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An Infrared Spectroscopic Study of the Adsorption of Carbon Monoxide on Silica-supported Copper Oxide

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Adsorption of carbon monoxide at room temperature (0.1–50 Torr) on silica-supported copper oxide was studied by infrared spectroscopy. Catalysts were prepared by deposition-precipitation or impregnation. After calcination two types of adsorbed CO were identified showing absorption bands at 2136 ± 3 and 2204 ± 1 cm^{-1}, which are ascribed to CO adsorbed on copper(II) oxide and on isolated copper(II) ions in the silica surface, respectively. Reduction and reoxidation removed the band at 2204 cm^{-1} with all samples and raised the intensity of the 2136-cm^{-1} band with the precipitated catalysts but not with the impregnation catalyst. Evidence is brought forward that the isolated copper ions are mobilized during reduction and generate new copper (oxide) surface. The change in background transmission of the samples could be used to obtain further information about the interaction of O_2 and CO with copper oxide.

INTRODUCTION

Several investigators (*1–4*) have reported on infrared spectra of carbon monoxide adsorbed on copper(II) oxide. The most intense absorption bands are in the spectral range 2100–2200 cm^{-1} and have been correlated with molecularly adsorbed CO. The remaining bands are found between 1700 and 1100 cm^{-1} and have been attributed to bicarbonate, carboxylate, and carbonate species; these bands are weak and hard to interpret. We wanted to investigate whether we could use the experimentally easily accessible strong absorption bands around 2150 cm^{-1} to characterize differently prepared and pretreated copper oxide catalysts. A similar study was made on reduced copper catalysts, on which we will report elsewhere (*5*).

The catalysts were prepared by deposition-precipitation. This preparation method assures a homogeneous dispersion of the copper oxide over the silica carrier. To compare our results with those in the literature, we also studied a catalyst which had been prepared by the usual method of impregnation and drying. Adsorption experiments were carried out both after calcination and after reduction and subsequent oxidation of the catalysts. The adsorption of carbon monoxide was studied at room temperature and at pressures from 0.1 to 50 Torr.

EXPERIMENTAL

Catalysts CU-1 and CU-2 were prepared by deposition-precipitation and contained 16.7 and 30 wt% of copper, respectively. In a suspension of silica (Aerosil 200 V) in a cupric nitrate solution, the hydroxide was homogeneously precipitated by the decomposition of urea at 90°C. In order to prevent nucleation of copper species in the solution instead of on the carrier surface it was necessary to keep the copper nitrate concentration below 0.02 mol/liter. Details about this preparation method are published by Van Dillen *et al.* (*6*). Catalyst CU-3 was prepared by the usual method of impregnating the carrier with a cupric nitrate solution and drying. This catalyst had a copper content of 10 wt%.

The samples were pressed into self-supporting disks for infrared transmission measurements, and placed in an all-glass cell. The cell had been permanently mounted in the sample compartment of a Perkin–Elmer

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580 B spectrophotometer and coupled to a vacuum and gas supply system. Sample treatments could be performed *in situ* at temperatures from 25 to 400°C. The infrared transmission spectra of the sample were recorded at room temperature, before and after the dosing of carbon monoxide. Though the carbon monoxide pressure was varied, the infrared spectra were usually measured at a pressure of 50 Torr (1 Torr = 133.3 N m^{-2}). Absorption of the gas phase was compensated for by means of an identical cell in the reference beam of the spectrophotometer, which was always used in the double-beam mode.

With calcined samples adsorption was carried out after keeping the samples for 15 h at 400°C in an oxygen flow and subsequent evacuation at the same temperature. Reduction was done at 300°C in a flow of 10% H_2/90% Ar and reoxidation at the same temperature (reoxidized samples).

RESULTS AND DISCUSSION

Calcined Catalysts

All copper oxide catalysts investigated showed broad absorption bands which are due to adsorbed carbon monoxide. The results on the calcined catalysts have been summarized in Fig. 1. The most intense peak ranges from 2080 to 2190 cm^{-1} with a maximum at 2136 cm^{-1} with CU-1, 2139 cm^{-1} with CU-2, and 2133 cm^{-1} with CU-3. These bands are attributed to carbon monoxide adsorbed on copper(II) oxide particles adhering to the silica carrier. Other authors have mentioned analogous bands (*1*, *3*).

As can be seen in Fig. 1, all calcined catalysts displayed a weak band at 2204 ± 1 cm^{-1}. Evacuation at room temperature for 15 min caused the band at 2204 cm^{-1} to disappear completely, whereas the main absorption band at about 2136 cm^{-1} still had a considerable intensity. This shows that carbon monoxide which gives rise to this peak is weakly adsorbed.

Though a band at 2204 cm^{-1} has never been reported for CO adsorbed on copper oxide, it has been observed with other oxidic surfaces, e.g., highly oxidized zinc oxide (*7*), nickel oxide on silica (*8*), and magnesium oxide (*9*). These high-frequency bands have been correlated with weakly held species, but the type of bonding has been debated. We shall present evidence which points to this band being due to carbon monoxide adsorbed on "isolated" copper ions incorporated in the silica surface.

Catalysts CU-1 and CU-2 have been prepared by homogeneous decomposition of urea at 90°C in a cupric nitrate solution in which the silica carrier had been suspended. At this temperature copper ions will react with silica to form (surface) copper(hydro)silicates, but copper hydroxide crystallites will be formed as well. After calcination (prior to reduction) these catalysts therefore exposed both "isolated" copper ions and copper ions present in copper(II) oxide crystallites. The presence of (surface) copper(hydro)silicate can be inferred from thermal analysis. A DTG (differential thermal gravimetry) curve recorded during the first reduction following previous dehydration showed two peaks,

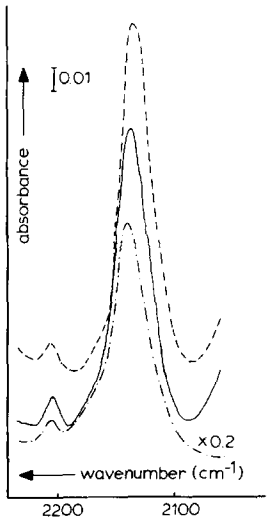

FIG. 1. Infrared spectra from CO adsorbed on calcined CuO/SiO_2 catalysts. (——) CU-1, (– · –) CU-2, and (– – –) Cu-3.

the first one corresponding to the reduction of the copper oxide crystallites and the second one (at a higher temperature) to the reduction of the isolated copper ions. Curve (a) in Fig. 2 shows these two peaks for catalyst CU-2. During the reduction the isolated copper ions are mobilized and coalesce into copper particles. After reoxidation a second reduction will therefore display only one peak in the thermogram. This is demonstrated by curve (b) of Fig. 2. The area under this peak appears to be about twice as large as that under curve (a). This is due to the fact that curve (a) was recorded after dehydration at 900°C, which converted the copper(II) oxide to copper (I) oxide. Curve (b) was recorded after reoxidation with oxygen at 300°C, which resulted in copper(II) oxide.

The mobilization of the isolated copper ions is also reflected by the infrared spectra of CU-1 and CU-2. After prolonged reduction at 300°C and reoxidation at the same temperature, carbon monoxide was again admitted. The infrared absorption bands are represented in Fig. 3. The first important difference with the calcined samples

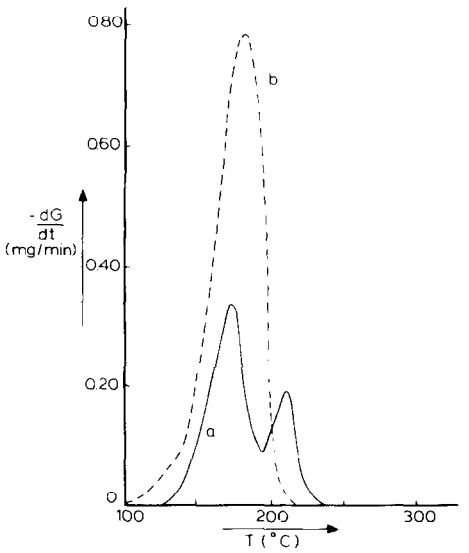

FIG. 2. Differential thermal gravimetric plot for catalyst CU-2. (a) During first reduction, (b) during second and next reductions.

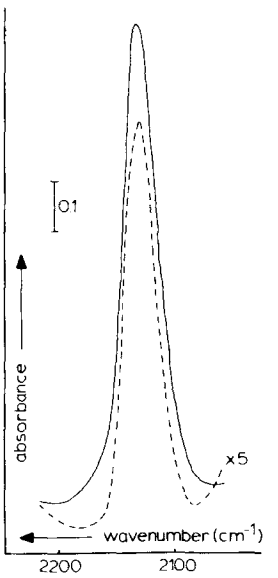

FIG. 3. Infrared spectra from Co adsorbed on reoxidized CuO/SiO_2 catalysts. CU-1 (——) and CU-3 (– – –).

(Fig. 1) is the absence of the high-frequency band. This is consistent with the isolated copper ions having formed copper oxide crystallites.

The change in intensity of the bands after reoxidation also points to the formation of copper oxide from atomically dispersed copper ions. In Table 1 the wavenumbers and absorbances at the peak maxima are summarized. With catalysts CU-1 and CU-2 the intensity of the absorption band has increased by a factor of 4 or more if compared with the calcined samples. The position of the peak did not change appreciably. We therefore assume that both absorption bands are due to carbon monoxide adsorbed on copper(II) oxide. The rise in the intensity of the absorption band consequently implies that during the reduction–oxidation cycle more copper oxide surface must have been generated, which agrees with the above explanation of the thermogravimetric data.

Another piece of evidence comes from activity measurements on copper oxide catalysts prepared by deposition-precipitation. The oxidation of carbon monoxide with

TABLE 1

Frequency and Absorbance at the Infrared Absorption Band Maxima[a]

Catalyst	Calcined		Reoxidized	
	Peak maximum (cm^{-1})	Absorbance	Peak maximum (cm^{-1})	Absorbance
CU-1 (16.7 wt% Cu)	2136 2203	0.118 0.014	2132	0.90
CU-2 (30 wt% Cu)	2139 2204	0.51 0.06	2130	>2
CU-3 (10 wt% Cu)	2133 2205	0.145 0.01	2129	0.16

[a] CO pressure = 50 Torr.

molecular oxygen was used as a test reaction. Comparison of the activities of the calcined and the reoxidized catalyst showed that the activation energy was the same (15 kcal mol^{-1}), whereas the preexponential factor in the Arrhenius equation had increased considerably by reduction and subsequent reoxidation. This points to an increase in the number of active sites for the catalytic oxidation of carbon monoxide. Details about these measurements will be published elsewhere.

For catalyst CU-3 the intensity had not increased by reduction and reoxidation. Here new copper oxide surface was not markedly formed. Impregnation of silica with a cupric nitrate solution at room temperature and evaporation of the solvent in a relatively short period of time leads to hardly any reaction between copper ions and the silica. Only during calcination at 400°C do some copper ions incorporate into the silica lattice. These isolated copper ions give rise to the weak band at 2205 cm^{-1}.

The results with the deposition-precipitated samples CU-1 and CU-2 show that a considerable fraction of the copper ions have reacted with the silica during the preparation. Although these catalysts contain many more isolated copper ions than the impregnated catalyst CU-3, the intensities of the high-frequency bands are comparable (Table 1). We therefore conclude that many copper ions are incorporated in the bulk of the silica lattice during deposition-precipitation and cannot contribute to the adsorption of CO.

Reoxidized Catalysts

Adsorption of carbon monoxide at a pressure of 50 Torr by the reoxidized catalysts gave rise to broad absorption bands, centered around 2131 ± 2 cm^{-1}, with all samples. Except for the intensity, the infrared absorption band is essentially the same with all catalysts (Fig. 3). Our results agree well with those of others (*1–3*).

Figure 4 shows the changes in background absorption of the catalysts on oxidation and subsequent adsorption of CO. After reoxidation of CU-1 and CU-2 the background absorption has increased considerably. The absorption decreased when CO was dosed and dropped further when CO was pumped off at room temperature. When the sample was subsequently evacuated at 150°C the transmission was almost the same as with the calcined sample. When carbon monoxide was dosed again, the background absorption did not change further.

The background absorption of the sample depended on the evacuation temperature after heating in oxygen. The transmittance of sample CU-1 at 2100 cm^{-1} after evacua-

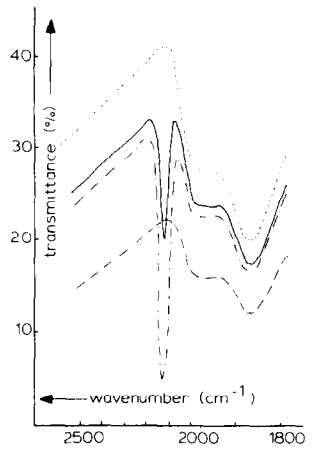

FIG. 4. Infrared spectra from reoxidized CuO/SiO_2 (catalyst CU-1). After reoxidation and subsequent evacuation at 300°C (– – –), after dosing of 50 Torr CO (– · –), after pumping off CO at room temperature (——), after evacuation at 150°C (– – –).

tion at 300 and 25°C was about 20 and 10%, respectively.

These results can be explained by the fact that copper(II) oxide takes up excess oxygen at its surface (*10*) and hence becomes a p-type semiconductor when heated in oxygen. The free charge carriers thus generated absorb infrared radiation of all frequencies and therefore increase the background absorption of the sample. When CO is dosed at room temperature, it reacts with the excess oxygen to form CO_2, which desorbs readily (*1*). When the CO has been evacuated the resulting copper(II) oxide is stoichiometric. As a result, the background absorption is minimized and repeated adsorption of CO does not influence the transmission of the samples. Carbon monoxide is not able to reduce copper(II) oxide at room temperature, which would cause it to be oxygen deficient.

Sample CU-3 did not exhibit these effects in the background absorption, probably because of the much lower specific surface area of this catalyst. We therefore think that under our experimental conditions the excess oxygen is concentrated at the surface of the copper oxide species and is appreciable only with very small particles.

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