AN INFRARED SPECTROSCOPIC STUDY OF THE ADSORPTION
OF CARBON MONOXIDE ON SILICA-SUPPORTED COPPER PARTICLES

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Infrared spectroscopy is used to study the adsorption of carbon monoxide (20°C; 0.1–100 Torr) on copper-on-silica catalysts differently prepared and pretreated. As determined by electron microscopy and X-ray line broadening, the catalysts contain copper particles having sizes of 60 to 5000 Å depending on the preparation procedure and the thermal treatment. Adsorbed carbon monoxide displays broad infrared absorption bands exhibiting a maximum at 2099 to 2146 cm^{-1}. The position of the maximum varies with the preparation and pretreatment of the catalyst. With deposition-precipitated catalysts (Cu-particles 60–120 Å) prolonged reduction at 300°C causes the maximum to shift from 2104 to 2139 cm^{-1}. The shift is attributed to initial facetting and subsequent rounding of the small copper particles. An impregnated catalyst (40–5000 Å) shows a shift from 2146 to 2129 cm^{-1} upon more severe reduction, which is ascribed to sintering to large copper particles.

1. Introduction

The vibrational spectrum of adsorbed carbon monoxide is a sensitive means for investigating the atomic structure of metallic surfaces. Van Hardeveld and Hartog [1], e.g., demonstrated this with nickel-on-silica catalysts. They found that different sites on the nickel surface gave rise to different absorption bands in the infrared spectrum of adsorbed carbon monoxide. These bands could be resolved at room temperature.

The adsorption of carbon monoxide on metals with filled d shells, such as copper, silver and gold, is much weaker than on metals which form bulk carbonyls. The binding is probably of an electrostatic nature, which can be understood in terms of quadrupole–quadrupole interaction between carbon monoxide and the metal. With this interaction the bond-strength depends on the coordination number of the copper atoms in the surface. Since the interaction is weak, differences in surface structure will not give rise to absorption bands displaying well resolved maxima, as with nickel. However, the extensive work of Pritchard [2] on copper single crystal surfaces has demonstrated that the surface structure of copper is at least correlated

with the position of the peak maximum of the absorption band of adsorbed carbon monoxide.

The tendency for copper particles to be facetted is relatively small. Sundquist [3] concluded to a small anisotropy of surface energy from an investigation of the shape of copper particles of the order of 1 μm. Later McLean [4] established that the degree of anisotropy of surface energy for copper was less than 4%. We therefore expect that small copper particles will have a large fraction of atomically rough areas in their surface. We wanted to investigate the relation between the surface structure of small copper particles and the vibrational frequency of adsorbed carbon monoxide more in detail. We feel that the experimentally easily accessible vibrational spectrum of adsorbed carbon monoxide can be a valuable tool for the characterization of the surface structure of copper catalysts.

Since we expect the particle size to affect the proportion of differently structured surfaces, we need copper catalysts of a particle-size distribution that is well known and as narrow as possible. As reduction must be performed at high temperatures for prolonged periods without too severe a loss of copper surface, an appreciable interaction between the metal and the carrier is, moreover, a prerequisite. Deposition—precipitation by means of hydrolysis of urea meets the above requirements. This method was used to prepare two copper catalysts of a different metal content. Another catalyst was prepared by the conventional procedure of impregnation and drying.

In the literature changes in the infrared absorption band of adsorbed carbon monoxide on copper catalysts have been attributed to incomplete reduction [2,5]. We wanted to discriminate between the influence of the surface structure of the metal particles on the one, and the degree of reduction on the other hand. We therefore varied the reduction temperature and time of the catalyst before admitting carbon monoxide. We, moreover, studied the interaction of carbon monoxide with oxygen adsorbed on copper. Adsorption of carbon monoxide was studied at room temperature in the pressure range 0.1 to 100 Torr.

X-ray diffraction line broadening and transmission electron microscopy were used to characterize the catalysts.

2. Experimental

Catalysts CU-1 and CU-2 containing 16.7 and 30 wt.% copper, respectively, were prepared by deposition-precipitation. In a suspension of silica (Aerosil 200 V) in a cupric nitrate solution the hydroxide was homogeneously precipitated by decomposition of urea at 90°C. X-ray diffraction line broadening yielded a value of 110 Å for CU-1 and 190 Å for CU-2 for the diameter of the copper particles after reduction of the catalysts at 300°C. Catalyst CU-3 was prepared by the conventional method of impregnating the carrier with a cupric nitrate solution and drying. This catalyst had a copper content of 10 wt.%.

After drying the samples were pressed into discs of approximately 0.1 mm thickness. A disc was placed into an all-glass cell with sodium chloride windows. The disc could be moved to a furnace section where the pretreatment could be carried out. Before reduction the catalysts were calcined in an oxygen flow at 400°C for 15 h. Reduction times and temperatures (200–400°C) were varied at a total pressure of 1 atm. with a mixture of 10% H_2 and 90% Ar.

The cell had been permanently placed in the spectrophotometer and coupled to a vacuum apparatus. After reduction the cell was evacuated for 30 min, with the catalyst at a temperature 25°C below the reduction temperature. Pressures as low as 10^{-7} Torr (1 Torr = 133.3 Nm^{-2}) could be maintained by means of an ion getter pump (Riber - 25 $\ell\,s^{-1}$).

Spectra were recorded at room temperature with a Perkin-Elmer 580 B infrared spectrophotometer. The absorbance of gaseous carbon monoxide was compensated for by means of an identical cell, placed in the reference beam of the spectrophotometer, and coupled to the measuring cell. It was checked that no adsorption of carbon monoxide appeared on the silica carrier under out experimental conditions.

Gaseous carbon monoxide (purity 99.997%) was obtained from L'Air Liquide and used without further purification.

For transmission electron microscopic studies the catalysts were reduced at 300°C and suspended in methylmetacrylate, which was polymerized at 60°C. Thin sections suitable for the electron microscope were cut with an ultra-microtome (Reichert). Two electron microscopes have been used i.e. a Philips EM 200 and a Jeol 200 C. The samples were studied both in bright and in dark field.

3. Results

3.1. Infrared spectra

With all copper particles studied, adsorbed CO showed broad infrared absorption bands at frequencies from 2040 to 2170 cm^{-1}. Consequently, differently bonded CO was always present at our copper surfaces. For reduced samples the position of the peak maximum did not vary markedly with the CO pressure. Usually spectra were recorded at a CO pressure of 50 Torr.

With catalyst CU-1 (16.7 wt.%) the influence of cyclic reduction—oxidation on the infrared absorption band of adsorbed CO was investigated. The reduction temperatures and times were varied with intermediate oxidation at 300°C in an oxygen flow of 1 atm. The results have been summarized in fig. 1 and table 1. The first three cycles shifted the band maximum from 2104 to 2139 cm^{-1}. This shift to higher wavenumbers is very well reproducible, as is apparent from an experiment with a fresh disc performed with another vacuum apparatus and infrared spectrophotometer (Grubb Parsons). After reduction for 12 h at 300°C we found the peak at 2099 cm^{-1}. Subsequent reduction for 17 h at the same temperature shifted the band maximum to 2131 cm^{-1}.
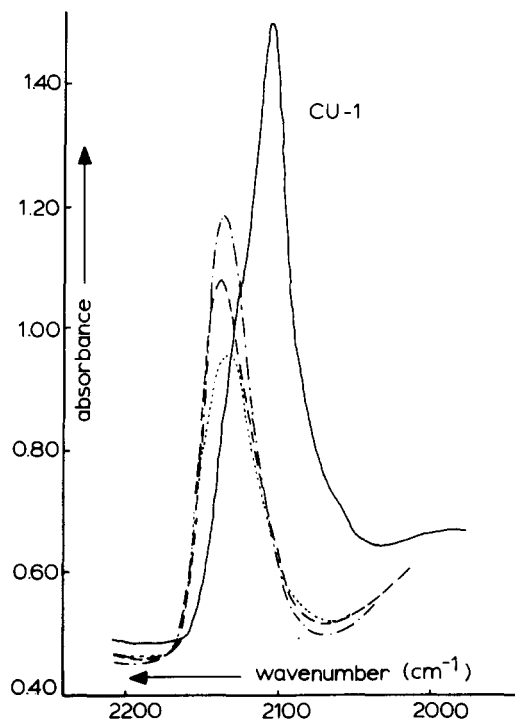
Fig. 1. Infrared spectra of CO adsorbed on Cu/SiO_2, sample CU-1. After reduction number 1 (———), 2 (.....), 3 (— — —) and 7 (— · — · —). See also table 1.

Evacuation for 20 min at room temperature removed the adsorbed CO almost completely. The behaviour of the absorption band on evacuation did not vary markedly with the reduction-cycle number.

Table 1
Influence of cyclic reduction and reoxidation on the infrared absorption band of adsorbed CO for catalyst CU-1, CO pressure 50 Torr

Reduction	Temperature (C°)	Time (hours)	Peak maximum (cm⁻¹)	Absorbance
1	300	15	2104	1.03
2	300	2	2131	0.52
3	300	15	2139	0.60
4	300	2	2139	0.56
5	300	15	2138	0.61
6	400	15	2136	0.77
7	400	15	2135	0.65

Reduction of copper oxide was already complete after 2 h at 300°C, as can be seen from the reductions 4 and 5 of table 1. Variation of the reduction temperature in the range 300–400°C had only a small influence on the infrared absorption band (reduction 5 and 6 of table 1). Thermogravimetric experiments have also established the rapid complete reduction of the copper species of the catalysts at 300°C. The shift of the band maximum is therefore not due to a different extent of reduction and thus a different content of not reduced copper ions.

The influence of oxygen on the infrared absorption band of adsorbed carbon monoxide was investigated with CU-1 after reduction 3. After dosing of 50 Torr CO the peak frequency was 2139 cm^{-1} and the absorbance 0.60 (table 1). Admission of 50 Torr O_2 shifted the band maximum to 2135 cm^{-1} and raised the absorbance to 1.20. On evacuation at room temperature the absorption band remained at a stable intensity of more than 40% of its original value. The different effect of evacuation at room temperature demonstrates that the interaction of CO is much stronger with an oxidized than with a reduced copper surface. The above results indicate that the stability of the absorption band against evacuation is a more reliable criterion for the degree of reduction of the surface than is the position of the band maximum.

Catalyst CU-2 was always reduced for 15 h, but now the reduction temperature was varied. Because of the high metal content of the catalyst (about 30 wt.%) the absorption bands were very strong and therefore difficult to measure accurately. The results have been summarized in fig. 2. After reduction at 200°C the absorption band was centered around 2130 ± 6 cm^{-1}. Intermediate oxidation and reduction at 300°C led to a peak maximum at 2136 ± 2 cm^{-1}. Prolonged reduction at 300°C did no more affect the band position and intensity of the absorption band. From fig. 2 it is apparent that the first reoxidation and reduction shifted the maximum of the CO absorption band to higher wavenumbers, as with catalyst CU–1. The shift of the maximum is, however, less pronounced than with CU-1.

Upon exposure to oxygen the band intensity of adsorbed CO increased, but the position did not change. As with CU-1 the adsorption on the oxidized surface was stronger.

The results for the impregnated catalyst CU-3 have been summarized in fig. 3 and table 2. It can be seen that the effect of more severe reduction is the reverse of that displayed by the other catalysts. After the first reduction (300°C) the peak maximum was situated at 2139 cm^{-1}. Another fresh disc of this catalyst reduced for 30 min at 300°C even displayed the peak maximum at 2146 cm^{-1}. Subsequent reduction at 400°C shifted the peak to 2129 cm^{-1} with a shoulder at 2100 cm^{-1}.

Reduction 3 of CU-3 (table 2) was carried out at 200°C after intermediate oxidation of the catalyst. After the third reduction the sample showed the same absorption band as when reduced for the second time at 400°C. This experiment therefore shows that the highest reduction temperature to which the sample previously has been subjected determines the peak position of the CO absorption band. Reduction at 200°C for 30 min is already sufficient to reduce the copper oxide crystallites completely.
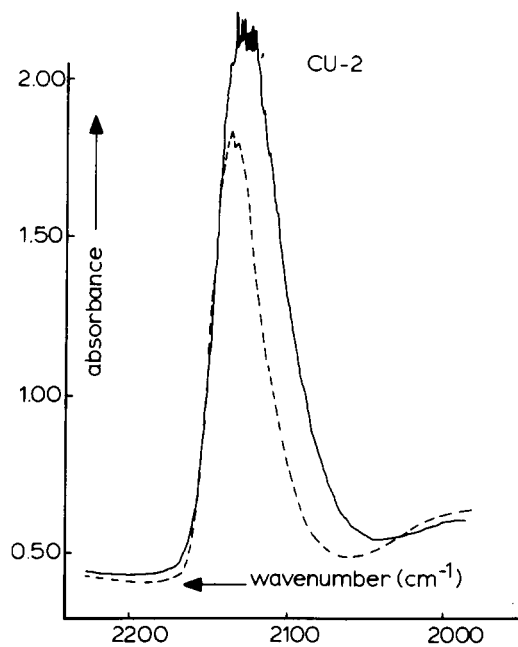
Fig. 2. Infrared spectra of CO adsorbed on Cu/SiO_2, sample CU-2. After reduction during 15 h at 200°C (———) and 300°C (———).
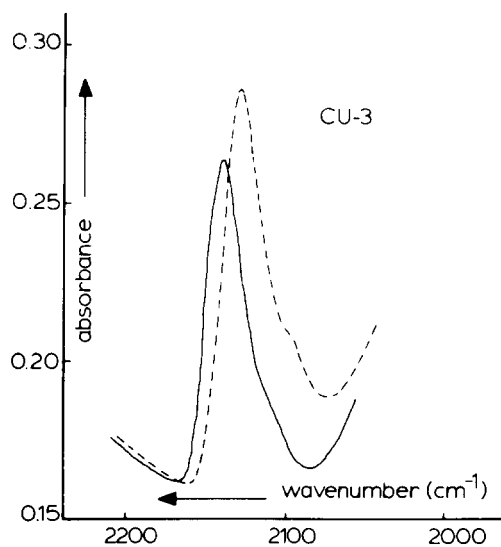

Fig. 3. Infrared spectra of CO adsorbed on Cu/SiO_2, sample CU-3. After reduction during 15 h at 300°C (———) and 400°C (———).

Table 2
Influence of the reduction temperature and time of CU-3 on the infrared absorption band of adsorbed CO. The catalyst was oxidized between reduction 2 and 3 only

Reduction	Temperature ($^{\circ}$C)	Time (hours)	Peak maximum (cm^{-1})
1	300	20	2139
2	400	15	2129
3	200	0.5	2129

When the copper particles have been prolongedly treated in hydrogen at high temperatures, they display infrared spectra of adsorbed CO that are closely related. This is apparent from fig. 4, in which the spectra for the severely reduced catalysts have been collected. The spectra for the deposition-precipitated samples CU-1 and CU-2 are equal when we ignore the differences in intensity, which are due to the different optical density of the discs and the different specific copper surface area of the catalysts. The impregnated catalyst CU-3 gives rise to a band at lower wave-numbers with a shoulder around 2100 cm^{-1}. This leads us to the conclusion that for comparing copper catalysts by their infrared spectra of adsorbed CO, the shift of the absorption band upon more severe reduction is at least as important as is the result after prolonged reduction.
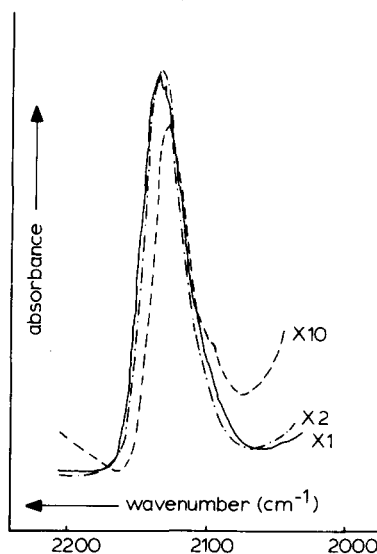

Fig. 4. Infrared spectra of CO adsorbed on Cu/SiO$_2$ after prolonged reduction at high temperature; sample CU-1 (−·−·−), CU-2 (———) and CU-3 (−−−).
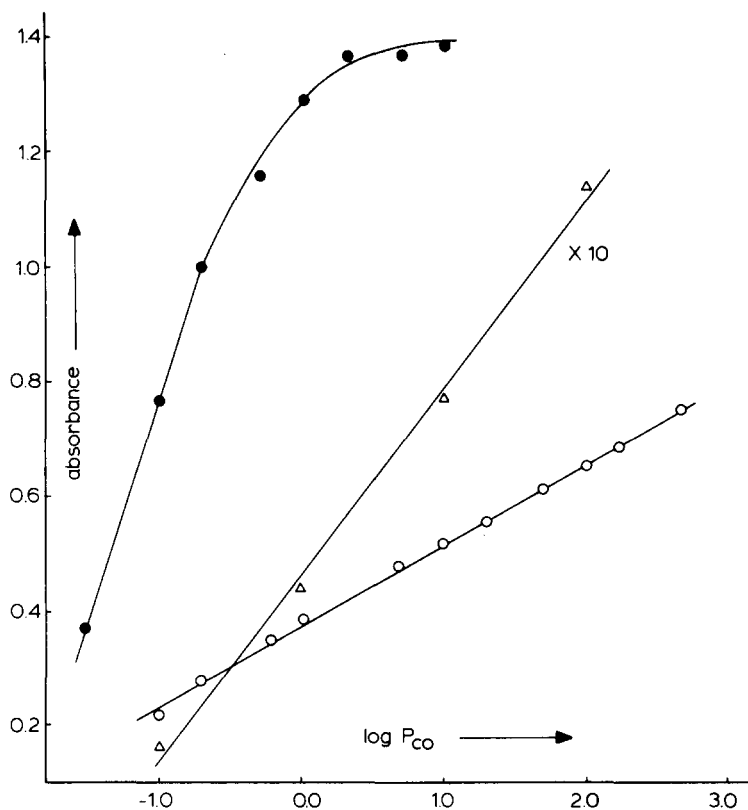
Fig. 5. The peak height of the absorption band of CO adsorbed on Cu/SiO_2 as a function of CO pressure; sample CU-1 (o), CU-2 (•) and CU-3 (△).

For all catalysts the absorbance at the peak maximum was measured as a function of the CO-pressure. The results have been collected in fig. 5. For catalysts CU-1 and CU-3 a linear relationship between the absorbance and the logarithm of the CO pressure exists. For CU-2 the band intensity seems to saturate at high pressures, but the large values of the absorbance causes the data to be less reliable.

A remark should finally be made about the importance of the vacuum conditions during these experiments. The spectra in fig. 6 have both been recorded after reduction of catalyst CU-3 at 300°C for 15 h. The more intense band at lower frequency was found after a leakage for a few minutes while pumping off the hydrogen at high temperature. Subsequent exposure to oxygen had hardly an effect on the absorption band which shows that the surface was already completely covered with oxygen.
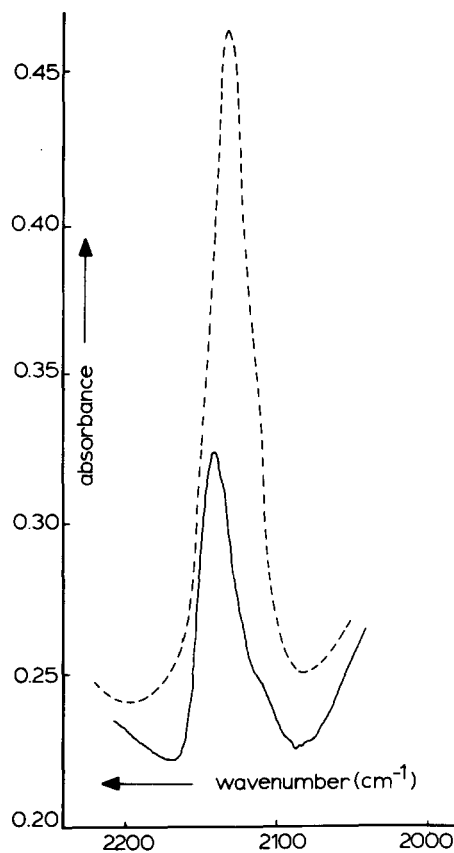
Fig. 6. Infrared spectra of CO adsorbed on sample CU-3 after reduction at 300°C and subsequent evacuation with (— — —) and without (———) a leakage.

3.2. Electron micrographs

Above we showed that the effect of the pretreatment of the catalysts on the infrared spectra of section 3.1 cannot be attributed to the degree of reduction of the copper species. We therefore investigated the catalysts in the transmission electron microscope. In figs. 7 and 8 electron micrographs are represented that have been selected from a large number of bright and dark field micrographs that provided consistent results. The catalysts prepared by deposition—precipitation (CU-1 and CU-2) show a very homogeneous distribution of copper particles over the carrier with a fairly narrow size-distribution. With CU-1 a small number of rather large particles (about 120 Å diameter) besides many particles that are smaller (about 60 Å) can be seen. Catalyst CU-2 shows the same bimodal particle-size distribution, but now the
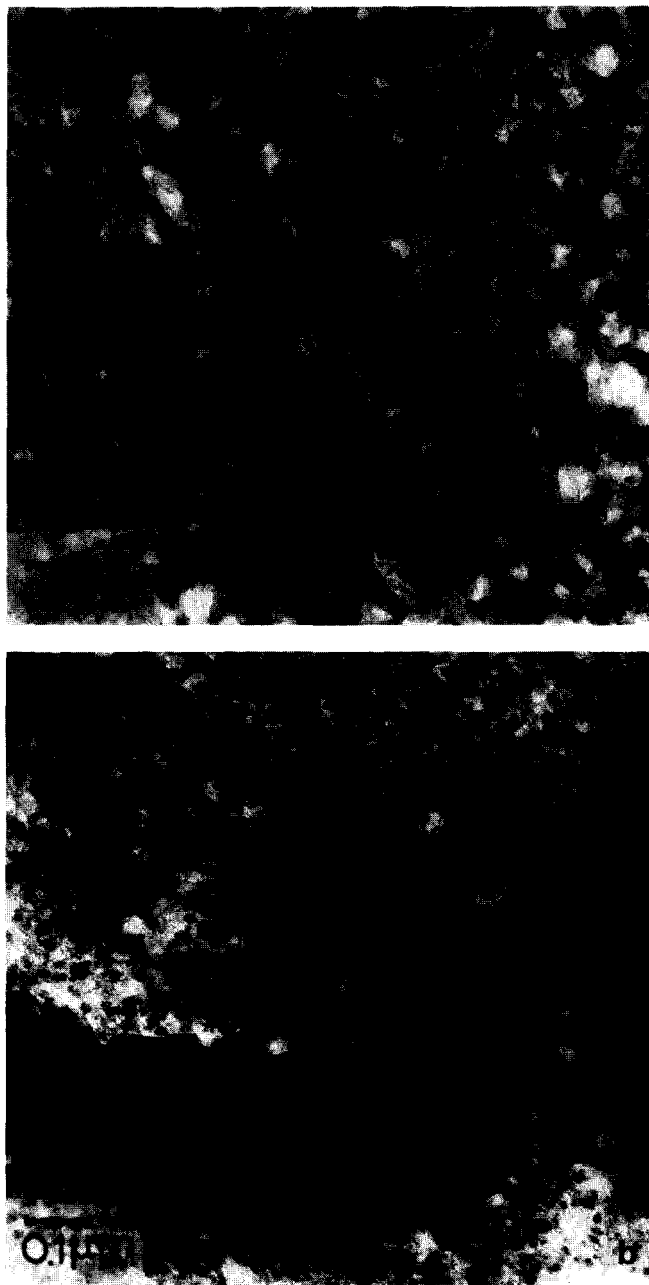
Fig. 7. Electron micrographs of Cu/SiO_2 catalysts, reduced at 300°C. (a) Catalyst CU-1, (b) catalyst CU-2.
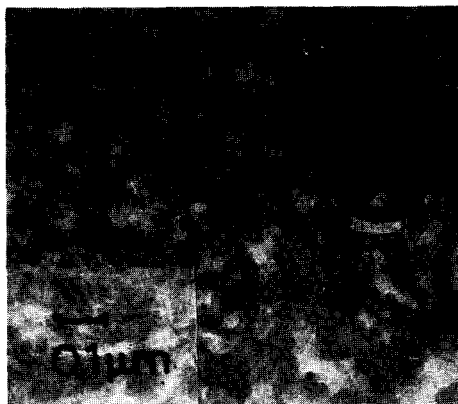
Fig. 8. Electron micrograph of catalyst CU-3, reduced at 300°C.

larger particles are more numerous. This is reflected in the (volume-) average diameter from X-ray line broadening of 110 and 190 Å for CU-1 and CU-2, respectively. The impregnation catalyst CU-3 has a very broad particle-size distribution, ranging from 40 to 5000 Å. We think that the dispersion of the metal by impregnation depends strongly on the drying procedure. Comparing results from different investigators for impregnation catalysts is therefore hardly possible. With our CU-3 there are still a large number of small particles (about 100 Å) which contribute appreciably to the total copper surface, but it is possible that other investigators have had mainly particles of 200 Å and larger.

4. Discussion

Using single crystals, vapour-deposited films and supported Cu-particles Pritchard and co-workers [2] investigated the adsorption of carbon monoxide on Cu-surfaces most profoundly. As a support they used SiO_2, Al_2O_3 and MgO. Sheppard and Nguyen [5] have published an excellent survey of infrared studies on adsorbed species dealing also with adsorption of CO on Cu.

With the closely packed (111) and (100) copper surfaces Pritchard et al. [2] recorded band maxima at 2070 to 2090 cm^{-1} on adsorption of CO at 77 K. The stepped (211), (311) and (755) surfaces showed a main maximum at 2100 to 2110 cm^{-1}. Especially the spectra of the (211) and (755) surfaces are important. These surfaces contain terraces having (111)-structure separated by (100)-like steps. The width of the (111) terraces on the (755) surface is larger than that on the (211) surface. In spite of the presence of (111) planes adsorption of CO on the (211) and (755) surface does not lead to frequencies characteristic of the flat (111) surface

(2070 to 2076 cm^{-1}). On the (111) and (100) surface CO is adsorbed in ordered structures as apparent from LEED experiments [6,7]. Since CO adsorbed in these structures shows frequencies from 2070 to 2076 cm^{-1} with the (111) surface, we feel that the structure of the adsorbed layer on extended (111) planes cannot be established on the relatively small terraces on the (211) and (755) surfaces. There is a density of steps on these surfaces that prevents adsorption of CO in an ordered structure exhibiting frequencies of 2070 to 2090 cm^{-1}.

Using Cu films deposited onto glass or alumina Pritchard et al. observed adsorbed CO to display frequencies of (2104 ± 2) cm^{-1}. Impregnated Cu/SiO$_2$ and Cu/Al$_2$O$_3$ catalysts reduced at 250°C or 350°C showed frequencies of (2105 ± 3) cm^{-1}, while alumina-supported catalysts containing more than 5% Cu showed frequencies from 2110 to 2120 cm^{-1}. The results with single-crystal surfaces suggest that both vapour-deposited Cu-films and supported Cu-particles mainly expose stepped surfaces. We cannot indicate precisely the critical step density where domains of adsorbed CO characteristic of the (111) or (100) surface cannot be markedly established. The step density of the films and supported catalysts is therefore not accurately known. Apparently Cu-crystallites present both in films and in supported catalysts interact differently with magnesia. Owing to the interaction Cu-crystallites on magnesia expose more extended closely packed planes. As a result CO adsorbed on Cu/MgO shows frequencies between 2079 and 2085 cm^{-1}.

Seanor and Armberg [8] recorded frequencies appreciably higher than 2110 cm^{-1} with silica-supported copper. They observed a frequency of 2143 cm^{-1}, which gradually decreased to 2130 cm^{-1} at an increasing number of reduction and degassing treatments at 400°C. With Cu/SiO$_2$ and Cu/Al$_2$O$_3$ Pritchard et al. also found a decrease in frequency from (2122 ± 2) cm^{-1} to (2105 ± 3) cm^{-1}, when the reduction temperature was raised from 140°C to 350°C. Admission of oxygen led to higher frequencies, which decreased again after reduction. Pritchard et al. therefore attributed bands at higher frequencies than about 2110 cm^{-1} to the presence of not completely reduced copper. CO adsorbed on CuO shows frequencies of about 2135 cm^{-1} [8,9].

Wavenumbers above 2104 cm^{-1} recorded in this work cannot be due to incompletely reduced copper. The data of table 2 demonstrate that reduction for 30 min at 200°C is sufficient to reduce the copper oxide in CU-3 completely. The most convincing evidence is from the deposition-precipitated catalysts, where more severe or more prolonged reduction shifted the frequencies to higher values. This was most pronounced with CU-1. After the first reduction (15 h at 300°C) the frequency peaked at 2104 cm^{-1}, which agrees with values published for films and severely reduced catalysts by [2]. Increase of the reduction time or temperature raised the frequency of the maximum to (2135 ± 4) cm^{-1}.

Since we measured a maximum above 2130 cm^{-1} with fully reduced supported copper catalysts, there must be still another structure of *metallic* copper surfaces. The structure must differ from that of flat closely packed or stepped surfaces. In the establishment of the structure of Cu-surfaces exhibiting frequencies above 2120

cm^{-1} we were guided by results published by Moskovits and Hulse [10,11]. These authors investigated copper—carbonyl complexes isolated in an argon matrix. With larger clusters of Cu-atoms they measured frequencies agreeing with those observed with films and stepped surfaces provided a red shift of approximately 15 cm^{-1} was taken into account. The red shift is commonly encountered in infrared spectra of argon-isolated species. The wavenumbers observed by Moskovits and Hulse corrected for the red shift are 2143, 2131 and 2127 cm^{-1}. Their results indicate that species in which CO is bonded to an isolated Cu-atom or to a Cu-atom strongly interacting with only a small number of other Cu-atoms are displaying frequencies above 2120 cm^{-1}.

The small anisotropy of the surface energy of copper [3,4] causes the equilibrium shape of Cu-crystallites to be rather spherical. Small equilibrated Cu-particles will therefore not contain straight steps of a considerable length in their surface, but curved steps only. The curved steps will consist of short straight rows of atoms containing a small number of Cu-atoms even down to two or one. Besides bonding of CO to protruding single Cu-atoms as a species similar to Cu—CO, bonding to the end of a step similar to Cu—Cu—CO or to both ends of very small rows similar to OC—Cu—Cu—CO can be expected with small equilibrated Cu-particles. To explain our infrared results we thus assume that small Cu-crystallites can expose surfaces having many protruding Cu-atoms or small clusters of Cu-atoms.

We next have to explain how the Cu-particles in our catalysts can expose both straightly stepped and atomically rough surfaces depending on the thermal treatment. Electron micrographs showed the impregnated catalyst CU-3 to contain well dispersed, very small, as well as strongly clustered copper nitrate particles. Since the amount of copper (II) ions atomically dispersed on the silica surface was small, the copper oxide was reduced fast. The completely reduced crystallites have therefore been rather prolonged at an elevated temperature during the first reduction (20 h) at 300°C. The very small copper crystallites resulting from the reduction of rather symmetrical copper oxide could therefore take up their equilibrium shape. The clustered larger copper crystallites ask for a considerable longer period to assume their equilibrium shape. The driving force for coalescence to large symmetrical crystallites, which is due to the local curvature of the surface is rather small, which causes the rate at which the equilibrium shape is taken up to be small. After the first reduction both the very small crystallites and the coalescing clusters of crystallites will consequently have atomically rough surfaces. As a result the completely reduced, impregnated catalyst CU-3 showed a band with a maximum at 2139 cm^{-1}. When the catalyst was reduced for 15 h at 400°C, the extent of reduction was not raised, but the clusters of Cu-crystallites coalesced to large single crystallites (up to about 5000 Å). Though the atomically rough surfaces of the small crystallites (100 ± 40 Å) were still dominating the spectrum, the stepped surfaces of the large particles exposed also a marked surface area. By calculations on assumed bimodal particle-size distributions we assessed the surface area of a limited fraction of large crystallites to be appreciable. The marked surface area of a small curvature leads to the

well resolved shoulder shown in fig. 3 at about 2100 cm^{-1}, which is characteristic of more extended stepped surfaces. A slight sintering of the small particles shifted the maximum of the main peak to 2129 cm^{-1}.

As we have demonstrated experimentally [9], a large fraction of the copper ions in the catalyst CU-1 had reacted with the silica support. On reduction of the fresh catalyst the copper oxide species deposited onto the silica, the copper ions of which have not reacted with the silica, rapidly reacts to small copper crystallites. The small copper crystallites subsequently capture copper atoms migrating over the silica surface. The migrating copper atoms are resulting from the reduction of copper ions atomically dispersed in the silica, which reduction was shown experimentally to proceed appreciably more slowly than that of the other copper oxide species. This brings about the copper crystallites to grow mainly parallel to the surface of the support. As a result flat, rather extended crystallites are obtained. The extended stepped top surface of these crystallites exhibits an absorption band peaked at 2104 cm^{-1}. Oxidation and reduction change the kinetically established flat crystallites into the more spherical crystallites of the thermodynamic equilibrium. Accordingly the frequency of the maximum shifts to 2131 cm^{-1}. The extended flat crystallites resemble the mono atomic rafts described by Prestridge et al. [12]. The thickness of our flat copper crystallites is of the order of that of the copper particles rapidly developed from the copper oxide species present on the silica surface. The small interaction of metallic copper atoms and the silica causes the copper particles to tend towards a spherical shape. As a result the thickness of our flat extended particles will be more than that of one or two copper atoms. After the first reduction of catalyst CU-1, the maximum of the absorption band is at 2104 cm^{-1}, which points to the presence of stepped surfaces of a low curvature. Fig. 1 shows also a marked intensity at $2070-2090$ cm^{-1} after the first reduction, which indicates more extended flat surfaces without steps to be also markedly present. The flat particles presumably have a larger copper surface area than the thermodynamically more stable crystallites present after oxidation and reduction. Provided the molecular intensity is not appreciably different, the drop in absorption from 1.03 to 0.52 (table 2) is due to the change in shape of the particles. With subsequent oxidation and reduction the about spherical copper particles are re-established.

With catalyst CU-2, which has a higher copper load, more copper species had been deposited onto the support. Owing to this the height of the copper crystallites resulting from the more easily reducible material is larger. Addition of copper atoms from the surface of the support to the larger crystallites leads to particles of a more hemispherical shape than with the freshly reduced catalyst CU-1. The resulting larger curvature of the surface causes the maximum of the absorption band to be situated at 2130 cm^{-1}. However, the marked absorption at 2100 cm^{-1} (fig. 2) indicates that extended flat crystallites were also present after the first reduction. Subsequent oxidation—reduction cycles shift the maximum to a slightly higher frequency (2136 cm^{-1}), while the intensity at 2100 cm^{-1} was appreciably reduced.

The catalysts CU-1 and CU-2 contain particles of a mean size of 60 and 120 Å,

respectively. Since both catalysts display absorption maxima at about the same frequency after equilibration, the particle size has not a very large effect. This is in keeping with the low anisotropy of the surface energy of copper.

The data published on Cu/SiO_2 catalysts show much diversity. We feel that this is due to the strong effect of the impregnation procedure and of details of the thermal pretreatment on the shape of the copper crystallites. Our results can be used to rationalize the data of the literature. The shift from 2120 to 2105 cm^{-1} on raising the reduction temperature from 140 to 250°C, found by Pritchard et al., may be due to formation of flat extended Cu-crystallites. Since the catalysts were not completely re-oxidized and again reduced, recrystallization to more spherical particles could not proceed. Since the reduction of copper oxide at 140°C is slow, the above shift may be due to the presence of remaining copper oxide, which adsorbs CO displaying a maximum at about 2135 cm^{-1}. The use of MgO as a support presumably leads to particles approaching the structure of rafts with a flat surface at the top. Seanor and Amberg reduced their Cu/SiO_2 longer at a more elevated temperature (400°C). Their Cu-particles could take up the equilibrium shape. Coalescence of clusters gradually shifted the maximum to lower frequencies.

In conclusion we can say that the vibrational frequency of carbon monoxide adsorbed on copper is a function of the surface roughness. The surface roughness depends upon the supply of copper atoms towards the particles during reduction on the one, and the particle size on the other hand. The diversity of data of infrared studies of CO adsorption on impregnated copper catalysts is caused by the irreproducible preparation and pretreatment of these catalysts. The differences are caused by large changes in particle shape and particle size distribution, and to a smaller extent to differences in the degree of reduction.

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