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CARBON MONOXIDE ADSORPTION ON ION-EXCHANGED COPPER AND COPPER-NICKEL ON SILICA CATALYSTS

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ABSTRACT

Copper and Copper-Nickel on Silica catalysts were prepared by the ion exchange method. Following reduction at different conditions the catalysts were characterized by adsorbed carbon monoxide Infrared Spectroscopy. After previous vacuum thermal pretreatment, an absorption band, from 2129 cm^{-1} to 2126 cm^{-1} (due to CO adsorbed on Cu^{+1} ions) was observed. The intensity of this band increased with the pretreatment from room temperature up to 773 K. However after hydrogen treatment, a downward shift (2126-2122 cm^{-1}) and intensity variations were observed depending on the reduction degree of the sample. The reduced samples (Cu°) did not adsorb carbon monoxide. When the catalysts were reduced in a CO atmosphere both the position and intensity of the absorption bands were dependent on the temperature, copper loading and CO/O_2 ratios. Ni^{+2} did not show CO absorption bands and it behaved as a diluent of Cu^{+2} ions hindering the $(Cu\text{-}O\text{-}Cu)^{+2}$ ion formation. Reduction with ethanol (483 K, P_{ol}= 5 KPa) led to a weak absorption band centered at 2123 cm^{-1}. In all cases, CO adsorption took place on Cu^{+1} and the frequency shifts (2128-2122 cm^{-1}) observed might be explained by electronic changes of their neighboring sites.

INTRODUCTION

The copper on silica catalysts prepared by the ion exchange method (Amara et al., 1987; Clause et al., 1989; Kohler et al., 1987; Stammbach et al., 1990; Wehrli et al., 1990; Clarke et al., 1993) and other similar techniques (deposition-precipitation (Van der Grift et al., 1989; Van Stiphout et al., 1988b), electrodeposition (Van Stiphout et al., 1988a) and coprecipitation) have been the subject of many contributions in the recent literature.

The most important industrial applications of these catalysts have been water gas shift reaction (Salmi and Hakkarainen, 1989) and low pressure methanol synthesis (Bartley and Burch, 1988; Burch and Chappell, 1988; Robbins et al., 1991; Robinson and Mol, 1991). Moreover, they have become important in hydrogenation and dehydrogenation reactions because of their high catalytic activity and low deactivation rate under reaction conditions.

Thus many researchers have studied in detail the structure of the precursors and the characteristic behavior of the reduced species on these catalysts. Most of them proposed that Cu^{+1} ions could play a very important role in reactions where CO or carbonilic compounds were involved, because these sites enhance CO adsorption.

Recently, Amara et al., (1987); Kohler et al., (1987) and Clause et al., (1989) concluded that the final structural characteristics of Cu/Silica catalysts were very dependent on metal loading, pH of the exchange solution, washing conditions and the chelating ligand properties of the exchanged complex. Thus from the literature two general kinds of ion exchanged catalysts can be distinguished:

a) Catalysts in which the amount of deposited copper is greater than the TEC(theoretical exchange capacity) of silica (considering that two hydroxyl groups are needed for each copper atom) (Kohler et al., 1987; Clause et al., 1989). The excess, deposited inside the support pores as hydroxo-ammoniacal complex (Kohler et al., 1987) is converted to copper hydroxide during the washing step (generally at pH≈7) as a consequence of the ammonium ligand replacement by hydroxo groups. Subsequent drying leads to highly dispersed $(OH)_2Cu$ which is transformed, after calcination, into CuO crystallite (<10 nm). After reduction, CuO is reduced to the metallic state. On these catalysts, the exchanged copper species remain attached to the surface through silanol groups and they

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can only be reduced to Cu^{+1} species. The combination of these two types of copper species might well be responsible for the unique behavior of this type of catalysts (Kohler et al., 1987).

b) Catalysts with copper loading lower than the TEC of the support. This was the specific case of the catalysts studied in this contribution. (See Experimental Section). During the exchange procedure (pH > 11) the tetrammine copper cation complexes are tight to the surface by electrostatic forces and subsequently converted into diammine copper species through the replacement of two ammonia ligands by two silanol groups during the drying step.

After calcination in air, at 723 K, two copper species are developed (Amara et al., 1987), namely $(Cu^{II}-O-Cu^{II})^{+2}$ and isolated Cu^{II} ions. The percentage of $(Cu^{II}-O-Cu^{II})^{+2}$ pairs depends on the degree of exchange. Below 20% of TEC of the support, isolated Cu^{II} are the predominant species. Within 20% to 70% approximately of TEC, $(Cu^{II}-O-Cu^{II})^{+2}$ pairs are developed. At higher copper loading hyperdispersed CuO could start to form.

On these catalysts, the stability of Cu^{+1} species depends on their coordination to the support. Amara et al. (1987), reported stable $(Cu^{II}-O-Cu^{II})^{+2}$ pairs, directly reduced to Cu^{+1} by evacuation up to 1073 K, while isolated Cu^{+2} ions were reduced to Cu° by CO above 623 K.

The valence state of copper ions, in conventionally supported and bulk catalysts, is often determined by IR Spectroscopy using CO as probe molecule (Clarke et al., 1993; Hollins, 1992; Kantcheva et al., 1992; Davydov et al., 1978; Busca, 1987; Kohler et al., 1989; Amara et al., 1987) but the obtained results are not always coincident. Accordingly, some authors suggested that CO did not form complexes with Cu^{+2} ions at room temperature. Only at 77 K could Cu^{+2} ions stabilize CO (Kantcheva et al., 1992) giving some bands in the 2180 to 2160 cm^{-1} range, probably due to the weak electron - acceptor ability of Cu^{+2} ions and/or to the high reactivity of the oxygen in the coordination sphere of copper. In all cases, however, carboxylate - carbonate structures are reported when CO adsorption is performed at room temperature as a consequence of the CuO reduction by the CO molecule. At room temperature, Davydov et al., (1978) and Amara et al., (1987) assigned the observed bands in the 2130-2115 cm^{-1} range to Cu^{+1}-CO carbonyl formation.

Nevertheless, other authors (Kohler et al., 1989; Jong et al., 1980) reported Cu^{+2}-CO carbonyl band formation, at room temperature, in a range (2130-2110 cm^{-1}) similar to that observed for Cu^{+1}-CO. The different behavior would probably be explained taking into account that the catalysts studied by these two researchers were characterized by the hyperdispersed CuO formation. The latter assumption is reinforced by the fact that while in bulk CuO catalysts, after the reduction to the metallic state, the infrared bands assigned to Cu°-CO appeared in the 2110-2080 cm^{-1} range, in the catalysts where hyperdispersed CuO crystallites are found (<10 nm) Cu°-CO chemisorption was reported in the 2115 to 2100 cm^{-1} range, showing a general trend that the increase of dispersion would promove infrared bands shift to relatively higher frequencies.

On the other hand, in those catalysts where Cu^{+2} ions remain as mono or binuclear copper species (i.e.: $(Cu^{II}-O-Cu^{II})^{+2}$ or isolated Cu^{II}), no carbonyl complexes on metallic centers but a high decrease in the Cu^{+1}-CO assigned band is observed after reduction in CO at 588 K (Amara et al., 1987). A similar behavior is reported in Cu/MgO solid solution catalysts after H_2 reduction (Davydov et al., 1978)and it is in agreement both with the low stability of the copper carbonyl complexes when the copper clusters range in size from monoatomic to four atoms particles (Huber et al.,1975; Moskovits and Hulse, 1977) and with copper organometallic complexes behavior in which Cu° carbonyl are difficult to be formed.

The present contibution is to report the behavior of the copper species on type (b) catalysts under several reduction conditions and their characterization by IR spectroscopy of chemisorbed CO. The role of the nickel ions, co-exchanged on the catalysts, is also investigated in order to establish the best conditions to stabilize Cu^{+1} while avoiding copper-nickel alloys formation.

EXPERIMENTAL

Support

Silica Davison G62, 60-100 mesh, 170 m^2/gr specific surface area, 9 nm mean pore diameter and 1.32 mmol OH/g Silica exchange capacity, is used as catalyst support.

Catalysts Preparation

The monometallic Cu/SiO_2 catalyst is prepared following the ion exchange method. An ammoniacal aqueous solution (1:1) is added to the support and the mixture stirred for 30 minutes. This being the standardized time for exchanging the silica protons by $(NH_4)^+$ ions. Then, copper ammoniacal complex solution $[Cu(NH_3)_4]^{+2}$ is slowly poured into the $(NH_4)^+$ exchanged silica under stirring conditions during 30 minutes. The pH of the solution is always higher than 11 and the amount of copper complex added is exactly the necessary to obtain the desired copper loading, which is kept below the exchange capacity of the support. After the exchange process the solution is colorless (all the Cu^{+2} complex was exchanged on the support). Then, the solution is filtered and the solid washed with distilled water. The catalyst is dried at 383 K for 4 hr and then calcined in air at 723 K for 4 hr.

Copper-Nickel catalysts are prepared by subsequent exchange of nickel and copper ammoniacal complex solutions as follows. After the exchange of the silica protons by $(NH_4)^{+1}$ ions, these are exchanged by the cation complex $[Ni(NH_3)_6]^{+2}$. The mixture is filtered, washed and dried at 383 K for 4 hr. Then, following the same procedure, after exchanging the silica protons by $(NH_4)^{+1}$ ions, the exchange of the copper ammoniacal complex is carried out. Finally, the catalysts are dried at 383 K and calcined at 723 K for 4 hr.

In all cases, the calcined samples present a blue colour.

Copper and Nickel Content

Metal loading of the catalysts samples are determined by atomic absorption spectroscopy in a Metrolab RC 250 AA spectrometer. The copper and nickel loading of the catalysts are shown in table 1.

TABLE 1

Metal loading of the monometallic and bimetallic catalysts

Catalyst Name	% Cu	% Ni
2% Cu	2.00	----
0.5% Ni + 0.25% Cu	0.25	0.50
0.5% Ni + 0.5% Cu	0.49	0.48
0.5% Ni + 1% Cu	0.85	0.48
0.5% Ni + 2% Cu	1.64	0.47
1% Ni + 0.5% Cu	0.41	0.82

Carbon Monoxide adsorption studies

Samples of each catalyst are finely ground and pressed at 4 tn/cm^2 into 1 cm diameter thin disks of 25 mg weight. A conventional glass high-vacuum system and an Infrared cell with KRS5 windows [thallium bromide (42%) - thallium iodide (58%)] are used to carry out different "in situ" pretreatments, .

The catalysts are pretreated, before CO absorption, under different conditions (vacuum, H_2, O_2, CO, ethanol) and the experiments performed at different temperatures. Reduction of the catalysts is carried out by flowing hydrogen either for 15 minutes or for 1 hr. Reoxidation of the samples, previously evacuated or reduced in hydrogen, is carried out in pure oxygen for 15 minutes at 13.3 KPa. In CO reduction experiments, the samples are pretreated with CO or O_2:CO (5:75) mixtures for 30 min at 10.6 KPa. In order to study the final state of the catalyst during the ethanol dehydrogenation reaction, samples are reduced with an ethanol-nitrogen mixture stream (Pol = 5 KPa), at 473 K and using several reaction times.

In all cases, after the different pretreatment and prior to CO adsorption, the cell is evacuated at room temperature (RT). The chemisorbed CO spectra are recorded under 10.6 KPa of CO at RT on a Perkin Elmer Model 683 spectrometer connected to a data station. Difference spectra are shown in the 2300 -1800 cm^{-1} region; the subtraction of the spectra is carried out with reference to the respective blank catalyst spectra.

RESULTS AND DISCUSSION

Carbon Monoxide adsorption on the Support

Spectra of carbon monoxide adsorbed on vacuum pretreated (423 K) silica (Fig.1) show the presence of two bands: one centered at 2143 cm^{-1}, assigned to C≡O stretching vibrations (gaseous carbon monoxide) (Straghan and Walker, 1976) and another at 2006 cm^{-1}.

Both bands disappear at pressures below 13.3 KPa. The band at 2006 cm^{-1} is assigned to carbon monoxide physically adsorbed on the support. On the other hand, no changes are observed in the O-H stretching region of hydroxyl groups at a pressure of 13.3 KPa, indicating no interaction between CO molecules and O-H groups at R.T.

To avoid the presence of gaseous CO and physically adsorbed CO bands the experiments are carried out at a pressure of 10.6 KPa.

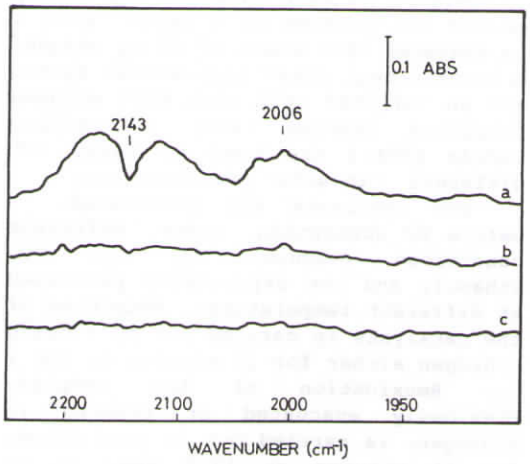

Fig. 1. *Infrared spectra of CO adsorbed on SiO_2 pretreated in vacuum at 473 K, under different CO pressures at RT. a) 80 KPa ; b) 13.3 KPa; c) 6.7 KPa*

CO Adsorption on 2% Cu/SiO_2 Catalysts. Evacuation

The spectrum of adsorbed carbon monoxide on Cu/SiO_2 catalysts, previously evacuated at RT, are shown in Fig. 2a. The intensity of the developed absorption band (2127 cm^{-1}) increases from 0.03 to 0.12 absorbance units after 90 minutes of contact time with CO (10.6 KPa) at RT (Fig. 2b). Simultaneously two weak absorption bands in the 1800-1500 cm^{-1} region assigned to carbonate and/or carboxilate species (Davydov et el., 1978) are observed (Fig. 9a). This behavior is explained by the oxidation of CO to CO_2 on Cu^{II} centers and the consequent reduction of them to Cu^{+1} sites that chemisorb CO. A similar behavior is reported by (Amara et al., 1987 and Davydov et al., 1978).

Fig. 2 shows the effect of the evacuation temperature (from RT to 723 K) previous to CO adsorption. In fact, a gradual increase (form 0.1 to 0.8 absorbance units) of the 2127 cm^{-1} band intensity as evacuation temperature increases can be observed. After vacuum pretreatment at temperatures higher than RT(ie: from 423 K to 723 K) the CO adsorption shows no contact time effect on the intensity of the absorption band at 2126 cm^{-1}. Consequently, the bands in the 1800-1500 cm^{-1} region are vanished or seriously diminished (Fig. 9).

For a sample pretreated at 723 K the intensity of the 2127 cm^{-1} adsorption band remains unaltered and only a broadening towards the side of low frequencies is observed after 24 hour of contact time probably due to CO adsorption on Cu^{+1} centers with different electronic environment (Clarke et al., 1993).

On the other hand, in Fig. 2 it is observed that the position of the absorption band after the different vacuum pretreatment, is almost the same (ie: 2128-2126 cm^{-1}) in all the temperature range. In a similar way, within the 1 to 10.6 KPa range, the band position does not show a significant shift (Hollins, 1992) probably due to the low copper loading and the special structural characteristics of the paired and isolated copper atoms.

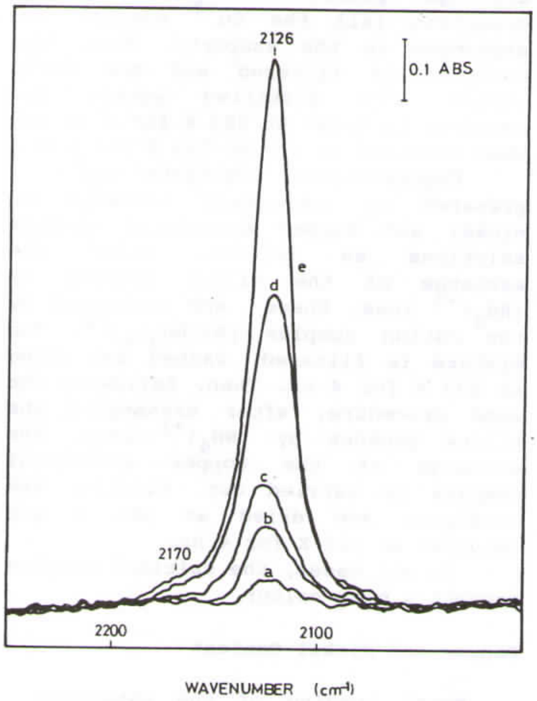

Fig. 2. *Infrared spectra of CO adsorbed on 2% Cu/SiO_2 under 10.6 KPa CO pressure, at RT. Sample pretreatment: evacuation for 30 min. at: a) 300 K and contact with CO for 1 min.; b) 300 K and contact with CO for 1 hr. 30 min.; c) 423 K; b) 573 K; e) 723 K.*

At high evacuation temperatures (> 573 K) a second weak absorption band appears as a shoulder at 2170 cm^{-1}. Also, as the samples are evacuated from R.T. to 573 K the blue original colour changes to pale yellow. These results are in agreement with those previously reported by Amara et al. (1987). These facts suggest that the vacuum thermal pretreatment leads to a reduction of

Cu^{+2} ions by decomposition of $(Cu^{II}\text{-}O\text{-}Cu^{II})^{+2}$ pairs as follows:

$$(Cu^{II}\text{-}O\text{-}Cu^{II})^{+2} \text{ ---> } 2\ Cu^{+1} + 1/2\ O_2.$$

The assignment of the 2127 cm^{-1} band to CO adsorbed on Cu^{+1} is in agreement with other author's reports for CO adsorbed on prereduced Cu catalysts on different supports (Amara et al., 1987; Davydov et al., 1978; Kantcheva et al., 1992).

The band at higher frequencies (2170 cm^{-1}), observed as a shoulder in the left side of the 2127 cm^{-1} peak, for samples preevacuated at high temperatures was also reported by Amara et al. (1987). It can be either, assigned to $Cu\text{-}C{\equiv}O^{+}$ species formation, in agreement with Hierl et al. (1981) and Gardner and Petrucci (1960), based on the existence of a relationship between the vibration frequency of adsorbed CO and the number of valence electrons associated with the copper centers, or, according to Amara et al. (1987) to carbonyl formation with the unreduced Cu^{II} centers arising from $(Cu^{II}\text{-}O\text{-}Cu^{II})^{+2}$ pairs.

The reoxidation degree of the samples, previously outgassed at 723 K, depends on temperature. Thus, at RT, no decrease in the intensity of the CO band is observed when CO is adsorbed. But, when the temperature under O_2 is increased, subsequent CO adsorption shows a decrease of the absorption band and a shift towards higher frequencies (2129 cm^{-1}). After reoxidation at 573 K, the intensity of the chemisorbed CO band is considerably small and the colour of the sample becomes blue indicating both that reoxidation is produced and that Cu^{+2} ions have recovered their water ligands probably by taking them from the support. Although the shift from 2126 to 2129 cm^{-1} is within the experimental error, it is systematically observed. It migh be explained by electronic effects of reoxidized Cu^{+2} ions adjacent to Cu^{+1} centers. Due to the Cu^{+2} neighbor ions the back donation of Cu^{+1} electrons to π^* antibonding CO orbitals is decreased, the Me-C bond is weakened and the C-O bond becomes strengthened with a consequent increase of the CO frequency.

Other experiments show that evacuated samples are easily oxidized at 300 K and turn blue in the presence of moisture from the air. When moisture is not present the oxidation process requires higher temperatures (> 373 K). A similar behavior was reported by (Huang, 1973a and b) on Cu^{+2} exchanged on Y Zeolites.

Reduction in hydrogen

Fig.3 shows that the principal absorption band intensity increases as reduction temperature in H_2 increases. It reaches a maximum in the range between 423 K and 473 K. At higher temperatures the intensity decreases and after 15 minutes of reduction at 673 K the sample turns reddish black and the absorption band disappears. The CO band continuously shifts from 2129 cm^{-1} to 2122 cm^{-1} as the reduction conditions become more severe.

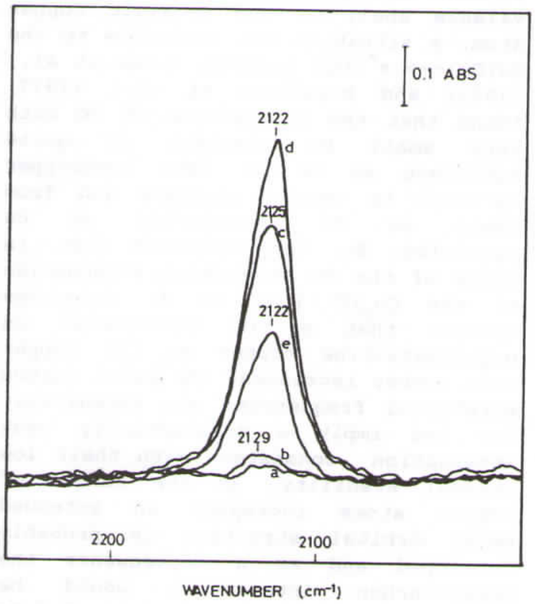

Fig. 3. *Infrared spectra of CO adsorbed on 2% Cu/SiO_2 under 10.6 KPa CO pressure, at RT. Sample pretreatment : reduction in hydrogen for 15 min at: a)300 K b) 353 K; c) 423 K; d) 473 K; e) 523 K.*

The changes in the intensity and frequency of the absorption band can be explained by changes in the oxidation state of the copper atoms close to that on which CO is adsorbed. After hydrogen treatment at 423 K the reduction of Cu^{+2} ions to Cu^{+1} is carried out in a great extent and it causes an increase in the intensity and a consequent shift of the band in the frequency from 2128 cm^{-1} to 2125 cm^{-1}. The last, due to the presence of Cu^{+1} ions that increased the magnitude of the back-donation. When the reduction temperature in H_2 and/ or when reduction time is increased, the transformation

Cu^{+1} -----> Cu°

is produced (curve a; Fig.4) which is observed by a decrease in the intensity of the absorption band. These Cu° sites do not adsorb CO at RT.

The decrease of the Cu^{+1}-CO adsorption band intensity after reduction is in agreement with Amara et al. (1987) results on Cu/SiO_2 catalysts prepared by a similar technique and also with those of Davydov et al., (1978) on CuO/MgO solid solution after H_2 reduction.

When isolated copper atoms are found on the catalyst surface and are not included in a metallic structure no CO adsorption can be predicted taking into account the stability of a filled 3d valence shell of the metallic copper atom, a situation not conducive to the $d\pi(Cu) \dashrightarrow \pi^*(CO)$ bonding. Huber et al., (1975) and Moskovits et al., (1977) found that the interaction of CO with very small Cu clusters is quite different as we go from monocopper carbonyl to copper clusters and from these to CO chemisorbed on Cu particles. So, they observed that, in spite of the CO stretching frequencies of the Cu_nCO (n=1 to 4) molecules aproach that of CO chemisorbed on polycrystalline copper as the copper atom number increases, the metal carbon stretching frequencies are anomalously low and imply a substantially weak interaction consistent with their low thermal stability. As the number of copper atoms increases an extended metal orbital structure is probably developed and as a consequence the Metal-Carbon interaction would be fortified giving the typical Cu°-CO chemisorption band reported in the literature.

The shift in frequency from 2125 cm^{-1} to 2122 cm^{-1}, after a more rigorous reduction is carried out on the partially reduced catalyst, can be explained by the presence of Cu° in the neighbor of Cu^{+1} sites. It produces an increase of the back donation and the CO π bond is weakened.

The CO adsorption after the catalysts are oxidized with oxygen (4 KPa and 13.3 KPa) at RT for 10 min, leads to an increase of the absorption band (spectra 4b and c) which indicates that metallic copper is reoxidized to cuprous ions. Subsequent oxidation at 373 K causes a decrease of the absorption band indicating that oxidation of cuprous to cupric ions takes place under those conditions (Fig. 4d). When the catalysts are treated with CO (10.6 KPa) for 50 hr at RT (Fig.4e), the intensity of the absorption band increases showing that the reduction of cupric to cuprous ions takes place again.

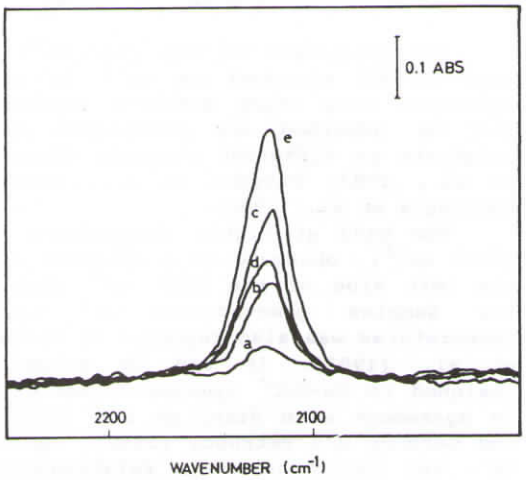

Fig. 4. *Infrared spectra of CO adsorbed on 2% Cu/SiO_2 under 10.6 KPa CO pressure, at RT.*
a) Reduction in H_2 for 1 hr. at 593 K.; b) Reoxidation with O_2 (4 KPa) for 10 min at RT; c) Reoxidation with O_2 (13.3 KPa) for 10 min at RT. d) Reoxidation with O_2 (13.3 KPa) for 10 min at 373 K.; e) Contact with CO (10.6 KPa) for 50 hr.

Reduction with carbon monoxide

Fig. 5 shows the changes of intensity and frequency of the CO absorption band when the catalyst is pretreated in a carbon monoxide atmosphere. After the pretreatment with a $CO:O_2$ (75:5) mixture at different temperatures two regions can be observed: one, below 503 K, where the band intensity rise up to 0.25 absorbance units (CO = 2129 cm^{-1}) and a second region, above 503 K, where a sudden increase of the band intensity and a shift in frequency towards 2123 cm^{-1} is observed. The sample becomes progressively dark and at 553 K it turns brown showing a decrease in the intensity of the absorption band. At 603 K no CO adsorption is observed. The reoxidation with oxygen cause an increase of the intensity of the peak and a shift towards higher frequencies (2126 cm^{-1}).

These two regions are less pronounced when the sample is reduced under pure CO (10.6 KPa). Under these last conditions, the changes in intensity and the shifts in frequency are smooth and continuous (Fig. 5).

These results lead to the following interpretations.

i) The Cu^{+2} ions are reduced with pure

CO in a degree that is very dependent on temperature. While temperature remains below 503 K the

$$Cu^{+2} \longrightarrow Cu^{+1}$$

reduction is the predominant process, but when temperature rises above 503 K, the Cu^{+1} to Cu° reaction becomes important. This process occurs simultaneously with the previous one. As a consequence of these phenomena a maximum in the CO - Cu^{+1} intensity band and a shift (2126 to 2120 cm^{-1}) in the band frequency is observed.

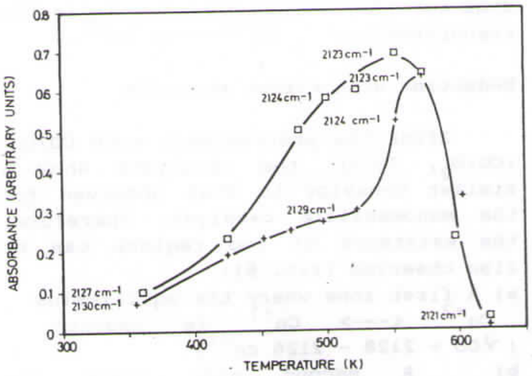

Fig. 5. *Intensity of the CO absorption band (under 10.6 KPa CO pressure, at RT) on the 2 % Cu/SiO_2 catalyst as a function of pretreatment temperature in a CO atmosphere.* □ *CO ;* + *$CO:O_2$, 75:5 mixture.*

ii) When the reduction is performed in a $CO:O_2$ mixture the presence of oxygen induces an equilibrium between the different Cu species :

$$Cu^{+2} \Longleftrightarrow Cu^{+1} \Longleftrightarrow Cu°.$$

Below 503 K, Cu^{+2} to Cu^{+1} is the predominant process which is limited by the oxygen presence. Due to this, the intensity of the CO-Cu^{+1} band remains in a plateau up to this temperature. Above 503 K, the transformation Cu^{+2} to Cu^{+1} continues while the transformation Cu^{+1} to Cu° begins and metalic sites appear. The intensity of the CO - Cu^{+1} band suddenly increases, passes through a maximum and decreases. This process is followed by a shift towards lower frecuencies. The intensity of the CO band is always lower than those observed after evacuation of the catalyst at 723 K (Fig. 2). This suggests that following the appearance of a certain ammount of Cu^{+1} ions these are suddenly reduced to the metalic state under CO atmosphere. Simultaneously, the oxidation of CO to CO_2 takes place.

The presence of carbonates and carboxylates adsorbed on the catalyst is only detected as very low intensity bands in the 1700-1300 cm^{-1} region when the samples are pretreated at R.T. At higher temperatures carbonates and carboxylates bands are missing (Fig. 9); because the sample is evacuated before CO is adsorbed and the spectra are recorded.

Reduction with ethanol

When the catalyst is pretreated under 5 KPa of ethanol at 473 K, the dehydrogenation reaction is carried out and acetaldehyde is produced. It is

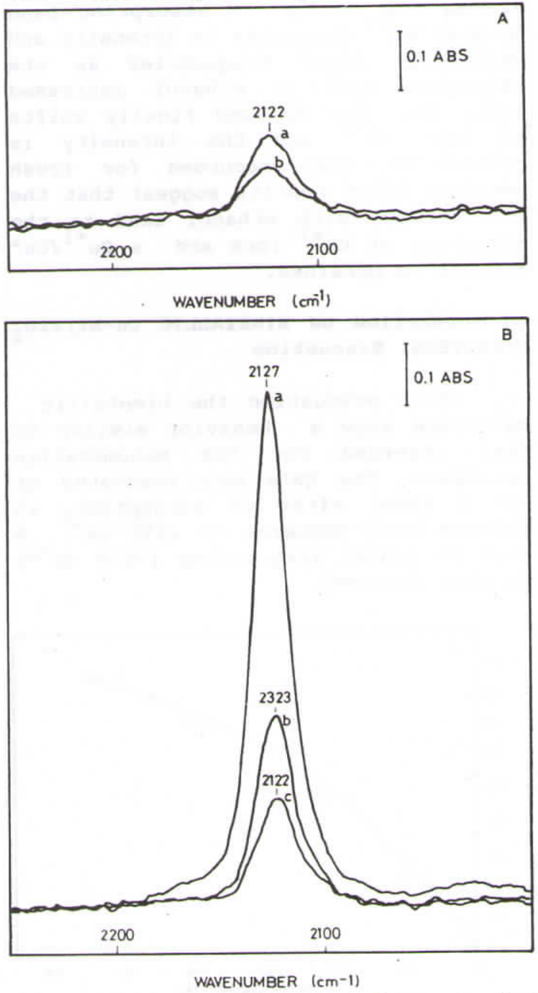

Fig. 6. *Infrared spectra of CO adsorbed on 2% Cu/SiO_2 under 10.6 KPa CO pressure, at RT. Sample pretreatment: reduction in ethanol at 473 K.*

A - *Fresh catalyst: a) 30 min. in ethanol; b) 1 hr. in ethanol.*

B - *Previously evacuated catalyst at 723 K: a) without reduction in ethanol; b) 1 hr. in ethanol; c) 2 hr. in ethanol.*

interesting to study the behavior of the catalyst under reaction conditions using CO adsorption as a characterization technique.

Two kinds of experiments are performed: (Fig. 6A and 6B).

A) A fresh catalyst sample is brought to reaction conditions and the catalyst analyzed at different reduction times.

B) Previous to the pretreatment with ethanol the sample is evacuated at 723 K.

In the first case a weak band at 2123 cm^{-1} remained practically unchanged at different reduction times. In the second case, after evacuation at 723 K, the intense CO absorption band at 2127 cm^{-1} decreases in intensity and shifts to lower frequencies as the reduction time in ethanol increased (fig. 6b). The CO band finally shifts to 2123 cm^{-1} and the intensity is similar to that recorded for fresh samples. These results suggest that the pretreatment with ethanol lead to the reduction of Cu^{+2} ions and a Cu^{+1}/Cu° mixture is obtained.

CO ADSORPTION ON BIMETALLIC $Cu-Ni/SiO_2$ CATALYSTS. Evacuation

After evacuation the bimetallic catalysts show a behavior similar to that observed for the monometallic catalysts. The catalysts evacuated at 723 K show, after CO adsorption, an intense band centered at 2126 cm^{-1}. A peak at higher frequencies (2170 cm^{-1}) is also observed.

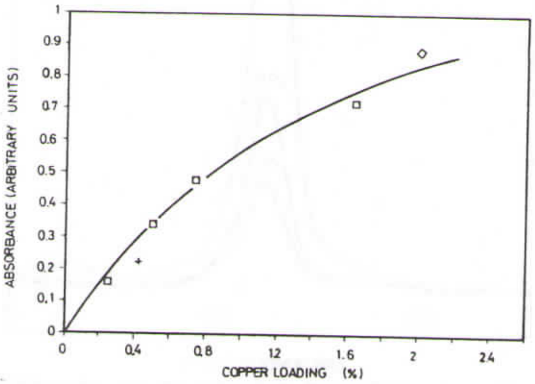

Fig. 7. *Intensity of the CO absorption band (under 10.6 KPa CO pressure, at RT) on Cu and $Cu-Ni/SiO_2$ catalysts, pretreated in vacuum at 723 K for 30 minutes, as a function of copper loading.* □ *0.5 % Ni, previously exchanged.*

\+ *1 % Ni, previously exchanged.*

◇ *Copper monometallic catalyst.*

Evacuation at 723 K, for 30 minutes, of a series of catalysts with 0.5 % nickel, which have been previously exchanged with different amount of copper, show an increase of the CO absorption band with increasing copper loading (Fig. 7).

The same figure includes the results obtained for a catalyst with higher amount of nickel (1 % Ni + 0.5 % Cu) and for the monometallic catalyst (2 % Cu). Both catalysts show a good fitting to the curve for catalysts with 0.5 % Ni and different copper loading.

These results suggest that nickel does not play a fundamental role in the transformation $Cu^{+2} \text{ ----> } Cu^{+1}$.

Reduction with carbon monoxide

After the pretreatment with CO/O_2 ($CO:O_2$, 75:5), the catalysts show a similar behavior to that observed for the monometallic catalyst. Therefore, the existence of two regions can be also observed (fig. 8):

a) A first zone where the equilibrium $Cu^{+2} \text{ <---> } Cu^{+1}$ is reached (ν CO = 2128 - 2126 cm^{-1}).

b) A second zone where the transformation $Cu^{+1} \text{ ---> } Cu^{\circ}$ is carried out (ν CO = 2123 - 2122 cm^{-1}).

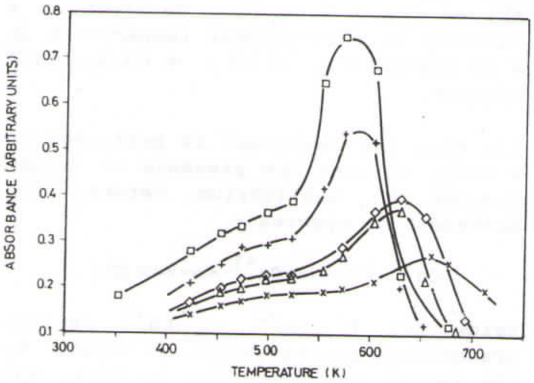

Fig. 8. *Intensity of the CO absorption band (10.6 KPa CO pressure, at RT) on $Cu-Ni/SiO_2$ catalysts as a function of the pretreatment temperature in a mixture $CO:O_2$, 75:5.*

□ *0.5% Ni - 2% Cu.*

\+ *0.5% Ni - 1% Cu.* △ *0.5% Ni - 0.5% Cu*

× *0.5% Ni - 0.25% Cu.* ◇ *1% Ni - 0.5% Cu.*

The transition temperature between the two zones depends on copper content. Low copper content samples present a high transition temperature. This dependence is in agreement with a high stability of Cu^{+1} species at low copper content, due to the presence of isolated Cu^{+2} species in high proportion and the subsequent transformation Cu^{+1} ---> Cu° at higher temperatures.

At high copper loading and low nickel contents the maximum of the curve (Absorption intensity vs treatment temperature, Fig. 8) shifts towards low temperatures; from 673 K for (0.5 % Ni + 0.25 % Cu) to 588 K for (0.5 % Ni + 2 % Cu) and 573 K for the copper monometallic catalyst. Above 673 K a sudden decrease of the intensity of the CO band is observed and the sample turns brown indicating the presence of metallic copper.

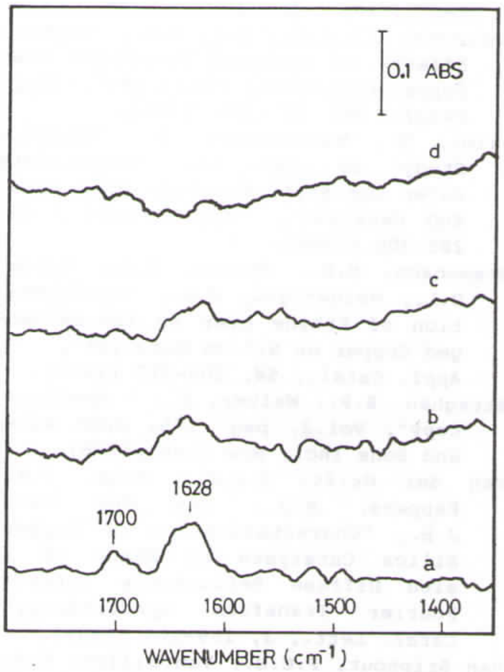

Fig. 9. *Infrared spectra of CO adsorbed on 2% Cu/SiO_2. 10.6 KPa of CO, at R.T. Sample pretreatment: a) Evac. 5 min. at R.T. and then 2.25 hr in CO. b) Treated in CO (10.6 KPa) at 373 K for 30 min. c) Treated in CO (10.6 KPa) at 473 K for 30 min. d) Treated in CO (10.6 KPa) at 723 K for 30 minutes.*

It seems that the nickel sites act as a diluent of copper atoms favoring the stabilization of Cu^{+1} sites; probably by hindering $(Cu^{II}\text{-}O\text{-}Cu^{II})^{+2}$ sites formation. Therefore, the temperature at which the transformation Cu^{+1} to Cu° begins depends upon copper content and the dilution effect of nickel sites.

CONCLUSIONS

Ion exchanged copper catalysts present the following behavior after evacuation and reduction in different atmospheric conditions.

a) Evacuation of the catalysts leads to Cu^{+1} ions formation as temperature increases. The reoxidation of previously evacuated catalysts restored Cu^{+2} sites.

b) Reduction with hydrogen at low temperatures leads to Cu^{+1} ions formation; high temperatures or long reduction times cause the transformation to the metallic state. Progressive reoxidation of the catalysts restores Cu^{+1} and Cu^{+2} sites.

c) After reduction with CO the transformation :

$$Cu^{+2} \text{ -----> } Cu^{+1} \text{ -----> } Cu°$$

occurs which depends upon: temperature, oxygen pressure, amount of exchanged copper and diluent effect of the nickel sites.

d) Reduction with ethanol at 473 K leads to a mixture Cu^{+1}/Cu° species, under reaction conditions.

In all cases CO adsorption is carried out on Cu^{+1} sites. The observed shifts in frequency are attributed to different electronic environment due to the presence of Cu^{+2} or Cu° adjacent sites.

NOMENCLATURE

R.T.	room temperature
ABS.	absorbance (arbitrary units)
Me	metal
Pol	ethanol partial pressure
π^*	unfilled π antibonding carbon monoxide orbitals.
ν	wavenumber (cm^{-1}).

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