Effect of the Reduction Treatment on the Structure and Reactivity of Silica-Supported Copper Particles

C. J. G. VAN DER GRIFT,[1] A. F. H. WIELERS,[1] B. P. J. JOGHI, J. VAN BEIJNUM, M. DE BOER, M. VERSLUIJS-HELDER, AND J. W. GEUS

Department of Inorganic Chemistry, University of Utrecht, Croesestraat 77a, 3522 AD Utrecht, The Netherlands

Silica-supported copper particles of high thermostability have been subjected to oxidation–reduction treatments after which the metal particle size, the surface structure, and the catalytic hydrogenolysis of methyl acetate were investigated. The metal particle size was assessed from the dissociative adsorption of nitrous oxide, X-ray line broadening, and transmission electron microscopy. The surface structure of the copper particles was derived from infrared spectra of adsorbed carbon monoxide. The hydrogenolysis of methyl acetate was used as a structure-sensitive test reaction to illustrate the effect of the surface structure on the activity of the catalyst. The copper particle size is not affected by reduction treatments up to 873 K, whereas the surface structure of the copper particles and thereby the oxygen uptake during dissociative adsorption of nitrous oxide and the activity of the catalyst in the hydrogenolysis of methyl acetate strongly depend upon the temperature and duration of the reduction treatment. Without a change of the copper particle size, prolonged reduction of the catalyst results in more densely packed copper surfaces that are more susceptible to penetration of oxygen during passivation with nitrous oxide and less active in the hydrogenolysis of methyl acetate. The rearrangement of the surface structure of the copper particles is reversible upon repeated oxidation–reduction cycles. © 1991 Academic Press, Inc.

INTRODUCTION

The catalytic properties of heterogeneous metal catalysts often depend upon the crystallographic structure of the exposed metal surface. Catalytic reactions depending upon the structure of the surface are known as structure-sensitive or demanding reactions, whereas reactions that are not affected by the surface structure are structure-insensitive or facile (*1*).

Copper metal catalysts exhibit a significant structure-sensitivity for a number of catalytic reactions. For instance, the water–gas shift reaction catalyzed by metallic copper has been shown to be structure-sensitive (*2*). Local oxidation of the copper surface by water and subsequent reaction of

the thus deposited oxygen with carbon monoxide has been proposed as the mechanism of this reaction. That the reaction is highly structure-sensitive is apparent from the fact that an amount of chlorine far less than a monolayer is sufficient to poison the carbon monoxide shift reaction completely.

The free copper surface area and particle size of the individual copper crystallites can be measured by a large number of techniques, viz., X-ray diffraction (XRD) (*3*), transmission electron microscopy (TEM) (*3*), a recently developed NMR-based determination (*4*), X-ray photoelectron spectroscopy (XPS) (*5*), and via chemisorption of suitable gaseous adsorbates. Since chemisorption provides a direct assessment of the free metal surface area, it is frequently used for catalyst characterization. Measurement of the freely accessible surface area by means of adsorption calls for adsorbates exhibiting a well-established (stable) adsorp-

Reference	Temp. (K)	Pressure (Pa)	Detection
Giamello et al. (13)	293–363	Pulse	Calorimetry
Osinga et al. (14)	293–423	7.9×10^4	Volumetry
Scholten and Konvalinka (15)	273–413	2.7×10^4	Thermal conductivity + mass spectrometry
Dvořak and Pasek (16)	298–333	Pulse	Chromatography
Evans et al. (17)	363	Pulse	Chromatography
Chinchen et al. (18)	298–363	Flow, 2.5×10^3 to 3.6×10^4	"Reactive frontal chromatography"
Luys et al. (19)	363	Flow, 1.3×10^3	Gravimetry
Bond and Namijo (20)	333	Flow, 1.01×10^5	Thermal conductivity

tion stoichiometry, i.e., the number of adsorbate molecules (or atoms) per metal surface atom. In the literature the adsorption of hydrogen (6, 7), carbon monoxide (8–11), oxygen (8, 12, 13), and nitrous oxide (13–20) have been used to determine the copper surface area.

From an evaluation of the adsorbates it appears that the copper particle size in supported catalysts is most frequently assessed by dissociative adsorption of nitrous oxide, using a variety of experimental procedures (Table 1). Controlled oxidation of only the copper surface atoms (passivation) can be achieved by decomposition of the nitrous oxide molecules at the metal surface giving rise to adsorption of oxygen atoms and molecular nitrogen being released into the gas phase. The dissociative adsorption of nitrous oxide is generally performed at temperatures ranging from 293 to 363 K (Table 1). It has been suggested that if one carefully passivates the copper surface even the application of higher temperatures does not result in migration of oxygen atoms into the bulk of the copper particles (21). The above adsorption temperature and the fast N_2O decomposition until complete surface coverage enable one to determine the copper sur-

face area in situ in a microreactor (18, 20). However, some uncertainty remains as to the precise number of adsorbed oxygen atoms per copper surface atom at saturation and the optimum passivation conditions needed to establish this stoichiometry without penetration of oxygen into the bulk of the copper particles. Generally, an adsorption stoichiometry of one oxygen atom per two copper surface atoms (Cu_s–O–Cu_s) is used to calculate the number of copper surface atoms from the amount of dissociated nitrous oxide (13–20).

Aiming at an in situ determination of the copper particle size, we developed a procedure based on measurement of the hydrogen consumption during temperature-programmed reduction (TPR) after complete bulk oxidation and after surface oxidation of the same catalyst sample. Surface oxidation (passivation) is performed by dissociative adsorption of nitrous oxide onto the reduced catalyst. The passivation conditions were varied in order to investigate the effect on the amount of oxygen adsorbed by the catalyst. Complete oxidation of the catalyst is brought about by reaction with molecular oxygen at an elevated temperature. The hydrogen consumption after complete oxidation provides a measure for the total amount of copper in the catalyst, whereas the hydrogen consumption after surface oxidation provides a measure for the number of copper surface atoms. Independent of our investigations Bond and Namijo developed an identical procedure, which has been published recently (20). In order to judge the reliability of this newly developed procedure, we compared the results with data obtained by in situ X-ray diffraction, and transmission electron microscopy. As it appeared that the reduction treatment preceding the passivation by nitrous oxide affected the oxygen uptake and thereby the calculated copper surface area, we also investigated the effect of the reduction treatment on the surface structure and reactivity of the copper particles. Both the temperature and the duration of the reduction were

varied. The effect of the reduction treatment on the surface structure of the reduced copper particles was derived from infrared spectra of adsorbed carbon monoxide. The hydrogenolysis of methyl acetate was used as a structure-sensitive test reaction to illustrate the reversible change of the copper surface structure brought about by repeated oxidation–reduction cycles.

EXPERIMENTAL

The silica-supported copper catalysts were prepared by deposition–precipitation using the hydrolysis of urea at 363 K to raise the pH homogeneously. Further details of this procedure are given elsewhere (22). After washing, the precipitates were dried in air at 393 K (overnight). The dried catalyst precursors are denoted fresh and are coded CuU10 to CuU40 according to their metal loading in weight percent (wt% = 100 × g Cu/(g Cu + g SiO$_2$)).

The fresh catalyst sample (approximately 100 mg, sieve fraction 500–850 μm) was pretreated in situ in a microreactor of an internal diameter of 8.0 mm. Prior to determination of the copper particle size the fresh catalyst was consecutively calcined, reduced, completely oxidized, and reduced once more. By this pretreatment procedure the catalyst precursor is converted into stable silica-supported copper metal particles (vide infra). The exact experimental conditions applied during the various pretreatment steps are given below. Calcination of the fresh catalyst was performed by heating the fresh sample from ambient to 723 K at 10 K/min in a 1 vol% O$_2$/He (Hoekloos) flow (50 ml/min) and keeping it at 723 K for at least 2 h. After calcination, the catalyst was cooled to room temperature in the 1 vol% O$_2$/He flow. At room temperature the reactor was flushed with pure nitrogen (50 ml/ min, 99.999 vol%, Hoekloos) for 10 min to remove the gaseous oxygen. Subsequent reduction of the catalyst was brought about by heating the sample from ambient to 723 K at 10 K/min in a 10 vol% H$_2$/N$_2$ (Hoekloos) flow (50 ml/min). At the end of the tempera-

ture ramp the reduction was continued at 723 K for at least 1 h. During the temperature-programmed reduction the hydrogen consumption was measured by means of a thermal conductivity detector (Gow Mac Instruments Co.). At the end of the reduction treatment the catalyst was cooled down to room temperature in the reducing gas atmosphere. At room temperature the reactor was purged with pure nitrogen (50 ml/min, 99.999 vol%, Hoekloos) for 10 min to remove the hydrogen prior to either complete oxidation with molecular oxygen or passivation with nitrous oxide. Complete oxidation of the catalyst was performed by heating the sample from ambient to 723 K at 10 K/min in a 1 vol% O$_2$/He (Hoekloos) flow (50 ml/min) and keeping it at 723 K for at least 2 h. After oxidation, the catalyst was cooled to room temperature in the 1 vol% O$_2$/He flow. At room temperature the reactor was flushed with pure nitrogen (50 ml/min, 99.999 vol%, Hoekloos) for 10 min to remove the gaseous oxygen. Subsequently the catalyst was reduced according to the procedure described above.

The copper particle size of the reduced catalyst thus obtained was determined by repeated passivation–reduction cycles. Passivation was performed by exposing the reduced catalyst to a flow (50 ml/min) of 5 vol% N$_2$O (99.998 vol%, Matheson) in N$_2$ (99.999 vol%, Hoekloos) at various temperatures (303, 333, 363, and 393 K) for different durations (10, 30, and 60 min). After passivation, the catalyst was purged with nitrogen (50 ml/min, 99.999 vol%, Hoekloos) for 10 min to remove the oxidant and subsequently subjected to TPR to assess the amount of oxygen taken up by dissociative adsorption of nitrous oxide. TPR was performed as described above.

X-ray line broadening during in situ temperature-programmed reduction up to 1000 K enabled us to calculate the average volume-weight crystallite size ($d_{v.w.} = (\Sigma n_i d_i^4)/(\Sigma n_i d_i^3)$) (3). In situ reductions were performed in a 10 vol% H$_2$/Ar dynamic gas atmosphere. The reducing gas mixture was

deoxygenated over BASF R3-11 and dried over Linde molsieve. Catalyst samples were heated from ambient to 1000 K in 60 h and subsequently kept at this temperature for at least 50 h. Furthermore, in order to study the effect of the duration of the reduction treatment on the copper particle size, catalyst CuU30 was heated from ambient to 723 K in 60 h and kept at this temperature for 110 h.

The X-ray diffraction patterns were obtained with a Guinier–Lenné high-temperature camera (Enraf Nonius, Delft, The Netherlands). Monochromatization was performed with a quartz crystal according to procedures described by de Wolff (23). A normal focus tube giving copper $K\alpha$-radiation, was used at 40 kV and 30 mA. The XRD reflections were taken from film (Industrex AA2, Kodak) with a modified computer-driven densitometer (Mikrodensitometer MD100, Jenoptik Jena GmbH, Germany). Volume-weighted crystallite-sizes ($d_{v.w.}$) were calculated using the Scherrer equation, $d_{v.w.} = L = K\lambda/\beta \cos \theta$, where K is the Scherrer constant, λ is the wavelength of the radiation (Cu$K\alpha_{1,2}$, $\lambda = 1.5418$ Å), β the line broadening of the peak due to the small crystallites (rad 2θ), and θ the corresponding angle of the diffraction peak (24). For K we used a value of 1.0. The full width at half maximum (FWHM) of the (111) reflection of copper was measured for calculation of the crystallite sizes. A correction for instrumental broadening was carried out; $\beta = (B^2 - b^2)^{0.5}$, where B is the total broadening and b is the instrumental broadening. The instrumental broadening was determined by measurement of the FWHM of the (113) reflection of α-Al$_2$O$_3$ (corundum) from the X-Ray Powder Diffraction Intensity Set SRM 674, National Bureau of Standards (25). The (113) reflection of α-Al$_2$O$_3$ was used since this reflection coincides with the (111) diffraction line of copper. The instrumental broadening was established to be $b = 0.0026$ rad 2θ. The accuracy of the crystallite size determined via this method is approximately 20% (23).

The copper particle size was also determined by transmission electron microscopy using a Philips EM420 microscope. Fresh catalyst samples (2–3 g) were calcined in air at 723 K for at least 10 h and subsequently reduced in a microreactor in a flow of 10 vol% H$_2$/N$_2$ (25 ml/min). The reduction procedure comprised heating the catalyst from ambient to 673 K at 5 K/min and keeping the catalyst at this final temperature for at least 16 h. The reduced catalysts were carefully oxidized by slow admission of air at room temperature. Then the catalysts were powdered and ultrasonically dispersed in ethanol. Droplets of the suspension thus obtained were brought onto a holey carbon film supported on a copper grid.

The surface structure of the copper particles after various oxidation–reduction cycles was monitored by infrared spectroscopic investigation of the CO absorption band. The vacuum equipment used for this investigation, described elsewhere (26), allowed us to pretreat the catalyst wafer in situ. The catalyst was calcined or oxidized in 1 vol% O$_2$/He or reduced in 10 vol% H$_2$/Ar. The catalysts were thoroughly oxidized at 723 K for 2 h and reduced at 573, 673, 773, 873, or 973 K for different periods of time. Thus the catalyst was subjected to similar reduction treatments as with the nitrous oxide surface oxidation experiments. After reduction, the samples were cooled to approx 300 K, evacuated for 1 h, and exposed to 133 Pa CO. Spectra were recorded in the presence of gas phase CO. A Perkin–Elmer 580B infrared spectrophotometer, connected to a 3500 Data Station was used to collect the spectra and handle the data.

The hydrogenolysis of methyl acetate was used as a test reaction to assess the effect of the reduction treatment on the activity of the copper particles. The equipment used for the hydrogenolysis measurements has been described elsewhere (27). After calcination at 723 K (air) 0.50 g of CuU20 (500–850 μm) was loaded into a microreactor and reduced at 573 K in a 20 vol% H$_2$/

N$_2$ flow (50 ml/min) for 2 h. After this first reduction the hydrogenolysis activity was measured in a flow (52.6 ml/min) of 5 vol% methyl acetate, 20 vol% H$_2$, balance N$_2$. Subsequently, the catalyst was completely oxidized in a flow of 2 vol% O$_2$/He for 2 h at 723 K and rereduced at 573 K for 2 h. After this second reduction the hydrogenolysis activity was measured as described above. Subsequently, the catalyst was reduced at 823 K for 24 h and the activity of the catalyst was measured as described above. Finally the catalyst was reoxidized in a flow of 2 vol% O$_2$/He for 2 h at 723 K and rereduced at 573 K for 2 h. After this fourth reduction the hydrogenolysis activity was measured once more.

FIG. 1. Temperature-programmed reduction profiles of catalyst CuU20; (a) after complete oxidation, and (b) after surface passivation.

RESULTS AND DISCUSSION

Dissociative Adsorption of Nitrous Oxide

By analogy with the procedure described by Bond and Namijo (20), determination of the copper particle size is based on measurement of the hydrogen consumption after complete oxidation of the catalyst, X, and after surface oxidation of the same catalyst, Y. After complete oxidation, X measures the total amount of reducible copper in the catalyst (Eq. (1), whereas Y is a measure for the number of copper surface atoms Eq. (2).

all copper atoms

CuO + H$_2$ → Cu + H$_2$O

hydrogen consumption = X   (1)

copper surface atoms only

Cu$_2$O + H$_2$ → 2Cu + H$_2$O
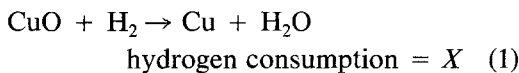
hydrogen consumption = Y   (2)
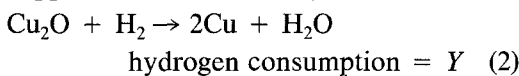
The hydrogen consumptions (X, Y) can be used to calculate a dispersion (D = N$_s$/N$_t$, with N$_s$ = number of copper surface atoms and N$_t$ = total number of copper atoms) (Eq. (3)).

$$D = (2 \cdot Y/X) \cdot 100\%. \quad (3)$$

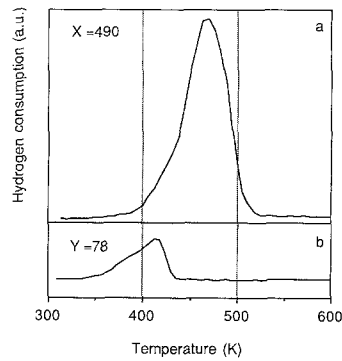From the literature, the area per copper surface atom in the (100), (110), and (111) planes is 0.065, 0.092, and 0.0563 nm^2, respectively (28). An equal abundance of these three planes gives an average copper surface atom area of 0.0711 nm^2, equivalent to 1.4×10^{19} copper atoms per square meter. Assuming a spherical shape of the copper metal particles and 1.4×10^{19} copper atoms per square meter, the specific copper surface area (S) and the average volume–surface diameter ($d_{v.s.} = (\Sigma n_i d_i^3)/(\Sigma n_i d_i^2)$) can be expressed as a function of X and Y (Eqs. (4) and (5)).

$$S = 2 \cdot Y \cdot N_{av}/(X \cdot M_{Cu} \cdot 1.4 \times 10^{19})$$
$$\approx 1353 \ Y/X \quad (m^2 \ Cu/g \ Cu) \quad (4)$$

$$d_{v.s.} = 6/(S \cdot \rho_{Cu}) \approx 0.5 \cdot X/Y \quad (nm) \quad (5)$$

with: N_{av} = Avogadro's constant = 6.02×10^{23} (mol^{-1}), M_{Cu} = relative atomic mass = 63.546 (g/mol), ρ_{Cu} = density = 8.92 (g/cm^3).

Temperature-programmed reduction of the completely oxidized CuU20 catalyst gives rise to the hydrogen consumption profile shown in Fig. 1a. In agreement with previous results, reduction starts at 420 K and the maximum hydrogen consumption is observed at 450 K (29). Repeating the complete oxidation–reduction cycles gives highly reproducible results for X.

TPR to determine Y after dissociative adsorption of nitrous oxide showed that reduction of the surface-oxidized copper particles

TABLE 2

Effect of the Passivation Procedure on the Y/X Ratio of Catalyst CuU20[a]

Exposure	303 K	333 K	363 K	393 K
10 min	N.D.	0.07	0.14	0.13
30 min	0.06	0.08	0.13	0.14
60 min	0.07	0.11	0.13	N.D.

Note. N.D., not determined.

[a] Results obtained after standard reduction for 1 h at 723 K.

proceeds at a temperature lower than that of reduction of the completely oxidized particles (Fig. 1b). The amount of oxygen taken up during passivation of the catalyst, as determined from Y, not only depends on the exact passivation conditions but also on the temperature and duration of the reduction preceding this treatment (vide infra). Having established the influence of the duration of the reduction treatment on the amount of oxygen taken up by the copper particles, the reduction treatment was standardized to TPR up to 723 K and continued reduction at this temperature for exactly 1 h. It is shown that this reduction procedure gives reproducible values for Y and a fair agreement of the calculated copper particle size with results obtained by XRD and TEM.

Using this standardized reduction procedure, the effect of the passivation treatment on the amount of adsorbed oxygen was investigated. The resulting Y/X ratios obtained after passivation of catalyst CuU20 at various temperatures for different periods of time are summarized in Table 2. At low passivation temperatures (303 K, 333 K), the amount of oxygen adsorbed at the copper surface depends on the duration of the N_2O exposure, whereas at higher temperatures (363 K, 393 K) the amount of nitrous oxide decomposed at the copper surface is constant and independent of the passivation duration. These results suggest that saturation of the copper surface by adsorbed oxygen can be established rapidly by N_2O decomposition at temperatures between 363 and 393 K. These findings are in line with results by other authors (*15, 17*). Since the constant Y/X ratio at 363 K most probably corresponds to full coverage of the copper surface by adsorbed oxygen, this value was used to calculate the dispersion (D), the copper surface area (S), and the copper particle size ($d_{v.s.}$) according to Eqs. (3), (4), (5) (results in Table 3).

X-Ray Line Broadening

In situ X-ray diffraction during reduction of the fresh catalyst precursors showed the genesis of copper metal particles at 500 K, in agreement with the reduction temperature determined during TPR (*29*). From X-ray line broadening the copper crystallite size was determined as a function of the reduction temperature and time at 1000 K (Fig. 2). Up to about 850 K, the copper particle size is constant. Regardless of the metal loading, reduction of the catalyst precursors results in copper particles which are about 5 to 7 nm in diameter. At temperatures above 850 K the crystallite size increases slowly indicating that some sintering occurs at these elevated temperatures. After 50 h at 1000 K in 10 vol% H_2/Ar the copper crystallite size has increased from 5–7 to 10–15 nm. In an additional experiment, sample CuU30 was kept at 723 K for 110 h to investigate whether prolonged reduction at this

TABLE 3

Copper Particle Size as Determined by Different Techniques

Sample	$d_{v.s.}$ (nm)[a]	$d_{v.w.}$ (nm)[b]	d (nm)[c]
CuU10	N.D.	N.D.	3.0–4.0
CuU20	4.0	5.0	3.5–5.0
CuU30	4.2	7.0	4.0–6.0
CuU40	N.D.	5.0	6.0–8.0

Note. N.D., not determined. Accuracy of the copper particle size ±20%.

[a] Oxidation-reduction procedure.

[b] X-ray line broadening.
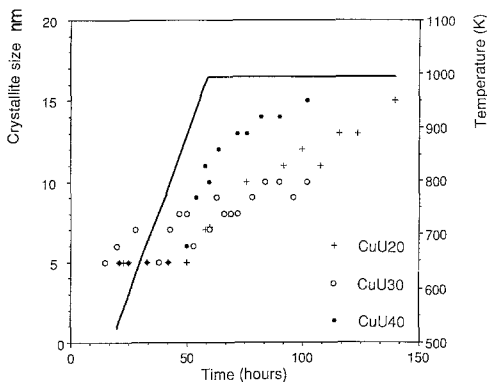
[c] Transmission electron microscopy.

FIG. 2. Crystallite size from X-ray line broadening.
Effect of the reduction treatment on the copper particle
size (solid line represents the temperature program).

temperature might induce a change in crystallite size. However, the crystallite size ($d_{v.w.}$ approx 6 nm) appeared to be independent of the duration of the reduction at this temperature. It is thus concluded that the varying oxygen uptakes during dissociative adsorption of nitrous oxide after reduction treatments up to 723 K are not caused by a real change in copper particle size.

The volume-weighted average crystallite size obtained from X-ray line broadening ($d_{v.w.}$ = 5–8 nm) is slightly larger than the average volume–surface particle size ($d_{v.s.}$ approx 4 nm) determined by the oxidation–reduction procedure. For mathematical reasons $d_{v.w.} = (\Sigma n_i d_i^4)/(\Sigma n_i d_i^3) \geq d_{v.s.} = (\Sigma n_i d_i^3)/(\Sigma n_i d_i^2)$, the difference between these averages depending on the particle size distribution (3). Thus, there is a fair agreement between the copper particle size as established from the standardized oxidation–reduction procedure and in situ X-ray line broadening.

Transmission Electron Microscopy

Finally, the copper particle size of the reduced and passivated catalysts (for definitions, see Experimental) has been investigated by means of transmission electron microscopy. In dark field the metal nuclei of the copper particles can be seen as bright

spots. By measuring the size of more than 200 randomly chosen metal nuclei, we arrived at the particle size range listed in Table 3. Since the electron micrographs show a fairly narrow homogeneous particle size distribution, it seems fair to assume that the particle size range given in Table 3 is representative for the entire copper particle size distribution. It should be stressed that due to exposure of the catalyst to air, the surface of the copper particles was oxidized and not observed in the dark field micrographs. Depending on the thickness of the oxide layer on the copper particles the values in Table 3 may be an underestimation of the actual particle size. However, on the other hand, very small particles ($d < 2$ nm) may completely oxidize and thus become invisible to TEM, causing the values in Table 3 to be an overestimation of the actual particle size.

Structure and Oxygen Uptake of the Copper Particles

In order to establish the influence of the reduction treatment on the oxygen uptake during interaction of nitrous oxide with the silica-supported copper particles in more detail, the temperature and duration of the reduction (preceding the passivation) were varied systematically. The passivation treatment was standardized to 30 min exposure of the reduced catalyst to a 5 vol% N_2O/N_2 flow (50 ml/min) at 363 K. The oxygen taken up by the catalyst is derived from the hydrogen consumption Y upon subsequent temperature-programmed reduction. The integrated hydrogen consumption Y thus measures the amount of oxygen adsorbed by the catalyst.

Typical TPR profiles obtained after reduction of the CuU20 catalyst at 773 K and passivation at 363 K are shown in Fig. 3. After prolonged reduction at 773 K the oxygen uptake corresponds to a hydrogen consumption Y of 109 (a.u.) (Fig. 3a). Reduction for 1 h at 773 K results in an oxygen uptake corresponding to 79 (a.u.), whereas reduction up to 773 K followed by cooling the
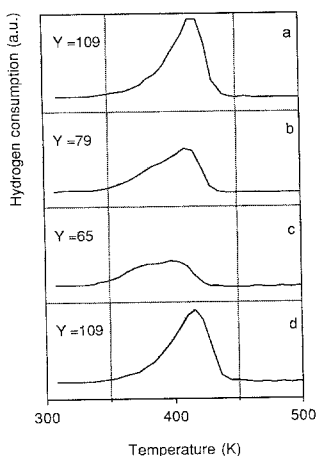
FIG. 3. Typical TPR profiles after an identical passivation treatment in chronological order; (a) after preceding reduction for 18 h at 773 K, (b) after preceding reduction for 1 h at 773 K, (c) after preceding reduction in 50 min from 273 K up to 773 K followed by direct cool down, and (d) after preceding reduction for 18 h at 773 K.

catalyst as soon as this temperature is reached gives rise to an oxygen uptake of 65 (a.u.) (Fig. 3b, 3c). Subsequent prolonged reduction at 773 K fully restores the oxygen uptake to 109 (a.u.) (Fig. 3d). As the results are completely reproducible, it is clear that the variation of the oxygen uptake is not due to an (irreversible) change of the geometric copper particle size. It is therefore likely that the amount of oxygen taken up during passivation does depend on the surface structure and reactivity of the equally sized copper particles.

The increased oxygen uptake after prolonged reduction may be due to either the availability of a larger number of adsorption sites at the surface or to the penetration of oxygen into the bulk of the copper particles. These explanations may both be correlated with the structure of the copper surface as established during the reduction preceding the passivation. By the formation of more densely packed copper surfaces the number of copper atoms per unit surface area increases, thereby raising the number of sites available to adsorb oxygen atoms. Based on

the assumption that dissociative adsorption of nitrous oxide gives rise to the formation of a monolayer of one adsorbed oxygen atom per two copper surface atoms, the oxygen uptake for equally sized copper particles is proportional to the number of copper surface atoms per unit surface area. The number of copper atoms per square meter varies widely with the crystallographic structure of the surface, for instance approx 1.09×10^{19} for (110) and approx 1.77×10^{19} for (111). Upon prolonged reduction treatments, a reconstruction of the copper surface to more densely packed surface structures may give rise to a significantly larger oxygen uptake by copper particles of an identical geometric size. Furthermore, the transparency of the copper surface for the penetration of oxygen into the bulk of the metal particle may depend upon the crystallographic structure obtained during the preceding reduction.

In an additional experiment the effect of the duration of the passivation treatment on the total oxygen uptake was investigated. Prior to passivation, catalyst CuU20 was reduced at 773 K for either 1 h or 16 h. The duration of the passivation treatment was varied from 10, 30 to 60 min in a flow (50 ml/min) 5 vol% N_2O/N_2 at 363 K. After reduction for 1 h at 773 K, the amount of oxygen taken up by the catalyst appeared to be independent of the duration of the passivation treatment suggesting that a stable surface coverage was established (Table 4).

TABLE 4

Oxygen Uptake Arbitrary Units during Passivation for Different Periods of Time, after Short (1 h) and Prolonged (16 h) Reduction at 773 K

Passivation time	1 h, 773 K[a]	16 h, 773 K[b]
10 min N_2O	80	99
30 min N_2O	79	109
60 min N_2O	79	182

[a] Reproducibility within 5% deviation from average value given in the table.

[b] Reproducibility within 20% deviation from average value given in the table.

TABLE 5

Effect of the Reduction Treatment on the Frequency of the CO Absorption Band (cm^{-1})

Reduction	1 h	16 h
573 K	2133	2133
673 K	2133	2126
773 K	2129 (2100)	2111 (2080)
873 K	2112 (2080)	2096 (2070)
973 K	2100 (2070)	2095 (2070)

Note. Numbers in parentheses show frequency of the shoulder at the CO-absorption band.

After reduction for 16 h at 773 K, however, the amount of oxygen taken up by the catalyst increased with the exposure to nitrous oxide (Table 4). Already after passivation for 10 min, the amount of oxygen taken up exceeds the stable amount of adsorbed oxygen after reduction for 1 h at 773 K. The increase of the oxygen uptake with prolonged exposure to nitrous oxide indicates a (slow) penetration of oxygen into the bulk of the copper particles.

In order to investigate whether the reduction treatment affects the surface structure of the reduced copper particles, we used infrared spectroscopy of adsorbed carbon monoxide. From the extensive work by Hollins and Pritchard (30), who studied the adsorption of CO on single crystals, vapor-deposited films, and supported copper catalysts, it is known that the frequency of adsorbed CO molecules strongly depends upon the (crystallographic) structure of the metallic copper surface.

The effect of the reduction treatment on the surface structure of the reduced copper particles in catalyst CuU20 was investigated by means of infrared spectroscopy. After *in situ* calcination and reduction of a fresh CuU20 catalyst wafer at 723 K, CO adsorbed at room temperature gives an infrared absorption band at 2100 cm^{-1}. Subsequent oxidation at 723 K and reduction at 573 K gives rise to a CO absorption band at 2133 cm^{-1} (Table 5).

These results are in line with previous data by de Jong *et al.* (*31*), who explained the observed frequencies in terms of different copper surface structures. After a first reduction, the copper particles expose a densely packed surface giving rise to CO absorption at approx 2100 cm^{-1}, whereas after subsequent oxidation and reduction at 573 K the high frequency of the CO band indicates adsorption on atomically rough copper surfaces exposing a large number of coordinatively unsaturated surface atoms (*31*). Subsequent oxidation at 723 K and reduction treatments at increasingly higher temperatures gradually shift the CO absorption maximum from 2133 to 2095 cm^{-1} (Table 5 and Fig. 4). After prolonged reduction at 973 K the catalyst was oxidized at 723 K and reduced at 573 K for 1 h. Subsequent adsorption of CO gives rise to an absorption band centered at 2107 cm^{-1}. Repeated oxidation–reduction cycles are needed to shift the CO absorption band to higher frequencies (2115 cm^{-1}).

By recording all IR spectra at a CO pressure of 133 Pa the observed change of the CO absorption frequency can only be due to a change of the surface structure of the copper particles. Comparing the CO absorption frequencies with data from the literature provides information on the surface
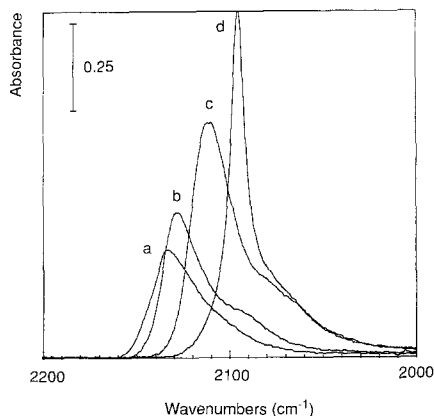

FIG. 4. Infrared spectra of 133 Pa CO adsorbed on catalyst CuU20; (a) after reduction up to 573 K, (b) after reduction for 1 h at 773 K, (c) after reduction for 16 h at 773 K, and (d) after reduction for 16 h at 973 K.

structure of the reduced copper particles in the catalyst. Guided by the results of Moskovitz and Hulse (*32, 33*), who studied copper–carbonyl complexes isolated in an Ar matrix, de Jong *et al.* (*31*) attributed frequencies of adsorbed CO above 2120 cm^{-1} to coordinatively unsaturated copper surface atoms or protroding Cu atoms. With stepped surfaces, (211), (311), and (755), Hollins and Pritchard (*30*) report CO absorption band maxima from 2100 to 2110 cm^{-1}, whereas with the more densely packed copper surfaces, (111) and (100), the absorption peaks at 2070 to 2090 cm^{-1}.

The results summarized in Table 5 thus indicate that, upon increasing the severity of the reduction treatment, the structure of the copper particles is changed from atomically rough, exposing a large number of coordinatively unsaturated surface atoms (2133 cm^{-1}), to stepped surfaces exposing small terraces (2110 cm^{-1}), to densely packed surfaces exposing larger flat terraces (2095 cm^{-1}). As long as the copper particle size is not increased by reduction at temperatures above 873 K, the change in surface structure is reversible upon repeated oxidation–reduction cycles.

Hydrogenolysis of Methyl Acetate

The hydrogenolysis of methyl acetate was used as a test reaction to illustrate the effect of the reduction treatment on the activity of the silica-supported copper particles. The major products of the hydrogenolysis of methyl acetate are methanol and ethanol. Transesterification of methyl acetate with methanol and ethanol gives rise to methyl formate and ethyl acetate, respectively. Hydrogenolysis of the products formed by transesterification results in the (re)formation of methanol and ethanol. At higher temperatures ($T > 540$ K) the formation of acetaldehyde, methane, and ethane is observed. As the product distribution depends on a set of reactions affected by the temperature and the conversion it is difficult to judge the selectivities of the catalysts and we confine ourselves to the conversion of methyl acetate as a function of the temperature. Al-
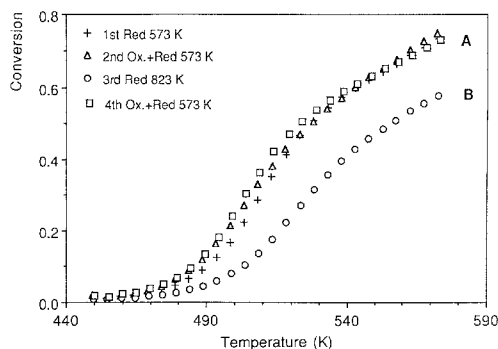

FIG. 5. Hydrogenolysis activity of CuU20 catalyst after different reduction pretreatments (see Experimental).

though information on the structure sensitivity of this particular reaction has not been found in the literature, Maire and Garin (*34*) deal with the structure-sensitivity of other hydrogenolysis reactions in their review on metal-catalyzed skeletal reactions of hydrocarbons.

After the first and second reduction treatments up to 573 K, with intermediate oxidation, the conversion versus temperature follows curve A in Fig. 5. Increasing the reduction temperature up to 823 K, in order to establish a more densely packed copper surface, causes a decrease of the hydrogenolysis activity (Fig. 5, curve B). Subsequently, the catalyst was completely oxidized and rereduced at 573 K to reestablish the more open copper surface structures. This treatment restored the initial activity of the catalyst illustrating that the change of the surface structure of the copper particles is reversible (Fig. 5, curve A). Complete reduction of the catalyst is already obtained at 573 K, whereas at temperatures up to 873 K no sintering occurs (vide supra). The results of this investigation clearly show that the activity of equally sized silica-supported copper particles can be reversibly changed by repeated oxidation–reduction cycles.

CONCLUSIONS

The copper particle size of silica-supported catalysts has been determined by dissociative adsorption of nitrous oxide, as

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well as by *in situ* X-ray line broadening and transmission electron microscopy. Provided the reduction and passivation treatments are chosen to give a stable (reproducible) oxygen uptake, the copper particle size as determined by the dissociative adsorption of nitrous oxide is in fair agreement with the results obtained by X-ray line broadening and transmission electron microscopy.

The temperature and duration of the reduction treatment affect the amount of oxygen that is taken up during the interaction of nitrous oxide with the reduced copper particles. Increasing the duration of the reduction treatment results in subsequent larger oxygen uptakes during passivation. The measurements were reproducible and reversible upon alternately short and prolonged reduction treatments indicating that the altered oxygen uptake does not reflect a change of the copper particle size.

The effect of the reduction treatment on the subsequent oxygen uptake during dissociative adsorption of nitrous oxide seems to be related to the surface structure of the equally sized copper particles. As shown by infrared spectroscopy of adsorbed carbon monoxide, a short reduction at relatively low temperatures (673 K) gives rise to the formation of an atomically rough copper surface exposing protruding copper atoms, whereas prolonged reduction at more elevated temperatures (873 K) gives rise to formation of more densely packed copper surfaces.

Silica-supported copper particles of an identical geometric size may exhibit widely different oxygen uptakes per unit surface area depending on the crystallographic structure of the surface. Notably, the copper particles with the more densely packed surfaces show a larger oxygen uptake due to (i) the larger number of copper atoms per unit surface area and (ii) the penetration of oxygen into the particles.

Measurements on the hydrogenolysis of methyl acetate after different oxidation–reduction pretreatments indicate that the activity of the catalyst is reversibly changed by transforming the surface structure of the equally sized copper particles. The more densely packed copper surfaces show a lower hydrogenolysis activity.

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