

CHARACTERIZATION AND QUANTIFICATION OF SILICA SUPPORTED
IONIC COPPER SPECIES BY I.R. SPECTROSCOPY AND GRAVIMETRY OF
ADSORBED PYRIDINE

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ABSTRACT

The pyridine chemisorption on ion exchanged Cu/SiO₂ catalysts with copper loading between 0.25% and 2% w/w was performed in order to characterize the surface species by infrared spectroscopy. Two types of Cu⁺² ions were identified, i.e.: isolated and occluded Cu⁺² ions and exposed pairs (Cu-O-Cu)⁺². A gravimetric technique was developed to quantify them. The dispersion of metal ions was determined assuming an arbitrary 1:1 stoichiometry. The catalytic activity for the dehydrogenation of ethanol was correlated with the amount of pyridine chemisorbed on Lewis acid sites constituted by Cu⁺² unsaturated centers. These copper ions present on the catalyst precursor are proposed to develop a "hydrosilicate like" structure.

INTRODUCTION

Infrared study of adsorbed pyridine (Py) has frequently been used to characterize the acid-basic properties of solid surfaces (Boehm and Knözinger, 1983; Peri, 1984; Kung and Kung, 1985). Thus, it is of great advantage in distinguishing between Brønsted and Lewis acid sites on solid catalysts.

Parry (1963), originally, has identified the adsorption levels of Py which correspond not only to the molecules chemisorbed on acid sites but also to those molecules bound by physical adsorption and hydrogen bonded (H-Py) to the surface. Its behaviour is followed spectroscopically, in the case of Lewis coordination (LPy) and H-Py, by checking the shift in frequency of Al ring vibration modes nominated 8a, 8b, 19a and 19b (Kline and Turtkevich, 1944).

On the other hand, adsorption on Brønsted acid centers is monitored by the appearance of bands at 1630 and 1540 cm⁻¹ assigned to the pyridinium ion (HPy⁺) (Parry, 1963).

Any surface force exerted by a catalytic material must cause a change in the symmetry of the probe molecules. The nature of this change can directly be related to the nature of the adsorption which also yields information

regarding the coordination properties of the surface site. Consequently, the presence of Lewis acid sites on oxides such as Al₂O₃ (Morterra et al., 1978), MgO (Morterra et al., 1973; Noller et al., 1980) and others (Schwartz et al., 1978; Hughes et al., 1969; Lefrancoise and Malbois, 1971) was determined by Py adsorption and some efforts have been performed in order to characterize the coordination state of ions such as Al⁺³, Mg⁺² and Zn⁺². Recently some transition metal on silica catalysts were characterized by this technique (Conell and Dumesic, 1987).

On ion exchanged catalysts, the transition metal ions are grafted on the silica support attached by oxygen atoms (Che et al., 1988) and they complete their coordination number with hydroxyl groups or labiles ligands such as water or ammonia, depending this of the previous history (Clause et al., 1989). Furthermore, these ligands can be removed by thermal or vacuum treatment leaving coordinatively unsaturated ions that can chemisorb Py. This behaviour was also observed on ion exchanged with transition metal ions zeolites (Vazquez et al., 1986; Huang, 1973).

The present paper reports the acid-basic characterization of ion exchanged copper-silica catalysts and their behaviour are compared with those of impregnated ones and chrysocolla (a natural copper hydrosilicate mineral).

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Furthermore, the amount of LPy, determined by a gravimetric technique, was correlated with the catalytic activity for the ethanol dehydrogenation reaction.

EXPERIMENTAL

Specific surface areas were measured by a gravimetric technique (Gonzo, 1982), while the pore size distribution was determined with an Aminco 60 K mercury porosimeter.

Davison grade 62 Silica gel, calcined in air at 1023 K during 5 hours, was used as support. The surface area was 150 m²/gr and the mean pore size 10 nm.

Copper acetate monohydrate from Mallinckrodt Chemical Co. of analytical grade was used to prepare all the catalysts.

The preparation techniques were:

a) Ion exchanged catalysts (I.E.):

The hydroxyl groups of the silica surface were exchanged with NH₄⁺ ions by immersing a given weight (usually 5 g.) of the support in 300 ml of 1:1 aqueous-ammonia solution. Then, 100 ml of Cu(NH₃)₄²⁺ solution (1:1 NH₄OH:H₂O) was slowly dropped (30 min.) into the stirred suspension of silica gel-ammonia solution. The copper complex concentration was just to obtain the desired amount of copper on the silica (from 0.25% to 2% w/w). After this treatment the solution was colorless indicating that all the complex was exchanged. The solution was stirred 30 minutes more in order to eliminate all Cu(OH)₂ traces that could be formed within the pore structure and to ensure that all the copper was grafted on the silica surface (Köhler et al., 1987).

Cu-Ni/SiO₂ catalyst was prepared by a successive exchange of both ions. Nickel was previously exchanged by a similar procedure to that above described. Nickel acetate tetrahydrate from Mallinckrodt Chem. Co. of analytical grade was used to prepare the hexamine nickel solution. After the catalyst was dried at 383 K for 4 hr it was immersed again in the ammonia solution and then the copper complex solution was dropped.

Each product was filtered and thoroughly washed with a 1:1 NH₄OH:H₂O solution and then with distilled water. The catalysts were dried at 383 K and calcined in air at 723 K for 4 hours.

The amount of copper and nickel on the catalysts was determined by atomic absorption spectroscopy and it was very close to the theoretical amount added

except for the 2% catalyst were the amount of metal determined was 1.87%.

b) Impregnated Catalysts:

They were prepared by using the required amount of copper acetate solution to just reach the point of incipient wetness of the support. Thus, 1.2 cc/g. of SiO₂, of salt solution of different concentrations was added in order to obtain catalyst with copper loadings from 0.5% to 2% w/w. The mixture was evacuated to ensure the pores filling.

The catalysts were dried at 383 K and calcined in air at 723 K for 4 hours. This temperature is high enough to decompose the copper salt into CuO. This was confirmed by I.R. spectroscopy.

Chrysocolia was obtained from the mineral collection of Natural Science Department of Salta University and it came from Chuquicamata mine of Chile.

The pyridine (Py) employed in the gravimetric and spectroscopic studies was obtained from Merck Chemical Co., and was reagent grade. It was used without further purification.

The infrared studies were performed on a Perkin Elmer model 683 spectrophotometer. The spectra were analyzed using a Perkin Elmer Data Station.

An Infrared cell fitted with KRS-5 windows obtained from Perkin Elmer Co. was used in the experiments. This enabled in situ treatments to be performed. In order to obtain the spectra the following procedure was used:

a) The sample was evacuated for 30 minutes at 473 K and cooled to room temperature (R.T.). The baseline spectrum was then recorded.

b) Gaseous Py (8 mmHg) was introduced to the infrared cell and the spectrum of physisorbed and chemisorbed Py on each sample was recorded at room temperature.

c) Physisorbed Py was eliminated by 2.5 hr evacuation (10⁻² mmHg) at room temperature. Following evacuation the spectrum was recorded. The difference spectrum was obtained by subtracting the baseline spectrum from that of the evacuated sample. They will be called "difference spectra".

The gravimetric analysis was carried out using a Cahn RG electrobalance. Prior to the Py adsorption, the samples were evacuated for 1 hr at 473 K.

Py vapors were admitted to the system at room temperature (8 mmHg) and were allowed to equilibrate with the sample. The change in weight was then measured and the weight loss under

dynamic vacuum at 323 K for six hours was recorded.

When no further loss in weight occurred the amount of chemisorbed Py was determined.

Catalytic activity measurements were carried out in a Pyrex flow system at atmospheric pressure (0.868 atm.).

Nitrogen (99.9%), previously purified by passing it through a MnO_2 trap and a Cu/Kieselgel trap, was used as carrier gas. It was saturated in a thermostatic vaporizer. The partial pressure of ethanol (Pol) was kept at 0.05 atm. and the nitrogen flow rate (FN_2) was fixed at 180 cc S.T.P./min. The catalysts were prereduced in this ethanol-nitrogen mixture at 473 K and the catalytic activity was determined after an activation period (3 hr) and when a plateau in the reaction rate was reached. The reaction mixture was analyzed by gas chromatography. The selectivity to acetaldehyde was near 100%.

RESULTS

When Py molecules interact with unsaturated surface sites, different Py chemisorbed species can be formed due to the available pairs of electrons on the nitrogen atoms. The nature of the adsorbed Py interaction can be very well studied using Infrared spectroscopy by considering the shift of the characteristic frequencies of the Py normal absorption modes or by the appearance of new bands in the 1400 cm^{-1} to 1700 cm^{-1} range.

These Py absorption bands, in the above indicated range, corresponds to the A_1 ring vibrations (i.e.: 8_a , 8_b , 19_a , 19_b) which are due to the presence of C-C, C-N and C-H bonds in an aromatic ring (Kline and Turkevich, 1944).

A strong dependence of the absorption frequency of the 8_a and 19_b vibration modes with the electronic deficiency of the acid site can be observed. Thus, shifts from 1580 cm^{-1} for liquid Py to 1630 cm^{-1} in the 8_a vibration mode have been reported when LPy is formed on Al^{+3} (Morterra et al., 1973) while for H-Py the shift is only 10 or 15 wave number above the frequency of the liquid Py.

On the other hand, Brønsted type adsorption (HPy^+) is monitored by the appearance of new bands at 1630 cm^{-1} and 1540 cm^{-1} as well as by a reversed intensity ratio of the modes at 1440 cm^{-1} and 1490 cm^{-1} (19_b and 19_a modes respectively) compared to the Lewis coordinated specie (Parry, 1963 and Morterra, 1973). Taking advantage of

this behaviour, it is possible to identify three Py chemisorbed species as follows:

- Hydrogen bonded Py (H-Py).
- Py bonded to Lewis acid sites (LPy).
- Pyridinium ion (HPy^+).

Their characteristic absorption bands are shown in the Fig. 1.

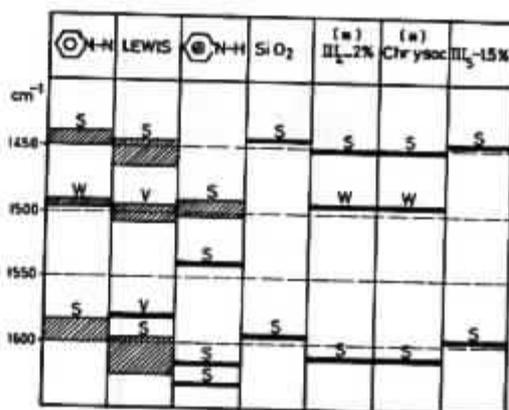


Fig.1: Intensity and absorption bands of different Py species interacting with solid surfaces. Band intensity: S strong, V Variable, W Weak. (*) after 2 hours evacuation (10^{-2} mmHg) at R.T. III₄: ion exchange catalysts. III₅: impregnation catalysts.

Pyridine-Support Interaction

The Py- SiO_2 interaction is very weak. Infrared examination of the Py interaction with silica previously evacuated at 473 K, shows the presence of hydrogen bonded species between free hydroxyl groups and the lone pair of electrons on the nitrogen atom with bands belonging to the 8_a and 19_b modes at 1595 cm^{-1} and 1447 cm^{-1} (Figs. 2 and 3).

It is important to note the absence of an infrared band in the $1485\text{--}1490\text{ cm}^{-1}$ range which is present when silica is pretreated at temperatures greater than 1123 K (Morrow and Cody, 1976).

The hydrogen bonded Py is easily removed by evacuation (10^{-2} mmHg) at room temperature. Fig. 2 and 3 show the effect of the evacuation time on this adsorbed species.

In the $4000\text{--}3000\text{ cm}^{-1}$ spectral region, bands assigned to the oxygen-hydrogen stretching vibration in OH groups are also observed. These bands are centered at 3740 cm^{-1} and 3650 cm^{-1} and are assigned to free hydroxyl groups and to hydrogen bonded hydroxyl groups respectively (Boehm and Knözinger, 1983; Peri, 1984).

Following Py chemisorption, the 3740 cm^{-1} band disappears and an asymmetric broadening of the band below 3650 cm^{-1} is observed (Fig. 2).



Fig.2: Py interaction with silica surface ($4000 - 3000\text{ cm}^{-1}$). a) SiO_2 without Py. b) $\text{SiO}_2 + \text{Py}$ (8 mmHg). c) $\text{SiO}_2 + \text{Py}$ after 2 hours evacuation (10^{-2} mmHg) at R.T.

Evacuation at 323 K for two hours regenerates the band due to free hydroxyl groups. This observation coincides with the disappearance of the 1598 cm^{-1} and 1447 cm^{-1} bands corresponding to the hydrogen bonded Py (Fig. 3).

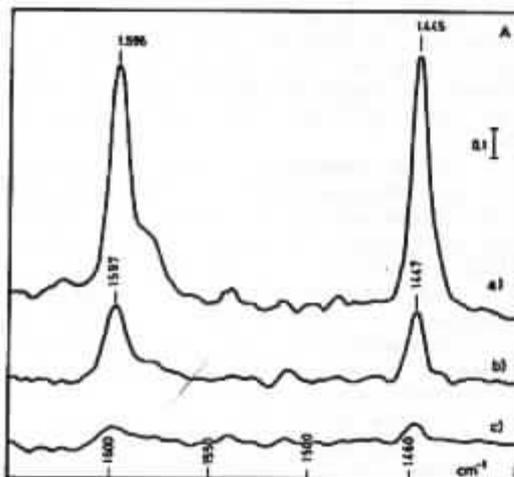


Fig.3: Py interaction with silica surface ($1650 - 1400\text{ cm}^{-1}$). Difference spectrum: a) $\text{SiO}_2 + \text{Py}$ (8 mmHg). b) $\text{SiO}_2 + \text{Py}$ after 5 minutes of evacuation (10^{-2} mmHg, R.T.) c) $\text{SiO}_2 + \text{Py}$ after 2 hours of evacuation (10^{-2} mmHg, R.T.).

Pyridine-Cu/SiO₂ Interaction

When Py vapor (8 mmHg) is equilibrated with an ion exchanged Cu/SiO₂ catalyst previously outgassed at 473 K, the infrared absorption spectrum is different to that observed on pure silica. This was specially noticeable in the region corresponding to the stretching vibrations of C-C and C-N bonds. In addition to the characteristic bands of Py adsorbed on the support, poorly resolved bands centered at 1610 cm^{-1} , 1487 cm^{-1} and 1451 cm^{-1} , were observed (Fig. 4).

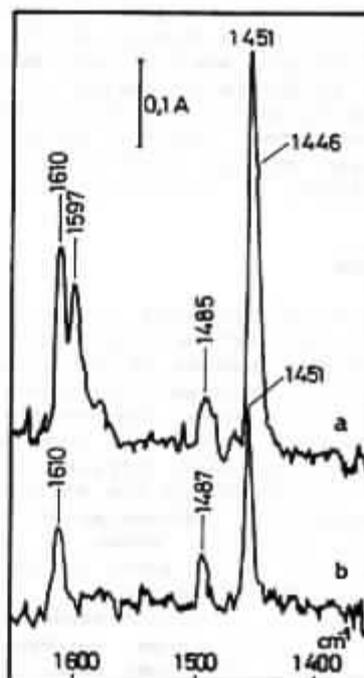


Fig.4: Py interaction with 2% ion exchanged copper catalyst. a) Py after 5 minutes of evacuation (10^{-2} mmHg, at R.T.). b) Py after 2 hours of evacuation (10^{-2} mmHg at R.T.).

These new bands appear initially masked by those of the physisorbed Py and H-Py but are completely defined after evacuation at room temperature (10^{-2} mmHg). They are assigned to the 8a, 19a and 19b modes of the LPy species. The 19a vibration mode, due to its low extinction coefficient, is only observed after evacuation at room temperature on Cu/SiO₂ catalysts which have a copper loading higher than 1% or on Chrysocolla (Fig. 1).

Evacuation at room temperature completely removed the 1598 cm^{-1} and 1451 cm^{-1} bands while the 1610 cm^{-1} , 1487 cm^{-1} and 1451 cm^{-1} bands remained

unaffected.

A semiquantitative picture of the amount of LPy chemisorbed on the catalyst as a function of the copper loading was obtained by integrating the area under the infrared bands corresponding to the 8a and 19b modes, respectively (Fig. 5).

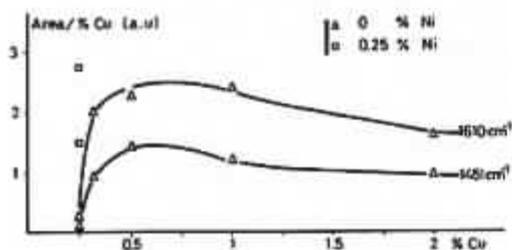


Fig. 5: Area of the peaks related to 18_a and 19_b vibration modes of the chemisorbed Py on Cu and Cu-Ni/SiO₂ catalysts vs. Copper loading. All the catalysts were prepared by ion exchange method. The area were determined after 2 hours of evacuation (10^{-2} mmHg at R.T.).

In this Figure it can be observed that for the 0.25% ion exchanged catalyst the amount of chemisorbed Py per total mol of copper is low, going through a maximum at a copper loading between 0.5% and 1%. A slight decrease was observed at higher copper loadings.

When 0.25% copper was exchanged over a previously exchanged 0.25% Ni/SiO₂ catalyst, the amount of chemisorbed Py per mol of copper increased.

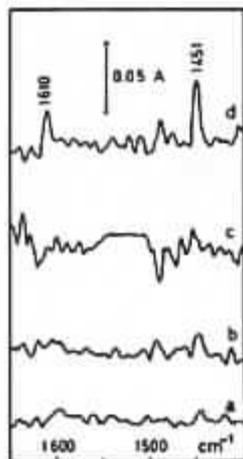


Fig. 6: Py interaction with Cu, Ni and Cu-Ni/SiO₂ catalysts. a) 0.25% Ni catalyst. b) 0.5% Ni catalyst. c) 0.25% Cu catalyst. d) 0.25% Ni - 0.25% Cu catalyst. (After 2 hours of evacuation at 10^{-2} mmHg at R.T.).

However, Lewis acid interaction with Py on pure Ni/SiO₂ catalyst, was not observed (Fig. 6).

It is also interesting to note that while Py adsorption on impregnated catalysts does not have a different behaviour to that observed on pure silica, the Py interaction found on the ion exchanged catalysts is similar to that observed on chrysocolla previously degassed at 473 K. (Fig. 1).

Gravimetric study

In an attempt to quantify chemisorbed Py adsorbed on ion exchanged copper catalysts, a gravimetric analysis as previously described was performed.

In Fig. 7 the dispersion of copper ($\%D_c$) is plotted as a function of copper loading. A 1:1 stoichiometry between Py molecules and surface copper ions was assumed.

DISCUSSION

Pyridine on silica

The adsorption of Py on silica shows that neither Brønsted nor Lewis acid sites are present on the support. The interaction is only characterized by the appearance of the 1598 cm^{-1} and 1447 cm^{-1} bands due to H-Py.

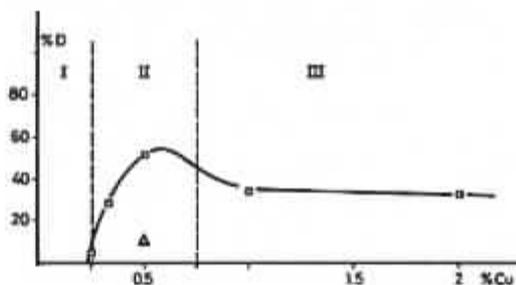


Fig. 7: Dispersion vs. Copper loading considering a 1:1 stoichiometry. Ion exchanged catalyst calcined in air at 1173 K, Δ . Ion exchanged catalysts calcined in air at 723 K, \square .

The weak nature of this interaction is clearly demonstrated since the observed bands can be completely removed by evacuation at 323 K. The surface groups responsible for such interaction are free hydroxyl groups. The admission of Py vapors causes the partial disappearance of the 3740 cm^{-1} band, which is characteristic of these surface sites and produces the broadening of the band below 3650 cm^{-1} as a consequence of the high polar effect of

the O-H...N bond (Peri, 1984).

Evacuation at room temperature produces a decrease in the intensity of the band below 3650 cm^{-1} and the reappearance of the 3740 cm^{-1} one. This behaviour, in addition to the restoration of the baseline spectrum between 1650 cm^{-1} to 1350 cm^{-1} (Fig. 3), shows that these groups are the responsible for that interaction.

Pyridine on Cu/SiO₂

The interaction of Py with Cu/SiO₂ catalysts is strongly dependent on the method of preparation of the catalysts.

The impregnated catalysts tend to form bulk CuO (tenorite) on the support following calcination in air at 723 K. On these catalysts Py absorption is similar to that observed on pure silica (Fig. 1).

These results can be explained if we consider the structure of the CuO crystalites of tenorite which have a characteristic monoclinic structure. Its surface is basic in character (Buzca, 1987) with the exposed oxygen and the Cu²⁺ ions (d⁹) being occluded and having a distorted octahedral coordination due to the Jahn-Teller effect (Huheey, 1981). Buzca (1987) reports, on tenorite, only absorption bands at 1593 cm^{-1} (8a) and 1442 cm^{-1} (19b) that could be assigned to H-Py or hardly to LPy arising from Py interaction with very weak Lewis acid centers. We didn't see any evidence of Py dimerization or Brønsted acidity on these catalysts.

On the other hand, the 1610 cm^{-1} , 1451 cm^{-1} Py absorptions bands in addition to the weak 1485 cm^{-1} band, found on the exchanged catalysts which have a high Cu loading, suggest that Py molecules interact with Lewis acid sites as a consequence of a coordinated unsaturated metal ion created on the surface by the ion exchange process.

On these catalysts the Cu²⁺ ions are inserted into the silica structure forming a hydrosilicate like surface. These copper ions are coordinatively unsaturated or have easily removable adsorbed water molecules (Kevan, 1987). They can be removed by increasing the temperature or by exchanging them with Py molecules, as expect from their position in the electrochemical series (Huheey, 1981).

These results are fully corroborated by those obtained with chrysocolia (Fig. 1).

It is interesting to note that on the exchanged catalysts the amount of LPy chemisorbed is a function of the

the copper loading. From this point of view we can distinguish three structural zones (Fig. 7).

In the first one, copper ions (probably having a stable high coordination or occluded into the silica structure), can not adsorb Py. These copper ions are inactive for the ethanol dehydrogenation (Fig. 8) because they are not exposed on the surface. The increase in the chemisorption of Py observed when Ni²⁺ ions (0.25%) are exchanged before the copper ions, suggests a structural promotor effect of the Ni²⁺ ions. Certainly, Ni²⁺ ions interact with the silica surface during the ion exchange process by developing a hydrosilicate like structure for higher nickel loadings (Bonini et al., 1991). However, for low loading of nickel the silica is only a matrix where the Ni ions are settled. These Ni ions occupy the high coordination sites allowing to the Cu²⁺ ions to occupy the more exposed ones. It is in agreement with the fact that the crystal field stabilization of copper ions in an octahedral field is smaller than that of the nickel ions (Huheey, 1981).

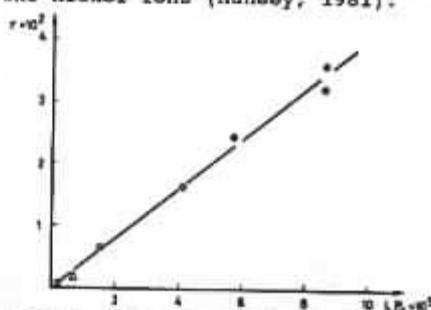


Fig. 8: Reaction rate (mol of aldehyde $\text{hr}^{-1}(\text{g}_{\text{cat}})^{-1}$) vs. LPy (mol of Py $(\text{g}_{\text{cat}})^{-1}$). Reaction conditions: 483 K, $P_{\text{O}_2}=0.05\text{ atm}$, $FN_2=180\text{ ml min}^{-1}$. Catalysts calcined in air at 723 K, \circ . Catalyst calcined at 1173 K, Δ .

On the other hand, it is possible to determine, based on the spectroscopic results (Fig. 5), that the dispersion of the Cu-Ni catalyst (assuming an arbitrary 1:1 stoichiometry) is higher than 100%. We could infer that the isolated ions, when are exposed, chemisorb more than one Py molecule per Cu atom.

For copper catalysts which have an intermediate Cu content (zone II) the copper ions interact with the silica surface by forming a hydrosilicate like monolayer. The copper ions are exposed to the surface and form coordinated unsaturated centers. These centers are the precursors of the sites responsible for the catalytic activity in the

dehydrogenation of ethanol. For the silica used, when the copper loading is between 0.5% and 0.75%, the copper atoms are separated by a distance which can be calculated to be between 2.66 Å and 3.26 Å. This value is close to the mean Cu-Cu distance found in several crystalline Cu-silicates (Heide et al., 1985; Kawamura, 1978). These copper ions are probably those forming Cu-O-Cu bridges reported by Amara et al. (1987) and they are attached to the silica by (Cu-O-Cu)⁺² groups.

Copper loadings of 1% or higher (zone III) result in a decrease in metal dispersion, probably due to segregation of a copper silicate phase (CuO/SiO₂). The copper oxide formation reported in the literature (Köhler et al., 1987), could be consequence of this hydrosilicate decomposition under high temperature conditions (higher than 723 K) or because the clustering of copper hydroxide during the drying step when an excess of copper ions is exchanged (more than one copper ions per two hydroxyl groups presents on the silica surface).

Catalyst calcination at 1173 K in air results in the segregation of the CuO phase due to the diffusion of copper ions to form small crystallites (Shimokawabe et al., 1982). These observation agrees with a lower Py adsorption (Fig. 7), as well as with a decrease in the total reaction rate. The results obtained both by the semi-quantitative spectroscopy technique and by quantitative gravimetric technique are in good agreement. The correlation of catalytic activity for the dehydrogenation of ethanol with the amount of LPy (Fig. 8) shows that the changes in activity are not due to changes in the type of active sites, but to the number of surface copper ions accessible on the catalyst, which in turn are strongly dependent on the copper loading.

CONCLUSIONS

There are two types of copper ions on the ion exchanged catalysts, i.e.: occluded Cu⁺² ions and exposed copper ions. The last ones can be assigned to (Cu-O-Cu)⁺² pairs reported by Amara et al (1987). The first ones are occluded to the Py molecules and are correlated to the isolated copper ions (Clause et al., 1989; Köhler et al., 1987 and Amara et al., 1987). The previous exchange of nickel expose them to the Py chemisorption.

The copper ions are interacting with the silica in a similar fashion as

in the hydrosilicate structure of chrysocolla.

There are not Brönsted acidity on this type of catalysts.

The amount of Py chemisorbed on the unreduced catalysts can be very well correlated to the catalytic activity for the dehydrogenation of ethanol.

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