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The relation between reduction temperature and activity in copper catalysed ester hydrogenolysis and methanol synthesis

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Zinc and manganese promoted silica supported copper catalysts show an activity increase in methyl acetate hydrogenolysis and methanol synthesis after high temperature reductive treatments. The effect of reduction can largely be reversed by applying a treatment in an inert atmosphere at reduction temperature, which results in a decrease in copper surface area as measured by N_2O chemisorption and which is accompanied by distinct changes in the XRD pattern of the catalyst. These phenomena could be explained with a model assuming the reversible formation of epitaxial, two-dimensional, copper particles on top of a mixed oxide phase.

Keywords: supported copper catalysts; zinc oxide; manganese oxide; promoter effects; methyl acetate; hydrogenolysis; methanol synthesis; epitaxy

1. Introduction

The hydrogenolysis of fatty methyl esters is an important step in the manufacture of alcohols from natural fats and oils. In industry, copper chromium oxide catalysts are widely used for this reaction. The use of chromium, however, poses an environmental hazard since process water streams containing hexavalent chromium are generated during catalyst manufacture and regeneration. Research is therefore focused on the development of chromium-free catalysts for the hydrogenolysis of esters.

In our group, silica supported copper catalysts have been developed which are active in the hydrogenolysis of fatty methyl esters [1]. The addition of zinc to silica supported copper catalysts results in an increased activity in ester hydrogenolysis [2]. For such zinc promoted silica supported copper catalysts, a remarkable effect of reduction temperature on hydrogenolysis activity was found. Upon reduction between 550 and 750 K a fivefold activity increase could be observed [3]. At that time, we could only derive from the crucial presence of zinc oxide and the nature of the reductive treatment that apparently formation of reduced copper particles in contact with zinc oxide caused the described effect. Puzzling, however, was that no concomitant rise in copper metal surface area could be detected by N_2O chemisorption. Simultaneous sintering of other copper species could be excluded on the basis that unpromoted silica supported copper catalysts did not show sintering under these conditions.

This paper describes a series of experiments we conducted to elucidate some of the phenomena behind the effect of reduction temperature on the activity of promoted copper catalysts in ester hydrogenolysis, combining reactivity data with N_2O chemisorption experiments. In a similar way we have tried to establish whether the results obtained during ester hydrogenolysis also are relevant for methanol synthesis from H_2 and CO.

2. Experimental

Silica supported copper catalysts were prepared by homogeneous deposition precipitation of copper nitrate trihydrate (Merck, >99.5% pure), zinc nitrate hexahydrate (Janssen, >98% pure) and/or manganese nitrate tetrahydrate (Merck, >98.5% pure) onto Aerosil 200 silica, according to the method described by Van de Grift et al. [4]. The pH was raised from 3 to 6.5 by the decomposition of urea (Aldrich, >98% pure) at 363 K. The precipitate was washed twice with doubly distilled demineralised water and dried at 363 K overnight, after which it was crushed and sieved to obtain the required particle size (125–212 μm). Both unpromoted Cu/SiO_2 and zinc and manganese promoted catalysts have been prepared containing (a) 14 wt% copper; (b) 14% copper in combination with 7% Zn and (c) 13% copper combined with 4% Mn, respectively (as determined by ICP/AES). Within experimental error, no other metals were detectable during ICP/AES analysis.

The copper surface areas were determined by a method described by Luys et al. [5]. About 400 mg of a

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catalyst sample was placed into a porous basket in a Setaram TG85 thermo-balance. Calcination was performed in a flow of 2 cm^3 s^{-1} air. The temperature was raised with 72 K h^{-1} to 750 K, where it was kept for 12 h. Reduction was performed in a flow of 2 cm^3 s^{-1} H_2/Ar mixture containing 67% hydrogen (Praxair, 99.997% pure) and 33% argon (Praxair, 99.999% pure, further purified using molecular sieves and an oxygen trap). The sample was heated to the required reduction temperature with 72 K h^{-1} and kept at this temperature for 1 h. After the reduction the thermo-balance was evacuated for a given time at either reduction temperature or 600 K, depending on the experiment. The sample was subsequently cooled to 363 K under a flow of argon. The actual copper surface area determination was performed with a flow of 2 cm^3 s^{-1} 1% N_2O/99% Ar at 363 K. The copper surface area was calculated by linear extrapolation of the sub-surface contribution to $t = 0$, assuming $Cu_s/O_{ads} = 2$ and a value of 1.46×10^{19} Cu_s atoms m^{-2} [6]. Most of the values reported have been measured twice and reproduced well within 5% of the measured value.

X-ray diffraction experiments were performed using a Siemens D 500 diffractometer, using Cu Kα radiation and equipped with a graphite monochromator with a reflected beam. An X-ray chamber-reactor [7] was used for the high-temperature registration of the spectra. Preceding the experiments, 100 mg of the $Cu/ZnO/SiO_2$ catalyst was calcined under a 80 cm^3 min^{-1} flow of air at 758 K for 8 h. The reduction was performed under a flow of 80 cm^3 min^{-1} hydrogen. The temperature was raised with 120 K h^{-1} to 693 K and kept there until no more changes were observed. After recording the XRD diffraction pattern of the reduced sample, the hydrogen flow was replaced by a flow of 80 cm^3 min^{-1} helium (99.999% pure and further purified using a Ni–Cr catalyst and CaA molecular sieves) and, as a function of time, a series of diffraction patterns was recorded.

Methyl acetate hydrogenolysis activity experiments were performed in a gas phase flow set-up. Samples (300 mg) were calcined in a flow of 1 cm^{-3} s^{-1} air. The temperature was raised with 72 K h^{-1} to 750 K, and was kept at this level for 12 h. Reduction was performed in a flow of 1 cm^3 s^{-1} hydrogen (Praxair, 99.999% pure and further purified using a copper catalyst and 5 Å molecular sieves). The sample was heated to the required reduction temperature with 72 K h^{-1} and kept at that temperature for 1 h. A mixture of 0.25 vol% methyl acetate (Merck, 99+% pure), 10 vol% hydrogen and balance nitrogen (Praxair, 99.999% pure and further purified using a copper catalyst and 5 Å molecular sieves) with a flow rate of 2 cm^3 NTP s^{-1} at a total pressure of 0.4 MPa was passed over the catalyst. The temperature was cycled between 420 and 520 K. The reaction mixture was analysed using a Chrompack 438A gas chromatograph equipped with a Hayesep S column and a FID detector. Most values have been measured twice and reproduced well within 5% absolute.

Methanol synthesis was performed with a mixture of $CO/H_2 = 1/2$ (Praxair, purified over an activated carbon column) at a total pressure of 0.2 MPa with a total flow of 7.5 cm^3 NTP min^{-1}. Catalyst samples (250 mg) were pre-treated as in methyl acetate hydrogenolysis. Methanol synthesis was measured between 440 and 530 K. The product mixture was analysed using a Chrompack 438A gas chromatograph equipped with two Porapack columns and a methanizer with a FID detector. All reported values have been measured twice and reproduced within 5% of the measured value.

3. Results and discussion

In fig. 1, the results are shown of experiments similar to those earlier published by Van de Scheur et al. [3] using a newly prepared set of Cu/SiO_2 and $Cu/ZnO/SiO_2$ catalysts with the addition of results of a $Cu/MnO_x/SiO_2$ catalyst. The methyl acetate hydrogenolysis activity versus catalyst reduction temperature is shown for a reaction temperature of 470 K. For Cu/SiO_2, about 10% conversion is found for all reduction temperatures in the applied range of 500 and 750 K. The $Cu/ZnO/SiO_2$ and $Cu/MnO_x/SiO_2$ catalysts, however, show a considerable increase in activity as the reduction temperature is increased.

A similar effect was described by Yurieva, Makarova et al. who investigated the interaction of hydrogen with unsupported mixed oxides of Cu/Cr and Cu/Zn [8–10]. They observed the formation of epitaxial, two-dimensional, copper particles on top of a CuCr and CuZn mixed oxide phase after treatment under flowing hydrogen at 533 K, which correlated with enhanced acetone hydrogenation activity.

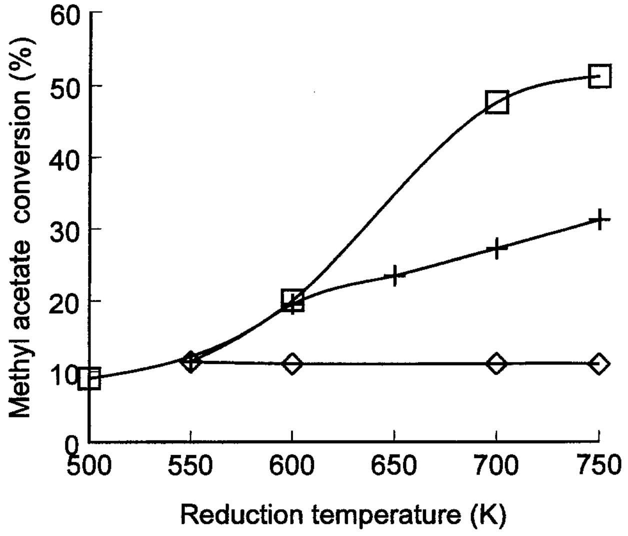

Fig. 1. Methyl acetate conversion as a function of catalyst reduction temperature. (◇): Cu/SiO_2, (□) $Cu/ZnO/SiO_2$ and (+) $Cu/MnO_x/SiO_2$.

The following model was suggested for the formation of epitaxial copper particles by these authors: during the reduction treatment, hydrogen adsorbs dissociatively and penetrates into the mixed oxide phase. Dissolved hydrogen interacts with copper ions, yielding H^+ and zero-valent copper atoms. The latter are able to migrate to the surface of the mixed oxide phase forming epitaxial, two-dimensional copper particles on top of the mixed oxide phase.

However, in our case, no clear rise in Cu^0 surface, as determined with N_2O chemisorption experiments, could be observed after high temperature reduction treatments [3]. Makarova et al. [8–10] have shown, however, that upon replacement of hydrogen by helium at high temperatures copper atoms migrate back into the mixed oxide phase, forming positively charged copper ions accompanied by hydrogen desorption.

It is clear from this model that, depending on the treatment, copper could reside in either zero-valent state particles epitaxially bound to the mixed oxide, or in a positively charged state in the Cu/Zn mixed oxide phase.

Preceding a N_2O chemisorption experiment, an evacuation treatment is performed at reduction temperature to desorb chemisorbed hydrogen. In view of the above, this could result in a lower measured copper surface area than is present under reaction conditions. To determine the influence of such an evacuation treatment, three series of copper metal surface area determinations have been performed with $Cu/ZnO/SiO_2$ and Cu/SiO_2 catalysts, one with short (5 min) evacuation at 600 K regardless of reduction temperature, the second with short evacuation at reduction temperature. A third series of experiments involved evacuation at a reduction temperature for 1 h.

The results of the N_2O chemisorption experiments are shown in fig. 2. Unlike previously obtained results with longer evacuation times [3], a steady rise in copper surface area is observed for the $Cu/ZnO/SiO_2$ catalyst when evacuated for 5 min at 600 K preceding N_2O chemisorption (circles). The $Cu/ZnO/SiO_2$ samples evacuated at reduction temperature only show a modest increase in Cu^0 surface area as a function of reduction temperature when evacuated for 5 min (triangles) and a decrease when evacuated for an hour (squares).

The Cu/SiO_2 samples also show increase in copper surface area going from 600 K reduction temperature to 700 K, where it more or less stabilises. The effect is, however, less pronounced as obtained with the $Cu/ZnO/SiO_2$ catalyst. The copper surface area of the unpromoted sample decreases significantly upon long evacuation times. However, the Zn promoted sample shows a threefold larger copper surface area loss upon prolonged evacuation compared to the unpromoted Cu/SiO_2 catalyst.

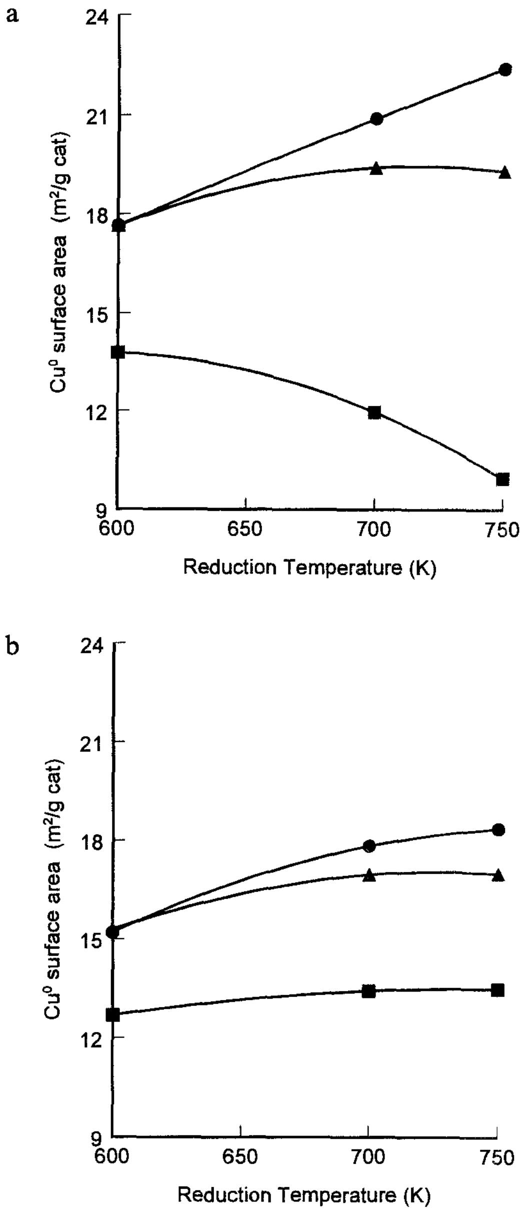

Fig. 2. Copper surface area as a function of reduction temperature for $Cu/ZnO/SiO_2$ (a) and Cu/SiO_2 (b) as determined by N_2O chemisorption. Evacuation treatment preceding N_2O chemisorption: 600 K for 5 min (●) reduction temperature for 5 min (▲) and reduction temperature for 1 h (■).

From the results of the N_2O chemisorption experiments, it is clear that an evacuation treatment has a pronounced effect on the copper metal surface area determined by N_2O chemisorption. As the reaction of N_2O with residual adsorbed hydrogen can be excluded [11] a realistic increase in copper surface area can be inferred as a result from the lower (600 K) evacuation temperature.

Berndt et al. [11], performing TPD and N_2O/CO pulse chromatographic experiments over supported Cu/ZnO catalysts, observed desorption of hydrogen in inert atmosphere at high temperature (500–700 K), ascribed to hydrogen dissolved in the zinc oxide phase. Long evacuation treatments, however, caused a significant decrease in copper surface area ascribed by the authors to the sintering of copper particles. In the absence of copper, zinc oxide did not show high temperature hydrogen desorption in their TPD studies. These phenomena could also be explained by the dynamic behaviour of copper described in the model above. In our view therefore, high temperature evacuation treatments should be applied cautiously in characterisation procedures of these catalyst systems.

To further evaluate the influence of an evacuation treatment, X-ray diffraction experiments have been performed with a Cu/ZnO/SiO_2 catalyst. The results are shown in fig. 3. The precursor catalyst, calcined in air at 758 K for 8 h is shown in curve 1. This curve shows one broad peak in the range of $2\theta = 32$–$39°$ most likely resulting from a mixed oxide phase. The freshly 693 K reduced catalyst (curve 2) shows two peaks at $2\theta \approx 43°$ and 49°, ascribed to (111)Cu^0 and (200)Cu^0 respectively. The mean particle size, calculated from the (111)Cu^0 diffraction line using the Selyakov–Scherrer formula is approximately 3.5 nm. Since no lines have been observed in the range of $2\theta = 30$–$40°$, the presence of crystalline ZnO in the reduced catalyst can be excluded.

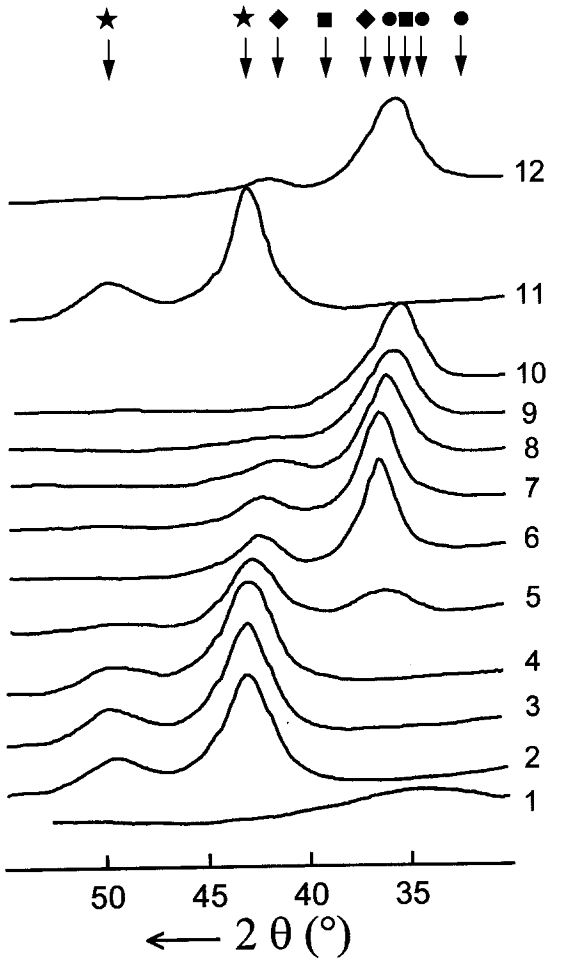

Fig. 3. X-ray diffraction patterns of Cu/ZnO/SiO_2. (1) calcined in air at 758 K for 8 h, (2) reduced in hydrogen at 693 K, (3) subsequent treatment in helium at 693 K for 30 min, (4) 80 min, (5) 100 min, (6) 120 min, (7) 140 min, (8) 160 min, (9) 180 min, (10) 200 min, (11) after subsequent reduction at 523 K and (12) treatment with helium for 200 min at 693 K. Assignments: (★) Cu^0, (◆) Cu_2O, (■) CuO, (●) ZnO.

Subsequently, hydrogen was replaced by a flow of helium at 693 K and a series of XRD patterns were recorded as a function of time (curves 3–10). After 80 min (curve 4), the lines at $2\theta \approx 43°$ and 49° clearly show a decrease in intensity, while after 100 min (curve 5) a line appears at $2\theta \approx 36°$. This suggests the transformation of metallic copper into an oxidised state of which the X-ray diffraction peak lies in between that of Cu_2O and CuO. This transformation is virtually complete after 200 min (curve 10); the peaks at $2\theta \approx 43°$ and 49° have completely diminished whereas the peak at $2\theta \approx 36°$ has risen considerably and is slightly shifted towards $2\theta \approx 35°$.

After the treatment in helium, the catalyst is reduced at 523 K under a flow of hydrogen. The XRD pattern obtained for this catalyst (curve 11) is comparable to the freshly 693 K reduced catalyst (curve 2). Apparently, the transformation of copper observed during a high temperature treatment in inert atmosphere can be reversed with reduction at relatively low temperatures.

Finally, the catalyst is treated with a flow of helium at 693 K for 200 min. The XRD pattern obtained for this catalyst, curve 12, is quite similar to the curve obtained after the first treatment in inert (curve 10) under the same conditions. Apparently, the transformation of copper from the metallic state into an oxidised state is completely reversible.

To examine the effect of an evacuation treatment on ester hydrogenolysis activity and to exclude the possibility of copper sintering during this procedure, activity experiments have been performed with subsequent treatments in reducing and inert atmospheres. In fig. 4, activ-

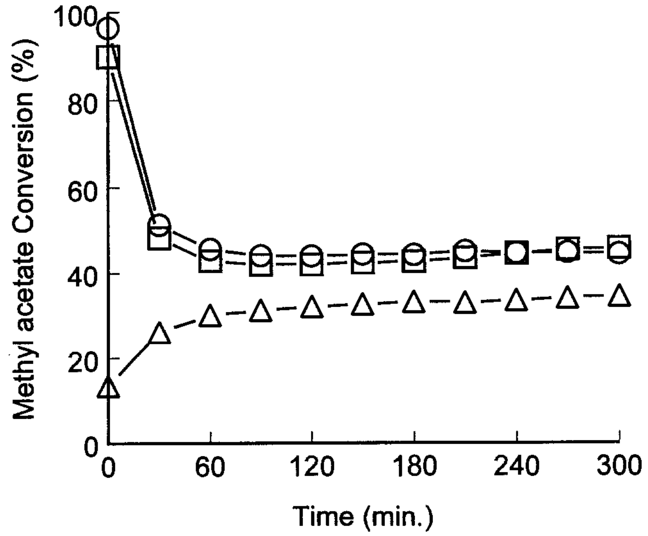

Fig. 4. Methyl acetate conversion as a function of time for Cu/ZnO/SiO_2 at three pre-treatment procedures: (○) reduction at 700 K in H_2 (1), (△) as (1) but followed by treatment in inert at 700 K (2), (□) as (2) but followed by reduction at 700 K in H_2 (3).

ity versus time for $Cu/ZnO/SiO_2$ catalysts with three different pre-treatments is shown. The samples have been pre-treated in the following ways: (1) reduction in hydrogen for 1 h at 700 K, (2) reduction as described in (1) but followed by a treatment in an inert atmosphere (N_2) at 700 K for 1 h, and (3) the same treatment as described under (2) but followed once more by a 1 h reduction in hydrogen at 700 K. It is clear from fig. 4 that treatment in inert atmosphere at 700 K (treatment (2)) results in a significantly lower ester hydrogenolysis activity than a reducing treatment only (treatment (1)). However, treatment (3) yields an activity that is comparable with treatment (1) implying that the deleterious effect of the second procedure can be reversed by a reductive treatment.

It can be concluded from these experiments that the evacuation treatment or treatment in an inert atmosphere results in a considerably lower ester hydrogenolysis activity. The fact that a subsequent treatment in a reducing atmosphere restores initial activity, excludes the possibility of copper sintering during high temperature evacuation or treatment in an inert atmosphere.

In view of the observations by Makarova et al. for acetone hydrogenation and these results in ester hydrogenolysis, it would be desirable to evaluate the influence of reductive treatments on the activity of the $Cu/ZnO/SiO_2$ catalyst in the highly relevant methanol synthesis reaction. Interestingly, Okamoto et al. also suggested formation of two distinct copper phases in 523 K reduced Cu–ZnO catalysts in a XPS study: Cu metal particles formed mainly from crystalline and amorphous copper oxide precursors and a two-dimensional Cu^+–Cu^0 epitaxial monolayer on top of zinc oxide derived from the mixed oxide precursor phase [12]. The importance of the epitaxial Cu species for methanol synthesis was proposed by the authors without performing reactivity experiments.

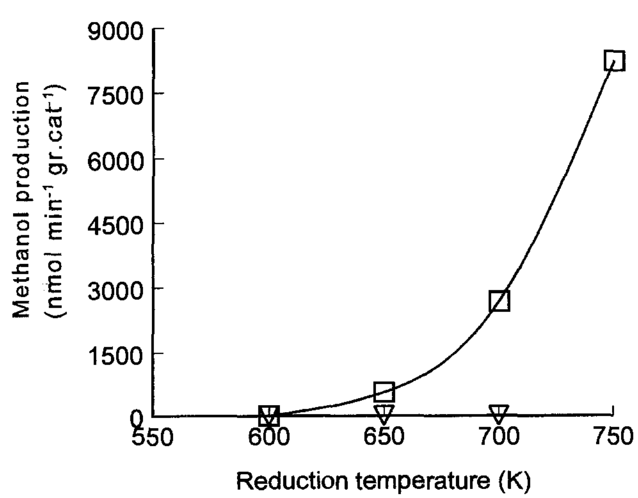

Fig. 5. Methanol synthesis activity as a function of reduction temperature at 470 K reaction temperature. (▽) Cu/SiO_2 and (□) $Cu/ZnO/SiO_2$.

A correlation between Cu^0 surface area and methanol synthesis activity has been observed by Waugh [13], whereas Klier suggests Cu^+ dissolved in ZnO to be the active species in methanol synthesis [14]. The present proposal would mean that these two species can be transformed into each other depending on reduction – and perhaps even reaction conditions.

In fig. 5 methanol synthesis activity at 470 K is shown for Cu/SiO_2 and $Cu/ZnO/SiO_2$ as a function of catalyst reduction temperature. Probably due to the relatively pure nature of the fume silica support applied, Cu/SiO_2 shows no measurable activity in methanol synthesis under the depicted conditions. This is consistent with work published by Nonneman et al. [15]. However, in our case a modest 500 nmol min^{-1} g-cat^{-1} methanol production is observed for Cu/SiO_2 at a reaction temperature of 530 K, which is approximately constant as a function of reduction temperature (see also fig. 6). The conversion of the $Cu/ZnO/SiO_2$ catalyst is thermodynamically limited under these conditions, so only the values at a reaction temperature of 470 K have been shown.

For $Cu/ZnO/SiO_2$, a very profound rise in activity upon high temperature reduction is observed, which is even more pronounced than in ester hydrogenolysis. The copper species present after a low temperature reduction treatment show considerable activity in ester hydrogenolysis, but not in methanol synthesis. This could be due to conventional three-dimensional copper particles. It has been shown that unpromoted silica supported copper shows ester hydrogenolysis activity, and that the TOF of low temperature reduced $Cu/ZnO/SiO_2$ catalysts is quite similar for this reaction [1]. Furthermore, a copper metal surface area of 13.8 m^2 g-cat^{-1} has been measured for the $Cu/ZnO/SiO_2$ catalyst after a 500 K reduction.

The influence of a treatment in inert atmosphere fol-

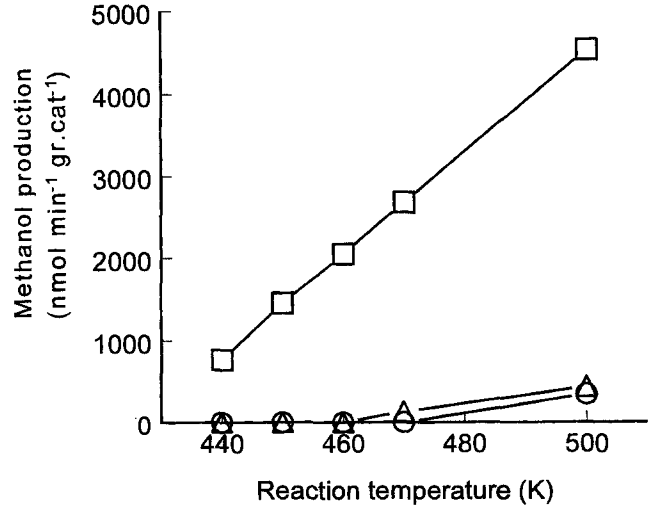

Fig. 6. Methanol synthesis activity for $Cu/ZnO/SiO_2$ as a function of reaction temperature for three different treatments: (□) reduction at 700 K in H_2 (1), (△) as (1) but followed by treatment in helium at 700 K (2), (○) reduction at 600 K in H_2.

lowing high temperature reduction is shown in fig. 6. This experiment was performed in order to establish whether the activity enhancement for methanol synthesis can be reversed by such a treatment. The $Cu/ZnO/SiO_2$ catalysts have been pre-treated in three different ways: (1) reduction in hydrogen for 1 h at 700 K, (2) reduction treatment as in procedure (1) followed by a treatment in an inert atmosphere at the 700 K for 1 h, and (3) reduction in hydrogen at 600 K for 1 h. The effect of inert gas treatment on methanol synthesis activity is dramatic; a tenfold decrease is observed, resulting in an activity that is comparable with the catalyst reduced at 600 K.

Alternative explanations for the observed phenomena could include the following. Reduction of zinc has been reported for these catalysts [3] and Kanai et al. [16] propose coverage of copper by zinc with formation of Cu–Zn alloys upon high temperature reductions. However, formation of alloys does not seem very likely in our case. First, the reversibility of the formation of the active species of the $Cu/ZnO/SiO_2$ catalyst by successive reductive and inert treatments, makes the formation of alloys a less probable explanation. Furthermore, an activity increase after high temperature reduction has also been observed for the $Cu/MnO_x/SiO_2$ catalyst (fig. 1). Formation of Cu–Mn alloys is in principle possible, but it is less likely than that of Cu–Zn bronzes because of the following. Kapteijn et al. [17] reported that during the reduction of supported and unsupported manganese oxides, preferentially a transformation to MnO occurs. The reduction of MnO towards metallic manganese ($\Delta G^0 = +125$ kJ/mol at 700 K) is thermodynamically much less favourable than the transformation of ZnO into metallic zinc ($\Delta G^0 = +85$ kJ/mol at 700 K). Our TPR results indeed suggest some ZnO reduction in $Cu/ZnO/SiO_2$ catalysts, but halting of MnO_x reduction at the MnO stage in $Cu/MnO_x/SiO_2$ catalysts implying that the formation of Cu–Mn alloys is unlikely under these conditions. The fact that the $Cu/MnO_x/SiO_2$ catalyst shows behaviour that is comparable to the $Cu/ZnO/SiO_2$ catalyst also makes it unlikely that the formation of alloys plays a key role in activity increase during reductive treatments. The XRD data of the $Cu/ZnO/SiO_2$ catalyst reduced at ~700 K (presented in fig. 3, line 2) more or less confirms this assumption. The 2θ value of the most important diffraction line (~43°) is a diffraction line characteristic for fcc-copper with Cu $K\alpha$ radiation [3]. If extensive formation of Cu–Zn alloys would occur, a shift of this diffraction line would be expected. This is not observed in this case nor in a previous study performed by our group. Finally, coverage of the copper particles by zinc oxide would give rise to a decrease in copper surface area, whereas we observe an increase with reduction temperature.

It is clear, however, that the silica supported catalysts reported in this paper show increased stability against over-reduction and sintering. Unsupported Cu/ZnO catalysts prepared by homogeneous precipitation are known to irreversibly sinter during reduction at temperatures above 600 K [18]. Possibly, the $Cu/ZnO/SiO_2$ catalyst exhibits increased resistance towards formation of Cu–Zn alloys as well.

Clausen et al. [19] reported a change of apparent copper co-ordination number of an unsupported Cu/ZnO catalyst and concomitant change in active surface area upon changing the oxidation potential of the gas phase. This is attributed by the authors to wetting/non-wetting phenomena. It is proposed that under relatively reducing conditions the copper atoms form disk-like shaped particles, more or less epitaxially grown on a zinc oxide phase, more or less in agreement with our proposal. Under less reducing conditions, however, they propose the formation of spherical copper particles. This is in contrast to our XRD results that suggest transformation of copper into an oxidised state. It should be noted, however, that this catalyst was reduced at 493 K, the lower limit of the range of reduction temperatures studied in this paper. The gas phase composition and treatment temperature were also drastically different from ours making direct comparison difficult. An additional complication is the fact that methanol synthesis gas mixtures always contained CO_2 in contrast to our methanol synthesis experiments, performed in a CO/H_2 mixture.

The very detection limit of the XRD technique, ca. 3 nm diameter crystallites, implies that the reversible migration of the copper particles of the promoted catalyst is not restricted to two-dimensional epitaxial platelets. Three-dimensional Cu^0 crystallites clearly are formed upon high temperature reduction and they disappear after treatment in inert atmosphere.

The N_2O chemisorption results confirm this picture. The copper surface area increases steadily in proportion with reduction temperature for the promoted catalyst, which was previously ascribed to formation of highly active two-dimensional copper particles on top of the mixed copper–zinc oxide matrix. A short evacuation period at the reduction temperature causes a decrease of the measured copper surface area, probably due to the re-migration of copper species in the mixed oxide phase. However, longer evacuation times give rise to a much larger decrease in copper surface, which no longer can be due to just the disappearance of the epitaxial layers.

An additional complication arises from the N_2O chemisorption results of the unpromoted Cu/SiO_2 catalyst. All effects described above for the promoted catalyst are to a lesser extent also observed for the unpromoted one. Consequently, also the copper–silica system allows some form of migration of the copper phase, but in this case the (very minor amount) of additional reduced copper formed upon reduction at high temperatures does not give rise to enhanced activity in the investigated reactions.

This, combined with the observation that the optimum reduction temperature for the $Cu/ZnO/SiO_2$ catalyst is much higher than for unsupported Cu/Zn or Cu/Cr catalysts [8–10] suggests that a ternary Cu–Zn–Si phase may be involved. Alternatively, the role of the support merely could be to prevent sintering of the mixed oxide phase already at sub-optimum reduction temperatures, whereas such sintering does cause the low temperature optimum for the unsupported catalysts.

The question remains, why the epitaxial copper particles show such high activity. In our view this can be due to, e.g., structure sensitivity, i.e. the epitaxy forcing copper to expose specific planes or causing some beneficial deformation of the Cu platelets. Alternatively, the contact with the ZnO could produce some activity enhancing charge transfer or render the Cu readily oxidisable [12] by, e.g., the synthesis gas reaction mixture; or maybe the enhanced occurrence of copper–zinc interfaces is the crucial factor when a dual site mechanism is operating. It is our intention to look further into these questions also studying the influence of more realistic reaction conditions.

4. Conclusions

A profound effect of reduction temperature on methyl acetate hydrogenolysis activity has been observed for Cu/ZnO/SiO_2 and Cu/MnO_x/SiO_2 catalysts in contrast with results obtained with unpromoted Cu/SiO_2. An even stronger effect of catalyst reduction temperature on methanol synthesis activity has been found for the zinc containing catalyst. The effect of reduction temperature on hydrogenolysis and methanol synthesis activity can be at least partially reversed, by a treatment in inert atmosphere at high temperature. The effect of reduction temperature and inert treatments can be explained by a model suggesting reversible formation of epitaxial copper particles as proposed in literature.

The copper metal surface area of the zinc promoted catalyst as determined by N_2O chemisorption, shows a steady rise upon reduction in the range of 600–750 K when the catalyst is evacuated at 600 K preceding the characterisation. Considerable decrease in copper surface area is observed after prolonged evacuation at reduction temperature prior to N_2O chemisorption. The copper metal surface area of the unpromoted Cu/SiO_2 catalyst also increases slightly going from 600 K reduction temperature to 700 K, where it more or less stabilises. Prolonged evacuation of the Cu/SiO_2 catalyst prior to N_2O chemisorption results in decrease of measured copper surface areas, but to a much lesser extent than in case of the Cu/ZnO/SiO_2 catalyst.

The transformation observed during evacuation preceding copper surface area measurements for the Cu/ZnO/SiO_2 catalyst is more or less confirmed by the X-ray diffraction experiments. A clear transition from copper in the metallic state to an oxidised state that is in between that of Cu_2O and CuO is observed after treatment in inert atmosphere at high temperatures. It is shown that this transformation can be reversed with a reductive treatment under relatively mild conditions.

These results combined with the ester hydrogenolysis and methanol synthesis experiments with treatments in inert gas atmosphere, suggest reversible migratory behaviour of the proposed epitaxial copper particles.

This implies that, depending on the treatment given before the characterisation, part of the copper could be present either as epitaxial metallic particles on top of zinc oxide or dissolved in the zinc oxide matrix in the ionic state.

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