannot be explained in terms of improved removal of heat by the added water as has been suggested by Sperber[2] for industrial conditions. We must therefore conclude that there is an interaction of the water with the catalyst under these reaction conditions. We suggested previously that formation of CO_2 takes place at sites on the silver on which weakly bound atomic oxygen (species I) is adsorbed.[9,10] It is thus probable that such species are deactivated by the presence of water, as has also been suggested by Kurina *et al.*[12] We suggest that weakly bonded surface oxygen is deactivated by the reaction

$$O_w + H_2O = 2OH_a.$$

Kurina *et al.* also suggest that water may terminate gas-phase reactions of formaldehyde to give CO,[7,8] but we showed[9] that the main side reaction is that which yields CO_2 and that this takes place on the silver surface. CO_2 is also the main by-product in commercial plants using unsupported silver. It is possible that in the work of Kurina *et al.*[7,8] water influenced the interaction of formaldehyde with the pumice support of the catalyst which they used. This idea is supported by the results of Petrova, Evseeva and Kurina,[20] who reported that the addition of water decreased the rate of carbon formation on the oxidic support. Furthermore, Ai[21] has shown that alumina has considerable activity in formaldehyde oxidation. Obraztsov *et al.*[22] have reported that the nature of the support indeed influences the rate of CO formation during methanol oxidation on supported silver catalysts.

Sperber[2] explains the effect of water on the selectivity of the reaction by suggesting that there is an increase in the thermal capacity of the mixture and that this decreases the reactor temperature. However, this cannot have a significant effect on our measurements because of the low reactant concentrations used; the thermal effect of the reactions is very limited compared with those encountered in an industrial adiabatically operated reactor.

No proof has been found of the interaction of water with the weakly bound oxygen in this study. However, it is possible that adsorption of water on weakly bound oxygen or competitive adsorption of water on sites related to weakly bound oxygen takes place at 500 °C and higher temperatures and in the continuous presence of water. Weakly bound oxygen itself is not stable under reaction conditions; it is thus impossible to study the interaction of water with weakly bonded oxygen under reaction conditions. The present results showed that at 200 °C interaction of water with oxygen species on silver is too weak to observe influences on t.p.r. and t.p.d. results after removal of water from the gas phase.

Conclusions

The reduction peak which occurs at 400 °C in t.p.r. experiments after oxidation of silver containing hydrogen and which was previously attributed to OH species is not caused by OH species on the surface and must be assigned to an OH species in the sub-surface of the silver.

No interaction of water with oxidized silver is observed at 200 °C and no interaction with bare silver is observed between 50 and 300 °C. The introduction of water during methanol oxidation decreases the conversion to CO_2, suggesting that an interaction of water with weakly bound oxygen exists under the reaction conditions.

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References

1 J. F. Walker, *Formaldehyde* (Reinhold, New York, 1964).
2 H. Sperber, *Chem.-Ing.-Techn.*, 1969, **41**, 962.
3 A. Trillat, *Bull. Soc. Chim. Fr.*, 1902, **27**, 797.
4 A. Trillat, *Bull. Soc. Chim. Fr.*, 1903, **29**, 35.
5 H. B. Uhl and I. H. Cooper, *U.S. Patent* 2,465,498 (1949).
6 N. Kh. Valitov and S. M. Lakiza, *Russ. J. Phys. Chem.*, 1975, **49**, 1853.
7 L. N. Kurina, N. V. Vorontsova and V. P. Morozoy, *Russ. J. Phys. Chem.*, 1973, **47**, 1230.
8 L. M. Kurina and V. P. Morozov, *Russ. J. Phys. Chem.*, 1976, **50**, 538.
9 L. Lefferts, J. G. van Ommen and J. R. H. Ross, *Appl. Catal.*, 1986, **23**, 385.
10 L. Lefferts, J. G. van Ommen and J. R. H. Ross, *Appl. Catal.*, 1987, **31**, 291.
11 L. Lefferts, J. G. van Ommen and J. R. H. Ross, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 3161.
12 L. N. Kurina, L. I. Novozhenova, L. P. Orlova, L. M. Koval and T. D. Dobrynina, *Russ. J. Phys. Chem.*, 1978, **52**, 867.

13 A. A. Plakidkin and L. N. Kurina, *Russ. J. Phys. Chem.*, 1980, **54**, 970.

14 C. A. Bazilio, W. J. Thomas, U. Ullah and K. E. Hayes, *Proc. R. Soc. London, Ser. A*, 1985, **399**, 181.

15 M. Bowker, M. A. Barteau and R. J. Madix, *Surf. Sci.*, 1980, **92**, 528.

16 C. T. Au, S. Singh Boparai, M. W. Roberts and R. W. Joyner, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 1779.

17 L. Wiedmann, N. L. Wang, R. Jede, L. D. An, O. Ganschow and A. Benninghoven, Springer Series in Chemical Physics, vol. 19, *Secondary Ion Mass Spectroscopy SIMS III* (Springer, Berlin, 1982), p. 42.

18 X. Bao and J. Deng, *J. Catal.*, 1986, **99**, 391.

19 L. Lefferts, J. G. van Ommen and J. R. H. Ross, *Appl. Catal.*, 1987, **34**, 329.

20 N. I. Petrova, Y. Yu, Evseeva and L. N. Kurina, *Zh. Prikl. Khim.*, 1978, **51**, 352.

21 M. Ai, *J. Catal.*, 1983, **83**, 141.

22 A. Ye. Obraztsov, M. P. Shashalevich, B. I. Popov, L. P. Taraban, N. P. Zharkova and A. G. Shevchenko, *Sov. Chem. Ind.*, 1970, no. 5, 26.

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