

THE REDUCTION BEHAVIOUR OF SILICA-SUPPORTED COPPER CATALYSTS PREPARED BY DEPOSITION-PRECIPITATION

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ABSTRACT

The reduction behaviour of silica-supported copper catalysts prepared by homogeneous deposition-precipitation has been studied by temperature-programmed reduction (TPR), differential thermogravimetry (DTG), in-situ diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy, and evolved gas analysis (EGA).

Preparation by homogeneous deposition-precipitation produces catalyst precursors in which the copper ions are highly dispersed over the silica support, and which show reduction behaviour similar to that of the mineral copper hydrosilicate, chrysocolla. Calcination of the catalyst precursors at 700 K leads to decomposition of the copper hydrosilicate, causing subsequent reduction to occur at a lower temperature.

During initial reduction of the chrysocolla-like precursors, the consumption of hydrogen and the release of water are not synchronous. Water formed by the reduction is retained in the catalyst, probably due to participation of water in a reorganization of the silica support. During the second reduction stage of silica-supported copper oxide particles, formed by previous reduction and re-oxidation of the chrysocolla-like precursor, the consumption of hydrogen and the release of water do occur simultaneously.

Finally, the influence of the composition of the reducing gas atmosphere on the reduction behaviour of the catalysts has been investigated. Increasing the hydrogen concentration in the reducing gas mixture from 5 to 50 vol.% does not affect the on-set of the reduction reaction, whereas addition of about 2.4 vol.% H₂O to the reducing gas mixture leads to significantly higher on-set temperatures. Once initiated, the reduction proceeds more rapidly at higher hydrogen partial pressures.

INTRODUCTION

For preparation of supported metal catalysts, an optimum dispersion of the metal over the support is desirable. A large number of preparation strategies aiming at high dispersion of the metal precursors has been

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described in the literature. Once the metal precursor has been brought onto the support, the catalyst is generally subjected to a thermal activation procedure (calcination, reduction, oxidation). The state of the highly dispersed metal precursor is likely to change during such treatments. Calcination (oxidation) may cause dehydration and decomposition of the metal species, whereas reduction will lead to formation of metal atoms which tend to agglomerize into (small) metal particles dispersed over the support. Extensive characterization of catalysts in different stages of the preparation and the pretreatment may facilitate elucidation of the relation between the catalytic properties and the procedures used during preparation and thermal activation. Temperature-programmed reduction provides a rapid 'fingerprint' of the dispersed metal species in the catalyst precursor. Detailed characterization of the reduction behaviour may provide an insight into the processes occurring during activation of the catalysts.

In a previous paper [1], we have dealt with the influence of the method of preparation on the reduction behaviour of differently prepared silica-supported copper catalysts. Preparation by means of homogeneous deposition-precipitation gives rise to formation of 'chrysocolla-like' catalyst precursors [1,2]. Chrysocolla is a mineral copper hydrosilicate with a high specific surface area and a two-dimensional dispersion of copper ions over corrugated silica sheets [3,4]. Since the formation of chrysocolla-like catalyst precursors allows the preparation of copper-on-silica catalysts of high metal dispersion (even at elevated metal loadings), we studied the reduction behaviour of these catalysts in more detail. The catalysts were prepared by homogeneous deposition-precipitation both under atmospheric and hydrothermal conditions. In order to investigate the effect of a thermal pretreatment on the reduction behaviour, the catalysts were either dried at 400 K or calcined at 700 K. To identify the processes occurring during temperature-programmed reduction of the catalyst precursors, the reduction behaviour was studied by several independent techniques. The reduction process was monitored by measurement of the consumption of hydrogen (TPR) or the weight loss (DTG) of the solid sample. Evolved gas analysis (EGA) was used to detect the release of water during reduction of the catalysts. In-situ diffuse reflectance infrared Fourier-transform (DRIFT) spectroscopy was used to study the effect of calcination and reduction on the structure of the solid catalysts. Finally, the partial pressures of hydrogen and water vapour were varied to study their effects on the reduction behaviour of the silica-supported copper catalysts.

EXPERIMENTAL

A series of catalysts was prepared by homogeneous deposition-precipitation of copper ions onto the surface of suspended silica (Aerosil; surface

area $230 \text{ m}^2 \text{ g}^{-1}$, Degussa), using the decomposition of urea at 363 K [2,5]. The copper loading was varied from 1 to 40 wt.%. The catalysts were coded CuU01 to CuU40, according to their metal loading. The decomposition of urea was also performed at 525 K under hydrothermal conditions. The catalyst prepared via this procedure had a copper loading of approximately 40 wt.% and was coded CuU40hy525. The influence of the conditions during the urea hydrolysis on the chemical and physical properties of the catalysts has been described in detail elsewhere [2]. The precipitates were thoroughly washed with distilled water and subsequently dried in air for at least 16 h at 400 K. The dried samples were ground to a sieve fraction of 0.3–0.4 mm.

With the TPR-experiments a mixture of 10 vol.% H_2/Ar (Hoek Loos) was passed through the catalyst sample at a flow rate of 50 ml min^{-1} . The catalyst sample (about 30 mg) was supported on a glass filter inserted in a quartz reactor (internal diameter, 8 mm). Water formed during the reduction was removed by a cold trap placed behind the reactor. The hydrogen consumption was measured quantitatively by a Thermal Conductivity Detector (Gow Mac HWD, model 40-202). The dried samples were subjected to the temperature-programmed reduction without any further pretreatment, whereas the calcined samples were dehydrated in situ at 700 K in 10 vol.% O_2/Ar . During temperature-programmed reduction the temperature was linearly increased (3.4 K min^{-1}) from 298 to 973 K. Optionally a second temperature-programmed reduction was performed after in situ re-oxidation of the sample. Re-oxidation was done by exposing the reduced catalyst to a flow of 10 vol.% O_2/Ar (50 ml min^{-1}) at room temperature, followed by raising the temperature to 700 K in this atmosphere. The oxidation was continued for at least 1 h at 700 K before cooling to room temperature in the oxygen-containing gas flow. Between oxidation and reduction treatments the reactor was purged with He (50 ml min^{-1}) at room temperature.

The influence of the hydrogen concentration on the reduction rate was investigated using the CuU30 catalyst. The hydrogen consumption was measured during reduction in 5, 10, 25 and 50 vol.% H_2/Ar . The total flow rate (50 ml min^{-1}) and temperature gradient (3.4 K min^{-1}) were kept constant. Second temperature-programmed reduction was performed after in situ re-oxidation as described above.

The influence of water vapour on the reduction behaviour of the CuU30 catalyst was investigated by addition of water vapour to the reducing gas mixture. At room temperature, the 10 vol.% H_2/Ar flow was saturated with water vapour (about 2.4 vol.%). After passing through the reactor, the reducing gas was dried over a Permapure column before entering the thermal conductivity detector. The total flow rate and temperature gradient were unaltered. Second temperature-programmed reduction was performed after in situ re-oxidation as described above.

With differential thermogravimetry (DTG) the weight loss caused by the reduction was measured using a thermobalance (Mettler TA2). Prior to

reduction, the catalyst samples (about 60 mg) were always dehydrated (calcined) in situ in 10 vol.% O₂/Ar at 700 K. Reduction was performed by heating the catalyst, in 50 ml min⁻¹ 10 vol.% H₂/Ar (Hoek Loos), from 298 K up to 973 K at a linear heating rate of 5 K min⁻¹. After in situ re-oxidation, the samples were subjected to a second reduction under identical conditions.

Evolved gas analysis (EGA) was performed during the reduction of catalyst precursors previously calcined in situ at 700 K in 10 vol.% O₂/Ar. The evolution of water during temperature-programmed reduction of the catalysts (about 1.5 g) was measured with a mass spectrometer (Leybold/Heraeus, Q200). With EGA the catalysts were reduced in a flow of pure hydrogen (50 ml min⁻¹) at a heating rate of 10 K min⁻¹.

For DRIFT spectroscopy the dried catalyst samples were powdered in an agate mortar, then diluted to approximately 20 wt.% in potassium chloride. A 'Praying Mantis' type diffuse reflectance accessory with a HVC-DR2CN reaction chamber (Harrick Scientific Corp.) was used. The infrared spectra were obtained with a Nicolet 7199 FT-IR spectrometer equipped with a medium bandpass MCT detector cooled by liquid nitrogen. The diluted samples were exposed to a small flow of either oxygen (purity 99.8%) or hydrogen (purity 99.98%). The temperature of the sample cup was increased step-wise to 820 K (as indicated in the Figures), although with hydrogen this maximum temperature could not be reached due to the high thermal conductivity of hydrogen. Furthermore, the actual temperature of the catalyst may have been 100–200 K below the temperature of the heating element due to the poor thermal conductivity of the samples. While keeping the catalyst at elevated temperature, one thousand interferograms were added and Fourier-transformed to obtain a resolution of 4 cm⁻¹. The spectra were standardised against a pure potassium chloride sample at the same temperature to correct for the reflectance of the background.

RESULTS

The precipitation of copper ions onto a suspended silica support by urea hydrolysis produces catalyst precursors which exhibit reduction profiles similar to that of the mineral copper hydrosilicate, chrysocolla [2,6]. It has been shown that the metal loading (up to 40 wt.%) does not affect the reduction behaviour of these catalyst precursors [2]. The structure of chrysocolla has been described by van Oosterwijck-Gastuche [3]. Despite the fact that the catalyst precursors are rather similar, some observations are more pronounced with the CuUhy-catalyst and, therefore, we shall deal with results on the reduction behaviour of both the CuU30 and the CuU40hy525 catalyst.

The reduction behaviour of these catalysts has been monitored by application of various techniques. As it was envisioned that the composition of the reducing gas atmosphere would affect the reduction process, we shall describe the influence of the partial pressure of hydrogen and water vapour on the reduction rate, at the end of this section.

Temperature-programmed reduction

The effect of the pretreatment on the reduction profile of catalyst CuU30 is shown in Fig. 1. Reduction of the dried catalyst precursor leads to a large hydrogen consumption peak entered at 485 K and a small peak at 530 K (Fig. 1a). After calcination for 2 h at 700 K, TPR shows only one hydrogen consumption peak at 460 K (Fig. 1b). It is known [3] that dehydration of the chrysocolla structure leads to the formation of copper oxide highly dispersed over the silica support. Apparently this copper oxide is more readily reduced than the copper ions in the original precursor. A second reduction, after intermediate re-oxidation at 700 K, shows the on-set of hydrogen consumption at 380 K with a maximum at 440 K (Fig. 1c). The hydrogen consumption peak at 440 K is characteristic of small copper oxide particles dispersed over the silica support [1]. The hydrogen consumption profile of the dried CuU40hy525 catalyst precursor also shows two peaks at 485 and 530 K (Fig. 2a). However, comparison with CuU30 reveals that, although the temperatures of the peak maxima are identical for both samples, with CuU40hy525 the hydrogen consumption at 530 K has significantly increased at the expense of the peak at 485 K. Calcination of CuU40hy525 for 2 h at 700 K,

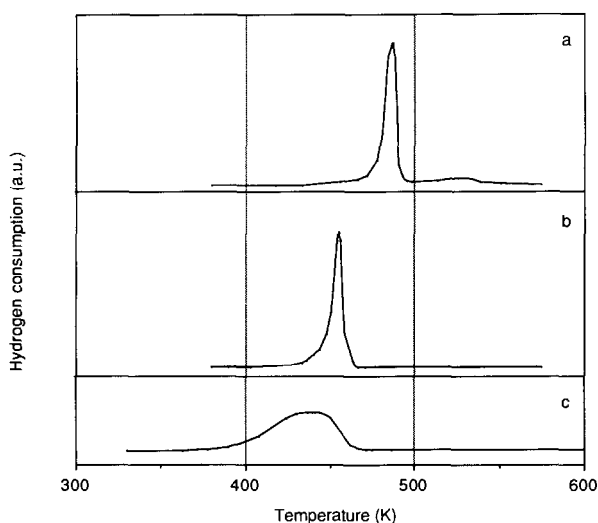


Fig. 1. TPR-profiles of CuU30: a, dried; b, calcined; c, second reduction.

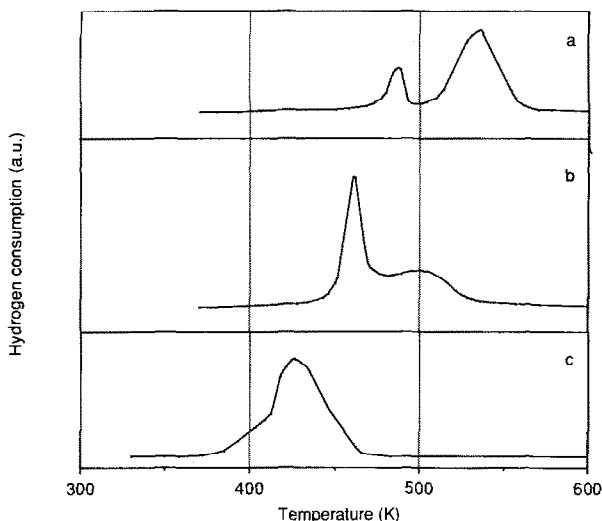


Fig. 2. TPR-profiles of CuU40hy525: a, dried; b, calcined; c, second reduction.

and subsequent TPR, results in a hydrogen consumption peak at 460 K with a shoulder at 500 K (Fig. 2b). A second reduction of catalyst CuU40hy525, after re-oxidation at 700 K, shows a single hydrogen consumption peak at about 440 K, similar to CuU30 (Fig. 2c).

DRIFT spectroscopy

The state of the copper species present in the catalyst precursors has been monitored by in-situ DRIFT spectroscopy during calcination in pure oxygen and reduction in pure hydrogen. Since CuU and CuUhy catalyst precursors show similar results, we shall only deal with spectra obtained with catalyst CuU40hy525 which exhibits the most intense absorption bands.

In Fig. 3 the effect of reduction on the spectra of a dried, but not calcined, catalyst CuU40hy525 is shown. Two hydroxyl-stretch bands are observed at 3740 and 3610 cm^{-1} (Fig. 3a). The band at 3740 cm^{-1} is due to isolate silanol groups present at the surface of the silica support [7]. The band at 3610 cm^{-1} is caused by copper-bonded OH-groups in the chrysocolla structure [6]. Besides these bands in the hydroxyl stretch-region, the dried catalyst also shows a band at 690 cm^{-1} which disappears upon calcination at 827 K, as well as upon reduction at 623 K (Fig. 3b). For basic copper nitrate, Secco and Worth [8] reported a Cu-O-H deformation vibration at 675 cm^{-1} . Tarte [9] investigated the frequency of OH vibrations in a variety of copper hydroxy salts in more detail. Based on frequency-shifts following OH-OD exchange, the band at 677–684 cm^{-1} was assigned unequivocally to the planar deformation vibrations of OH-groups associated with Cu-ions (δ Cu-O-H) [9]. The bands at 3610 and 690 cm^{-1} are,

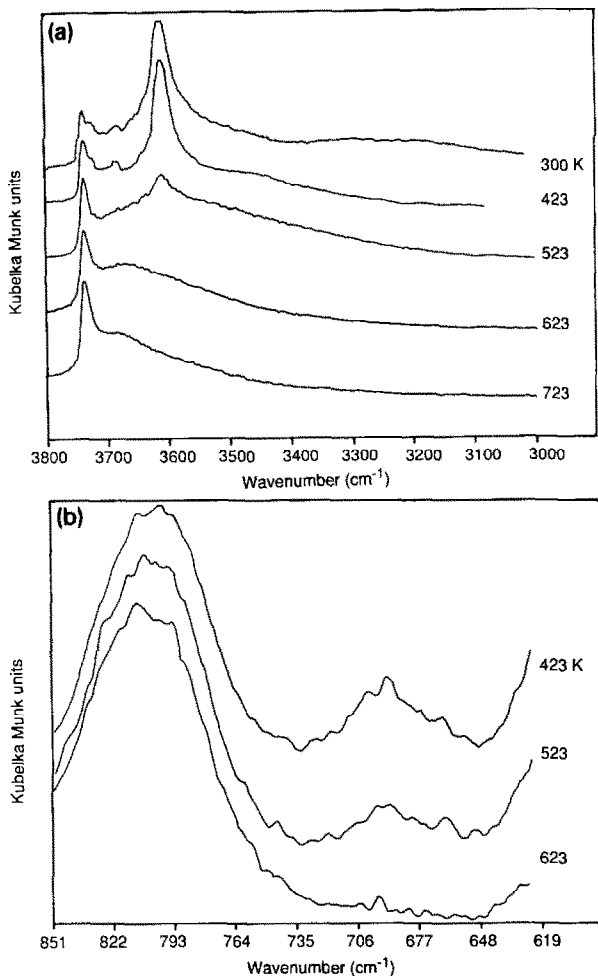


Fig. 3. Kubelka-Munk plot of dried CuU40hy525 during reduction at indicated temperature; 1a, OH-stretch vibrations ($3800\text{--}3000\text{ cm}^{-1}$ region); b, OH-planar deformation vibrations ($850\text{--}620\text{ cm}^{-1}$ region).

therefore, ascribed to the same chrysocolla-associated surface hydroxyl groups, so these bands can be used to monitor the presence of this compound in the catalyst precursor.

Upon reduction of the dried catalyst in hydrogen, the bands at 3610 cm^{-1} and 690 cm^{-1} disappear, whereas the band at 3740 cm^{-1} increases (Fig. 3). From the spectra recorded at increasingly higher temperatures it is clear that the chrysocolla-associated hydroxyl groups are removed during reduction of the dried catalyst precursor, starting at 523 K. During reduction, the copper atoms agglomerate into silica-supported metal particles, leading to denudation of the silica support and causing an increase of the silanol-band at 3740 cm^{-1} . Since the bands at 3610 cm^{-1} and 690 cm^{-1} due to the chrysocolla-like structure of the catalyst precursor show identical behaviour, we shall de-

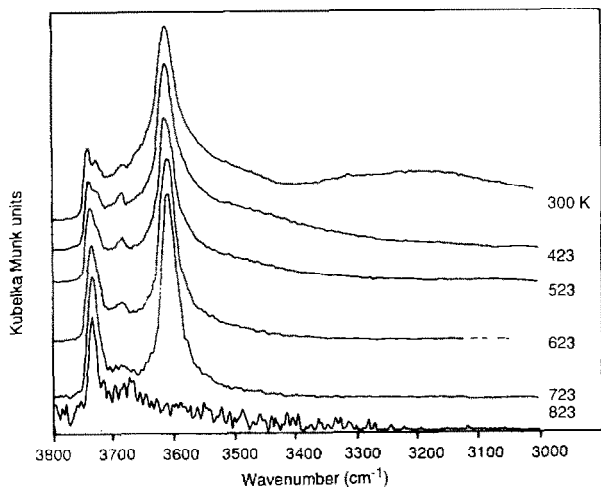


Fig. 4. Kubelka–Munk plot of CuU40hy525 during calcination at indicated temperatures.

scribe only the behaviour of the more intense hydroxyl-stretch band at 3610 cm^{-1} during calcination and subsequent reduction.

The DRIFT spectra obtained during calcination of sample CuU40hy525 at increasingly higher temperatures are shown in Fig. 4. Upon increasing the temperature, the broad band in the hydroxyl-stretch region ($3800\text{--}3000\text{ cm}^{-1}$) due to physisorbed water and hydrogen-bonded hydroxyl groups decreases. As a consequence the hydroxyl vibrations due to isolated silanol (3740 cm^{-1}) and to the copper-related hydroxyl groups of chrysocolla (3610 cm^{-1}) become more distinct. Upon calcination at 823 K the band at 3610 cm^{-1} disappears completely, whereas the intensity of the isolated silanol group strongly declines. The complete disappearance of the band at 3610 cm^{-1} indicates the decomposition of the chrysocolla structure to silica-supported copper oxide. Although the temperature of the sample during the recording of the spectra could not be assessed accurately (see Experimental), the spectra of Fig. 4 indicate a rather abrupt decomposition of the copper hydrosilicate structure at temperatures above 723 K .

After calcination at 823 K , the CuU40hy525 sample was cooled to room temperature in oxygen, degassed, and subsequently exposed to a flow of hydrogen. The spectra obtained during the subsequent temperature ramp are shown in Kubelka–Munk units (Fig. 5). The spectrum obtained at low temperature essentially shows the isolated silanol group at 3740 cm^{-1} . At temperatures where reduction of the catalyst precursor is known to proceed (about 450 K), the intensity of the band at 3740 cm^{-1} increases and a broad band appears in the region $3700\text{--}3000\text{ cm}^{-1}$. This band is due to water set free by reduction of the copper ions. At higher temperatures it disappears and the band due to silanol groups becomes even more intense. This can be explained by agglomeration of copper atoms into metal particles, leading to

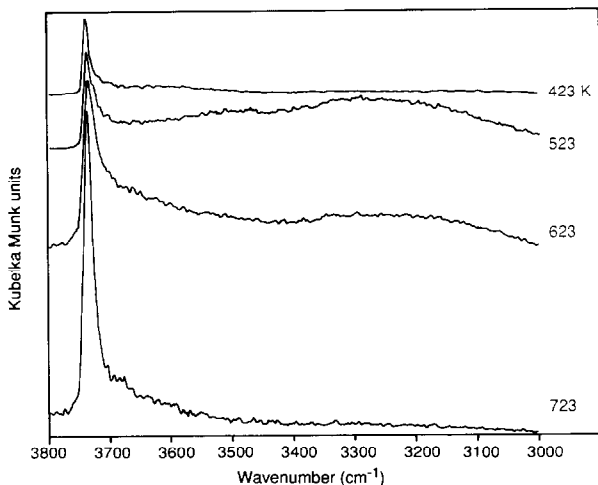


Fig. 5. Kubelka–Munk plot of a pre-calcined CuU40hy525 catalyst during reduction at indicated temperatures.

denudation of the silica surface and reappearance of hydroxyl-groups on the silica surface.

From the intensity changes of the 3610 and 690 cm^{-1} bands recorded by in-situ DRIFT spectroscopy during calcination and reduction, it can be concluded that the ‘chrysocolla-like’ structure of the catalyst precursors is decomposed by calcination at 823 K as well as by direct reduction at 550 K .

Differential thermogravimetry and evolved gas analysis

The differential weight loss curves obtained during the first and second reduction stages of the CuU30 and CuU40hy525 catalyst are shown in Figs. 6 and 7. Prior to reduction in the thermobalance, the samples were calcined in situ at 700 K to avoid weight changes due to desorption of water formed by decomposition of the hydrosilicate structure. Consequently the weight changes shown in Fig. 8 are due entirely to the release of water formed during the reduction.

The DTG-results show that the weight loss during first reduction of both catalyst precursors proceeds in two peaks at 460 and 530 K . With the CuU30 catalyst the major weight loss occurs at 460 K (Fig. 6a), whereas with the CuU40hy525 catalyst the weight loss at 530 K is more pronounced (Fig. 7a). Comparison of these DTG-results to TPR-profiles measured during first reduction of the calcined catalysts (Figs. 1b and 2b) shows a striking difference, suggesting that the consumption of hydrogen and the release of water do not proceed synchronously. In fact, the DTG-curves obtained upon reduction of the calcined catalysts show an unexpected resemblance to the hydrogen consumption profiles measured during reduc-

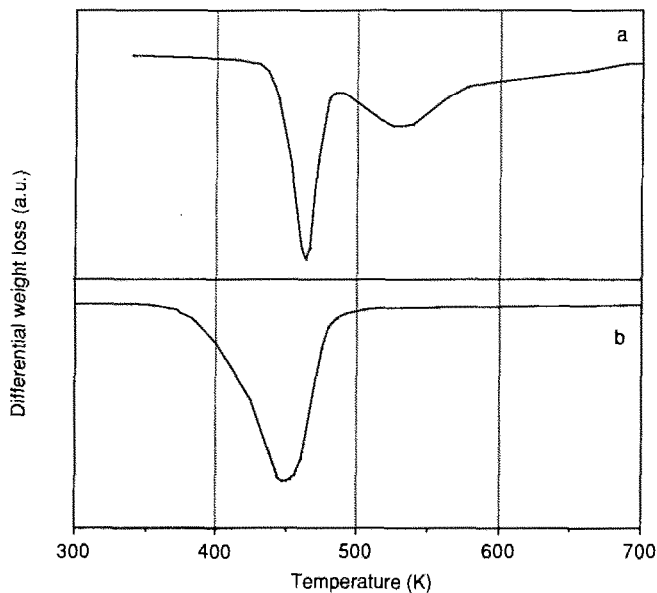


Fig. 6. DTG-profiles of CuU30: a, first reduction; b, second reduction.

tion of the dried catalysts (Figs. 1a and 2a). The comparison of DTG and TPR results indicates the important effect of water on the reduction behaviour, as described in more detail in the Discussion section.

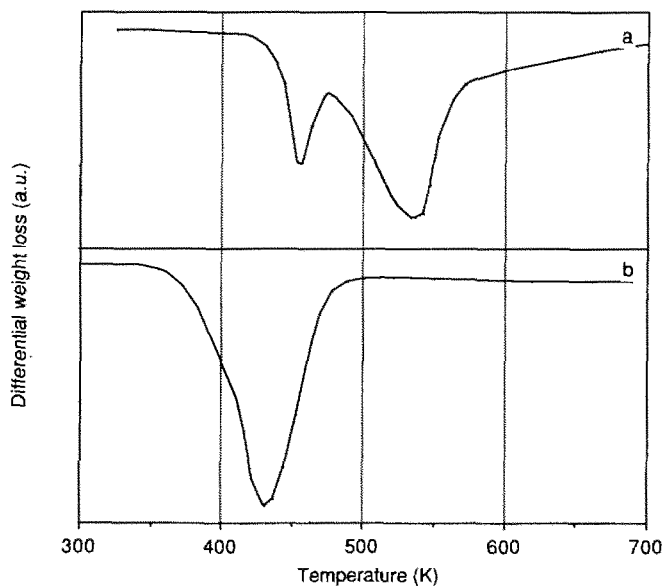


Fig. 7. DTG-profiles of CuU40hy525: a, first reduction; b, second reduction.

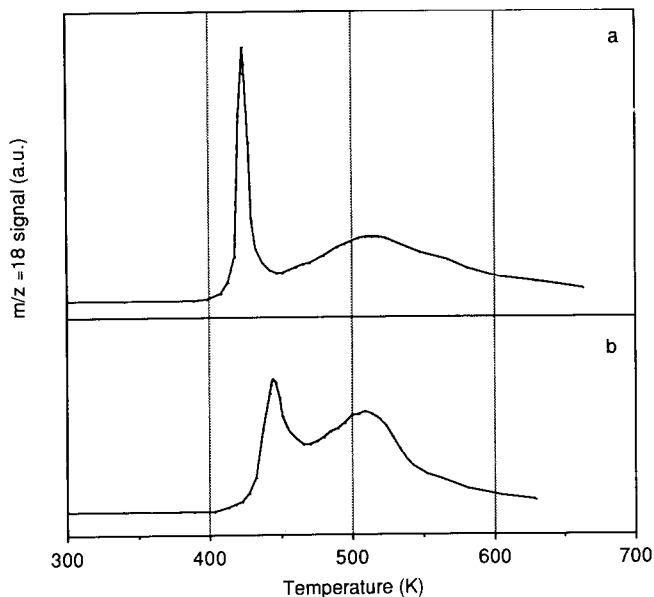


Fig. 8. Evolved gas analysis: a, first reduction of calcined CuU30; b, first reduction of calcined CuU40hy525.

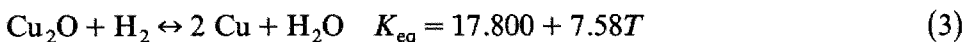
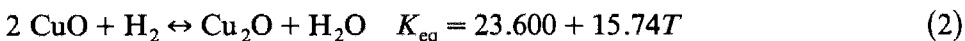
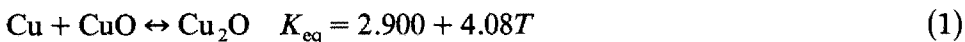
Second reduction of both catalysts shows a single weight-loss peak with an on-set temperature of 380 K and a peak maximum at 440 K (Figs. 6b and 7b). Upon second reduction, the DTG-curves are close to the corresponding TPR-profiles suggesting that in this situation the hydrogen consumption and the weight loss do occur simultaneously.

To investigate the consumption of hydrogen and the release of water during the TPR-experiments in more detail we performed evolved gas analysis. The difference in the TPR and DTG results obtained during the first reduction might be attributed to the fact that, because of the experimental set-up, the gas flow did not pass through the catalyst sample in the DTG experiments, whereas in the EGA and TPR experiments it did. The profiles of the evolved water curves are similar to the weight loss curves obtained in the thermobalance, indicating that, as expected, the weight loss is due solely to release of water (Fig. 8). The slight shift in peak positions as compared to TPR is due to different experimental conditions (heating rate, amount of catalyst, dynamic gas atmosphere, etc.).

Combination of the results of TPR, DTG, and EGA leads to the conclusion that, during first reduction of the calcined catalysts, the hydrogen consumption and the release of water do not proceed simultaneously. Unexpectedly the DTG-curves obtained during reduction of the calcined catalysts show close resemblance to the TPR-profiles obtained during reduction of the dried but uncalcined catalyst precursors. During second reduction of the catalysts the weight loss and the hydrogen consumption do occur simultaneously.

Effect of hydrogen and water vapour pressure on the reduction behaviour

In addition to characterization of the reduction behaviour by several independent techniques, we explored the effect of hydrogen and water vapour pressures on the TPR-profiles. To establish whether the change in dynamic gas atmosphere affects the reduction behaviour through a shift of the thermodynamic equilibria, we shall first consider the equilibrium between copper metal, copper(I) oxide and copper(II) oxide, and between these components and hydrogen and water vapour. Since no thermodynamic data on chrysocolla are available, we use copper(II) oxide to represent the catalyst precursor. Since high accuracy is not needed, the temperature dependence of the heats of formation and the entropies [10] are not taken into account.



The positive value of the equilibrium constant for reaction (1), where no gas phase reactants participate, indicates that the equilibrium is completely at the right-hand side. As a result copper and copper(II) oxide cannot coexist in equilibrium; they react to copper(I) oxide until either copper or copper (II) oxide has been depleted. The equilibrium constants for reactions (2) and (3) show that these two equilibria are completely at the right-hand side. For the reduction at 473 K of copper(I) oxide to copper, the ratio of the water and hydrogen partial pressures must be lower than 7.7×10^9 , which is the case for all practical TPR conditions. Thus, in the presence of hydrogen, thermodynamic analysis predicts complete reduction of both copper oxides to the metal. However, the following experiments shows that the kinetics of the reduction reaction are strongly affected by the partial pressures of hydrogen and water vapour.

Figures 9 and 10 show the influence of the hydrogen concentration on the reduction of CuU30. During the first reduction the on-set of the low-temperature reduction peak (about 450 K) is not affected by the hydrogen partial pressure, whereas the position of the peak maximum is shifted to lower temperatures with increasing hydrogen concentrations (Fig. 9). By contrast, the on-set temperature and position of the hydrogen consumption peak at about 530 K are not affected by the hydrogen concentration. However, the relative size of this peak as compared to the low-temperature peak increases as the hydrogen partial pressure is raised. We suggest that higher hydrogen partial pressures cause a more rapid reduction of copper ions, leading to a temporarily higher water vapour pressure within the pores of the catalyst.

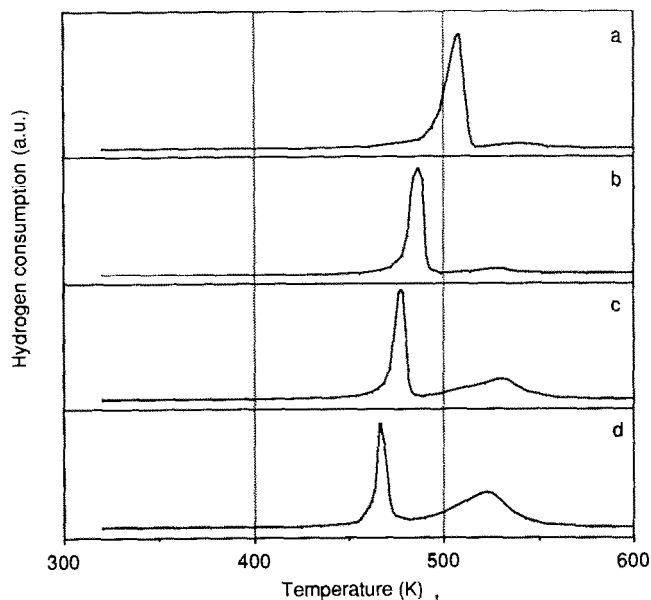


Fig. 9. The influence of the hydrogen concentration of the first reduction of dried CuU30: a, 5 vol.% H₂/Ar; b, 10 vol.% H₂/Ar; c, 25 vol.% H₂/Ar; d, 50 vol.% H₂/Ar.

Due to the increased water vapour pressure, a larger amount of residual copper species can only be reduced at a higher temperature, i.e. 530 K (see Discussion section).

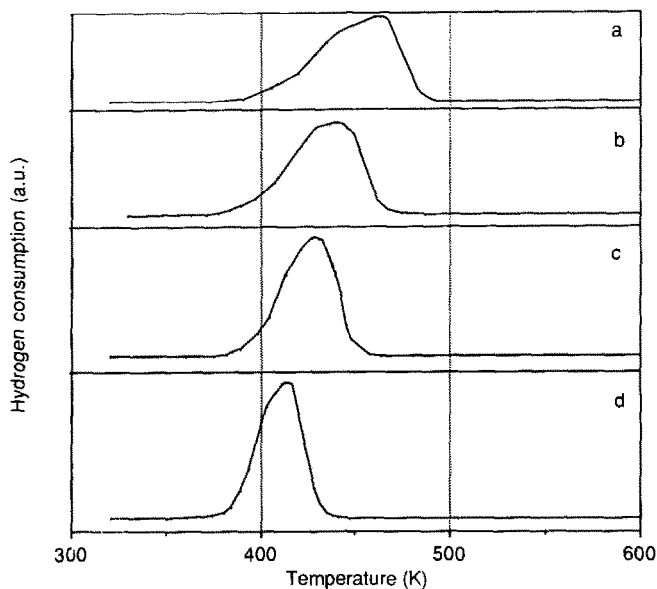


Fig. 10. The influence of the hydrogen concentration on the second reduction of CuU30: a, 5 vol.% H₂/Ar; b, 10 vol.% H₂/Ar; c, 25 vol.% H₂/Ar; d, 50 vol.% H₂/Ar.

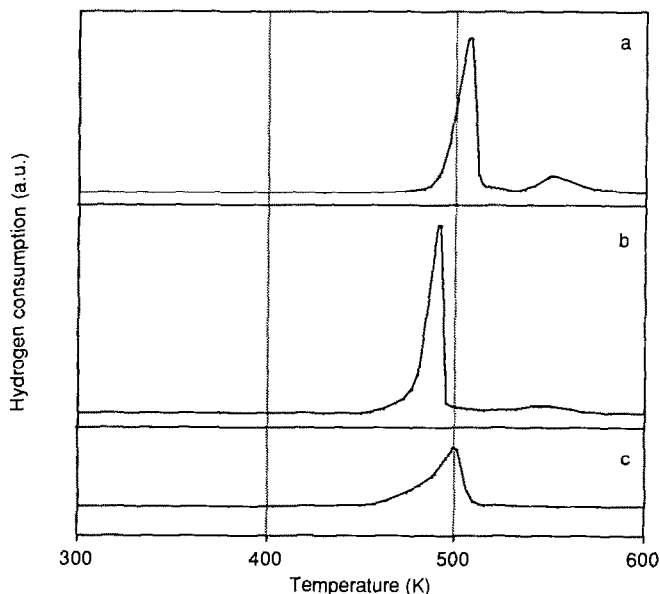


Fig. 11. TPR-profiles of CuU30 in 10 vol.% H_2/Ar containing about 2.4 vol.% H_2O : a, dried; b, calcined; c, second reduction.

After intermediate re-oxidation, the second TPR shows that increasing the hydrogen concentration shifts the peak maxima to lower temperatures, whereas, within experimental error, the reduction on-set temperature remains constant at about 380 K (Fig. 10). Repeating the oxidation–reduction cycle does not affect the reduction profiles obtained in subsequent TPR experiments.

Addition of water vapour (about 2.4 vol.%) to the reducing gas, i.e. 10 vol.% H_2/Ar , results in a shift of the hydrogen consumption profile to higher on-set temperatures (Fig. 11). Temperature-programmed reduction of the dried CuU30 catalyst with the wet reducing gas shows hydrogen consumption at 510 K and 550 K, whereas reduction with dry gas occurs at 485 K and 530 K (Fig. 1). Wet reduction of the calcined CuU30 catalyst shows hydrogen consumption at 490 K, as well as the re-appearance of the high-temperature reduction peak at 550 K. The second reduction, after intermediate oxidation, is also significantly retarded by the presence of water in the reducing gas atmosphere. Both the reduction on-set (450 K) and the hydrogen consumption peak maximum (500 K) are shifted to higher temperatures (compare Figs. 1 and 11). It is thus concluded that the presence of about 2.4 vol.% H_2O in the reducing gas significantly retards the reduction of copper ions in both the chrysocolla-like catalyst precursor as well as the once reduced and re-oxidized copper catalyst.

DISCUSSION

The reduction behavior of dried and calcined catalysts

Comparison of the results obtained by TPR, DTG, and EGA after various pretreatments of the catalyst precursors provides an insight into the processes taking place during the reduction of the catalyst. The results with the calcined catalyst precursors show that the consumption of hydrogen and the release of water do not proceed synchronously. Compared with the hydrogen consumption, the release of water formed by the reduction is retarded. In fact, it has been found that the weight loss curves obtained during reduction of the calcined catalysts resemble closely the TPR-profiles obtained during reduction of the dried but uncalcined catalyst precursors. This indicates that during reduction of the dried catalyst precursor the progression of the reduction reaction is hampered by the slow release of water. The retarded release of water during first reduction of the catalyst precursors can be caused by different phenomena, viz., continuous adsorption-desorption giving rise to (slow) temperature-dependent transport of water molecules out of the pores, and/or participation of water in the reorganization of the silica support.

The slow transport of water out of the porous silica support might be ascribed to continuous adsorption and desorption at the pore walls. It is well known that the transport of molecules which exhibit a significant interaction with the pore wall, and thus a high residence time in the adsorbed state, is slow. The exponential dependence of the residence time on the temperature might lead to the second weight loss peak during the temperature-programmed experiments. Persorption of water molecules in narrow interstices in the silica, remaining after extraction of the copper(II) ions by the reduction, may also lead to a slow release of water occurring only at elevated temperatures.

Another explanation for the retention of water is the participation of water in the reorganization of the silica support. As described in more detail in a previous paper [2], reduction of the chrysocolla-like catalyst precursors is accompanied by a considerable decrease of the specific surface area. Upon first reduction, the specific surface area (S_{BET}) of catalyst precursor CuU30 decreases from 462 to 275 $\text{m}^2 \text{g}^{-1}$, whereas the specific surface area of CuU40hy525 decreases from 466 to 393 $\text{m}^2 \text{g}^{-1}$. During reduction the copper atoms agglomerate into three-dimensional metal particles and the total surface area of the silicate structure is decreased due to reorganization of the silica support. It is well known that water participates in the reactions (hydrolysis of siloxane bonds and polymerization of silanol groups), which proceed during this reorganization [11], explaining the retarded release of water during reduction of the catalyst precursor. The retarded release of

water is only observed during first reduction of the chrysocolla-like catalyst precursors.

Although the present results unequivocally show that the impeded release of water is associated with the presence of (freshly) calcined chrysocolla in the catalyst precursors, it is hard to distinguish between the above explanations.

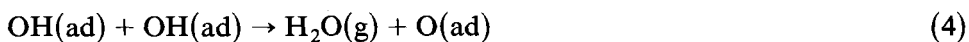
In the literature dealing with the reduction of silica-supported copper catalysts [5,12], the weight loss at 460 K is ascribed to the reduction of copper oxide, whereas the weight loss at 530 K is associated with the reduction of the more stable copper hydrosilicate. However, on the basis of our present results we propose an alternative explanation. The reduction behaviour of the catalyst precursors is very similar to that of the mineral copper hydrosilicate, chrysocolla. In this particular hydrosilicate all the copper ions are octahedrally surrounded by hydroxyl, water, and oxygen atoms belonging to the silicate structure [3]. Since TPR of the pure copper hydrosilicate also shows two hydrogen consumption peaks, at 460 and 530 K, it is probably incorrect to correlate these peaks to different copper species in the catalyst precursor (or mineral). As evidenced by DRIFT spectroscopy, dehydration of the chrysocolla structure during calcination in oxygen does not occur at temperatures below 600 K (Fig. 4). In a hydrogen atmosphere, however, the chrysocolla structure is reduced at temperatures below 600 K (Fig. 3). This implies that the copper(II) ions in chrysocolla are directly reduced without prior decomposition to copper oxide and water. Therefore, the two peaks in the hydrogen consumption profile cannot be due to sequential reduction of copper oxide and copper hydrosilicate, but merely indicate a discontinuity in the rate of reduction of the chrysocolla-like catalyst precursors. The relative contribution of the hydrogen consumption or weight loss peaks, at 460 and 530 K, to the total reduction of the catalysts depends on the preparation conditions, and the thermal pretreatment of the catalyst.

During second reduction of copper oxide on silica, as obtained by reduction and re-oxidation of the catalyst precursors, the hydrogen consumption and the release of water proceed synchronously in one peak centered at 440 K (Figs. 1c, 6b and 7b). As evidenced by DRIFT spectroscopy, and by other experimental data [5], the structure of the catalyst is irreversibly changed during its first reduction. Therefore, the copper oxide obtained by dehydration of the chrysocolla-like precursor exhibits a reduction behaviour different from that of the copper oxide obtained by reduction and re-oxidation of the same precursor.

The effect of the hydrogen and water vapour pressures on the reduction rate

We shall now discuss the influence of the composition of the reducing gas on the kinetics of the reduction reaction. The constant reduction on-set

temperature suggests that initiation of the reduction reaction does not depend on the hydrogen partial pressure within the range of 5 to 50 vol.%. The reduction on-set marks the temperature at which dissociation of molecular hydrogen becomes feasible, giving rise to formation of reactive (adsorbed) hydrogen atoms, capable of forming OH-groups at the surface of the copper precursor. The formation of OH-groups has been evidenced by in situ DRIFT spectroscopy (Fig. 5). Subsequent reaction of two OH-groups, Eqn. (4), or an OH-group and an adsorbed hydrogen atom, eq. (5), corresponds to reduction of the copper species.



As apparent from the different reduction on-set temperatures observed with the chrysocolla-like catalyst precursor (about 450 K) and the silica-supported copper oxide particles obtained after reduction and re-oxidation (about 380 K), the ease of hydrogen dissociation depends on the state of the copper catalyst. Dissociation of molecular hydrogen on the chrysocolla surface clearly requires a higher activation energy than dissociation on the supported copper oxide particles.

After initiation of the reduction, at an on-set temperature controlled by the state of the copper ions at the silica support, the reduction reaction proceeds at a rate determined by the hydrogen partial pressure. The reduction proceeds faster with increasing hydrogen pressures, indicating that the thermally-activated dissociation of hydrogen is no longer rate-determining. Apparently, small copper (metal) particles being formed in the initial stages of the reduction act as catalytic centres for the dissociation of molecular hydrogen. In fact, the reduction kinetics of both bulk [13] and supported copper oxide [14] indicate an autocatalytic reduction according to the nucleation model of ref. 15. By increasing the hydrogen partial pressure the amount of adsorbed hydrogen atoms is raised, causing the net reduction to proceed at a higher rate. It is well documented that the rate of reduction of copper oxide shows a first-order dependence with respect to the hydrogen concentration [13,16,17].

The addition of about 2.4 vol.% water to the reducing gas mixture of 10 vol.% H₂/Ar results in a significant retardation of the on-set of reduction. The effect of water vapour on the initiation of the reduction is probably due to adsorption of water at the surface of the catalyst, blocking sites needed for hydrogen dissociation [18]. The adsorbed water may be present at the catalyst surface either as hydroxyl groups or as strongly held molecular water. Only above a certain temperature does desorption of water occur, releasing the sites needed for dissociation of hydrogen and marking the on-set of the reduction reaction. Measurements by Delmon et al. [18] on the reduction of bulk copper oxide by hydrogen showed activation energies of

59–71 kJ mol⁻¹, in good agreement with the value reported by Gentry et al. of 67 ± 10 kJ mol⁻¹ [19]. The higher activation energy reported by Delmon was found when metallic copper nuclei were present, accelerating the reduction and thereby causing a higher in-situ water vapour pressure. Thus both the addition of water to the reducing gas atmosphere, and rapid in-situ formation of water as a product of the reduction reaction result in higher activation energies for reduction of copper oxide by hydrogen. With TPR experiments the addition of water to the reducing gas atmosphere shifts the on-set of reduction to higher temperatures (Fig. 11), whereas in-situ formation of water, indirectly varied by using different hydrogen partial pressures, affects the progression of the reduction reaction reflected in the TPR-profile (Fig. 9).

CONCLUSIONS

The reduction behaviour of silica-supported copper catalysts, prepared by homogeneous deposition–precipitation, is identical to that of the mineral copper hydrosilicate, chrysocolla. Furthermore, characterization of the catalyst precursors by IR spectroscopy shows the presence of two typical OH-absorption bands at 3610 and 690 cm⁻¹, also observed in chrysocolla. It is, therefore, concluded that preparation of the silica-supported copper catalysts by homogeneous deposition–precipitation gives rise to the formation of chrysocolla-like catalyst precursors. The precipitation conditions affect the exact TPR-profile, in that hydrothermally prepared catalyst precursors are more difficult to reduce than the catalyst precursors prepared under atmospheric conditions.

Calcination of the catalyst precursors causes dehydration of the copper hydrosilicate and formation of highly dispersed silica-supported copper oxide which is reduced more easily. During reduction of the calcined catalyst precursors the release of water set free by the reduction does not proceed synchronously with the consumption of hydrogen. Water formed by the reduction reaction is temporarily retained in the catalyst. This retention of water is only observed during the first reduction of the calcined (ex-chrysocolla-like) catalyst precursors. The retarded release of water may be explained by the participation of water (adsorption, persorption) in the reorganization of the silica support. During the second reduction, after intermediate re-oxidation, the hydrogen consumption and the release of water do occur simultaneously.

The hydrogen concentration in the reducing gas mixture (5 to 50 vol.%) does not affect the on-set of the reduction. The on-set temperature at which dissociation of hydrogen becomes feasible depends only on the state of the copper species (chrysocolla or copper oxide) and the presence of water in the reducing gas atmosphere. Addition of water vapour to the reducing gas

mixture leads to significantly higher reduction on-set temperatures. The progression of the reduction, measured during the temperature programme, depends on both the state of the copper species and the composition of the dynamic gas atmosphere. After initiation, the reduction proceeds more rapidly at higher hydrogen partial pressures, whereas water retards the reaction.

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