

Structural and acidic properties of copper–silica catalysts

1. A differential scanning calorimetry and Fourier transform-infrared/photoacoustic study

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Abstract

Adsorption of pyridine on copper–silica catalysts is studied by differential scanning calorimetry (DSC) and Fourier transform-infrared/photoacoustic spectroscopy (FT-IR/PA), in the region of mid-frequency vibrations as well as in the region of hydroxyl groups. The adsorption of pyridine on copper–silica catalysts shows three modes of sorption in the 1650–1400 cm^{-1} region: physisorption or hydrogen-bonded (HPY), and two sites of Lewis acid sorption (LPY(I) and LPY(II)).

The Lewis band at 1609 cm^{-1} was very strong compared with the 1450 cm^{-1} band since the former band showed a shift to higher wavenumbers whereas the latter showed a shift to lower wavenumbers. A relationship was found between the DSC scans, in the low temperature range (240–140°C), and the 1450–1443 cm^{-1} band. On the other hand, the high temperature DSC scans (400–360°C) were correlated with the behaviour of the 1609–1612 cm^{-1} band.

The volumetric results of pyridine adsorption on 9 and 15 wt.% Cu catalysts show a constant behaviour; however, this constancy was also reflected by carbon monoxide adsorption, demonstrated by a similar behaviour of both 2128 and 2259 cm^{-1} bands. This was attributed to the blocking of the small pores of silica earlier at the 9 wt.% Cu loading.

A new broad band at 2248–2259 cm^{-1} , not identified in the ion-exchange catalysts, was obtained and attributed to CO adsorbed on agglomerated copper clusters.

Keywords: Adsorption; Copper–silica catalysts; Differential scanning calorimetry; Fourier transform-infrared/photoacoustic spectroscopy; Pyridine

1. Introduction

Crystalline silicates are much more strongly acidic than silica gel, although the weak acid strength of silica gel, which is sometimes profitably used as a catalyst for some organic reactions [1,2], can be activated by introducing metal cations or metal complexes onto the silanol group [3–5].

Lewis acid sites are generated on silica by employing different dopant cations such as Sc^{3+} , Mg^{2+} , Fe^{3+} , Al^{3+} , Zn^{2+} and Ga^{3+} [6–8]. The great difficulty in differentiating between the Lewis acid sites which might originate on an oxidized metal-support on solid [9] surfaces led us to eliminate that interference through the use of both differential scanning calorimetry (DSC) and Fourier transform-infrared/photoacoustic (FT-IR/PA) techniques.

Pyridine is widely used as a molecular probe for

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determining the concentration of acid sites present on the surface of oxide catalysts [10].

Most investigations agree that IR spectroscopy, which is sensitive and informative, can detect pyridine coordinated to Lewis acid sites (LPY band), and weakly hydrogen bonded pyridine (HPY band) [11].

Many debates on Cu–SiO₂ catalysts concerning the dispersion and increase in the mean copper particle size with increasing extent of copper loading [12,13] indicate that detailed studies should be carried out. Copper-on-silica catalysts prepared by different methods have been subjects of recent interest [12–14]. However, there is some concern regarding the evaluation of acid sites for these systems because of the attempts at structure clarification of these catalysts.

On the basis of the requirement for detailed knowledge of copper–silica catalysts, the present study is intended to investigate the different Lewis acid sites as well as the surface structure of these catalysts through the adsorption of carbon monoxide, using Fourier transform-infrared/photoacoustic spectroscopy and differential scanning calorimetry techniques.

2. Experimental

The silica used is reagent-grade Kieselgel 60 from Merck. The silica gel is thermally pretreated for 15 h in air up to a temperature of 773 K, and showed a specific surface area of 450 m² g⁻¹ and a maximum incremental pore volume of 0.11 cm³ g⁻¹.

Three samples of Cu–SiO₂, containing 3–15 wt.% Cu, are prepared by the impregnation method in which 25 ml of an aqueous solution of cupric nitrate (Analar grade; B.D.H.), molarity range from 0.1 to 0.5 M, are added to 4 g of the support to give the desired loading. The slurry is evaporated to dryness at 393 K, and then calcined at 773 K for 15 h. The resulting samples are again heated to 723 K (at 5 °C min⁻¹), for 3 h, using a gas volumetric apparatus connected to a high vacuum system (Mercury diffusion+rotation pump) in order to allow a pressure reduction to 10⁻⁴ Torr. More

information about the apparatus can be found elsewhere [15].

The dehydrated and degassed samples are treated with pyridine, in situ, at its saturated vapour pressure on the sample, for 2.0 h at 423 K, and are evacuated at the same temperature for 0.5 h.

The adsorption of CO gas, for previously calcined and degassed catalysts at 723 K, is performed at an equilibrium pressure of 40 k-Pa. Carbon monoxide determination is also carried out using the gas volumetric apparatus.

2.1. Characterization of the samples

The IR spectra are recorded by use of a Nicolet 5-DXB Fourier transform-infrared spectrometer using a MTEC-100 photoacoustic detector (PAS). The spectra were recorded with 4 cm⁻¹ resolution and a mirror velocity of 0.16 cm s⁻¹, and 500 scans are averaged. Happ Genzel apodization is used and the single-beam spectra obtained in this way were ratioed against the background photoacoustic spectrum of carbon black.

After the reaction and degassing, the samples are stored in a glove box purged with dry nitrogen.

The photoacoustic cell, which is also enclosed in the glove box, is purged with ultradry helium.

For the DSC measurements, 12 mg of the sample are placed in an aluminium crucible, treated in a Perkin-Elmer DSC7 unit and scanned from 40 to 500 °C at a rate of 10 °C min⁻¹. Aluminium metal is used as a reference and a nitrogen purge of 50 ml min⁻¹ is used during the experiment.

Thermograms of pyridine desorption are obtained by heating the sample until a stable signal is reached. The sample is then cooled down to room temperature without opening the cell.

A mixture of pyridine and nitrogen gases is injected and the procedure is repeated as above.

3. Results and discussion

3.1. DSC thermograms of copper–silica samples

The DSC thermograms of pyridine desorbed from silica gel 60 (parent sample) and from silica

gel containing different amounts (wt.%) of copper are illustrated in Fig. 1. The figure reveals a broad endothermic peak with a maximum at 148 °C for the parent sample (Fig. 1a), and this may be due to the physisorption of pyridine by the surface hydroxyl groups of the silica gel.

The 3 wt.% Cu sample (Fig. 1b) exhibits a very large endothermic peak at 116 °C, a large endothermic peak at 160 °C and a very small exothermic peak at 385 °C. The peak at 116 °C can be attributed to the desorption of physisorbed pyridine. It is then possible to attribute the peak at 160 °C to a Lewis acid site since a shift occurs from 148 °C in the parent sample to 160 °C upon the addition of copper. This peak gives a heat of reaction (ΔH) value of 12.2 J g⁻¹. Copper oxide supported on

silica usually shows two distinct phases: dispersed cupric oxide and a copper silicate species [16]. However, increasing the copper loading may affect both phases, and induces a considerable change in the particle diameter as well as in the structure. Therefore, it is then possible to correlate the exothermic peak with a ΔH value of -0.13 J g⁻¹, obtained at 385 °C, with the initial effect of the particle size of the 3 wt.% Cu sample which may give rise to another type of Lewis acidity.

For 9 and 15 wt.% Cu samples (Figs. 1c and 1d), a large double endothermic peak is obtained. The low temperature peak of the doublet shows an observable shift, with increasing copper loading, to a lower temperature to give peak maxima at 79 °C and 77 °C for 9 wt.% and 15 wt.% Cu,

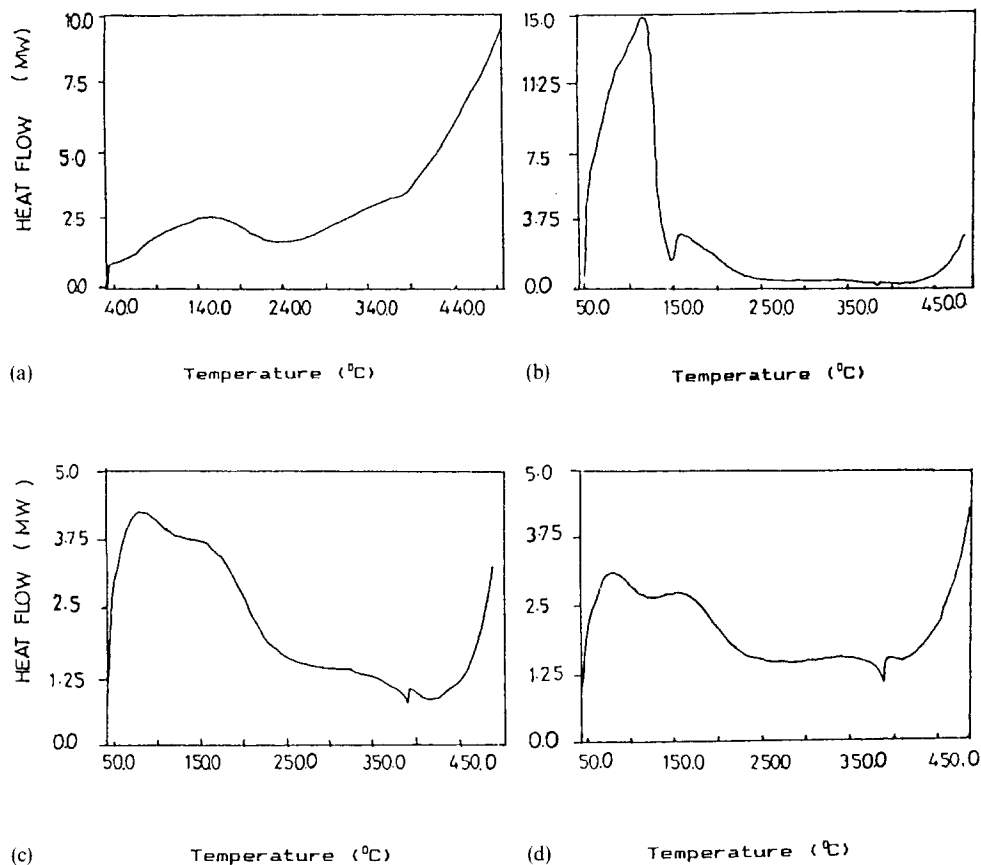


Fig. 1. DSC thermograms of pyridine desorbed from (a) silica gel 60 calcined at 773 K, (b) silica gel 60 modified with 3 wt.% Cu calcined at 773 K, (c) silica gel 60 modified with 9 wt.% Cu calcined at 773 K, and (d) silica gel 60 modified with 15 wt.% Cu calcined at 773 K.

respectively, whereas the high temperature peak of the doublet (attributed to Lewis acidity) reveals maxima of 149°C and 153°C for 9 wt.% and 15 wt.% Cu, respectively.

The complete overlap between the doublet peaks, influencing the accuracy of deconvolution, prevents us from obtaining the magnitude of the heat of reaction ΔH obtained during pyridine desorption from the Lewis acid site.

The high temperature peak (exothermic) of the 9 wt.% Cu sample, showing a maximum at 388°C, indicates a ΔH value of -1.02 J g^{-1} whereas the 15 wt.% Cu sample a maximum at 386°C gives a ΔH value of -1.4 J g^{-1} reflecting the strength of the latter site.

The above-mentioned two types of Lewis acidity obtained at both the medium temperature range (140–240°C) and the high temperature range (360–400°C) reveal the strength of the Lewis acidity at the latter temperature range, whereas the small magnitude of the peak corresponding to the latter site (360–400°C) indicates that this is of a lower concentration compared with the former type (140–240°C).

3.2. Mid-infrared desorption frequencies for pyridine adsorbed on the 9 wt.% Cu/SiO₂ catalyst

The desorption of pyridine from the 9 wt.% copper sample, in the range 1650–1400 cm^{-1} , is studied after evacuation at progressively higher temperatures ranging from 373 to 663 K (Fig. 2). The desorption frequencies are listed in Table 1.

Spectrum a shows bands for three distinct pyridine adsorption sites. The first set of bands is due to physisorbed or hydrogen-bonded pyridine on Cu–SiO₂ with absorption bands at 1435 and 1458 cm^{-1} , which appears as a shoulder. The latter band (1458 cm^{-1}) was seen for silica (parent) with a band at 1440 cm^{-1} not large enough to indicate Lewis acidity, i.e. only hydrogen-bonded pyridine was observed on silica with no evidence for proton acidity. The second set of bands is due to Lewis sites (LPY(I)) on Cu–SiO₂ with the 8a band at 1609 cm^{-1} and the 19b band at 1450 cm^{-1} . The third set of bands is due to another Lewis acid site (LPY(II)) with the 19a band at 1488 cm^{-1} and another band at 1520 cm^{-1} . The broad 1624 cm^{-1}



Fig. 2. FT-IR/PA spectra of pyridine desorbed from silica gel 60 containing 9 wt.% Cu, in the (1650–1400 cm^{-1}) range, at the following temperatures: spectrum a, 373 K; spectrum b, 410 K; spectrum c, 450 K; spectrum d, 523 K; spectrum e, 663 K.

Table 1
Infrared absorption frequencies (cm^{-1}) of pyridine desorbed from the 9 wt.% Cu–SiO₂ catalyst (spectra given in Fig. 2)

Type	Band	Evacuation temperature				
		373 K	410 K	450 K	523 K	663 K
HPY	19b	1435	1435	1435	1430	1425
		1458sh	1458	1458	—	—
LPY (I)	19b	1450	1450	1450	1445	1443
		8a	1609	1610	1611	1612
LPY (II)	19a	1488	1488	1483	1483	1480
		1520	1505	1515	1517	1520
		8a	1624	1624	1624	1624

Key: HPY, physisorbed or hydrogen-bonded pyridine; LPY (I), Lewis acid bonded pyridine site 1; LPY (II), Lewis acid bonded pyridine site 2; sh, shoulder.

band which appears as a doublet cannot be attributed to Brönsted acidity or to an artefact, because of our experimental conditions. Therefore the most probable assignment for this band is to Lewis acidity since it shows a prominent existence at temperatures up to 663 K.

The desorption of pyridine, as seen in spectra b–e, indicates that the physisorbed pyridine first gives rise to a shift to lower wavenumbers, followed by pyridine appearing on Lewis acid sites.

The 19a bands near 1488 and 1520 cm^{-1} reveal that these bands are attributed to mixed Lewis acid sites. The Lewis band at 1520 cm^{-1} could be due to coordinatively unsaturated Cu^{II} tetrahedral sites and the band at 1488 cm^{-1} can be assigned to anion vacancies over a tetrahedral and octahedral cation [17].

Splitting of the 19b band at 1450–1439 cm^{-1} is obtained at 663 K. Moreover, the 8a bands at 1609 and 1624 cm^{-1} give another indication of the presence of two distinct types of coordinatively unsaturated copper cations.

The desorption of pyridine also led to an upward shift in the peak maximum occurring at 1609 to 1612 cm^{-1} and a downward shift in the peak occurring at 1450 to 1443 cm^{-1} after complete evacuation at 663 K.

The integrated areas under the infrared bands at 1450 and 1609 cm^{-1} and their ratios are used to determine the relative concentration of pyridine adsorbed on the Lewis sites (Table 2). The concentration of the Lewis acid sites at 1450 cm^{-1} decreases initially with extent of evacuation.

The ratio of the areas under the IR bands at

1450 and 1609 cm^{-1} undergoes an initial decrease and then increases with extent of evacuation. This reflects the substantial decrease in the area under the 1609 cm^{-1} band compared with the 1450 cm^{-1} band.

It seems that the 1609 cm^{-1} band is much stronger than the 1450 cm^{-1} band since the former is characterized by a significant shift to higher wavenumbers (1609–1612 cm^{-1}) whereas the later shows a shift to lower wavenumbers (1450–1443 cm^{-1}).

Therefore, the significant increase in intensity shown by the 1450 cm^{-1} band compared with the 1609 cm^{-1} band reflects only the relative concentration of these sites.

3.3. The 4000–400 cm^{-1} spectral region

The changes in the hydroxyl group regions as the loading of copper increases (3, 9 and 15 wt.% Cu, oxidized form) apparently do not affect the nature of the surface hydroxyl groups on silica gel, especially at a low amount of copper (3 wt.%). At high copper content, the number of free hydroxyl groups (3745 cm^{-1}) is significantly reduced.

The maximal decrease in the number of free hydroxyl groups was 20% for the sample with 15 wt.% copper; this was obtained by comparing the integrated intensity of the free OH band with the SiO_2 overtone band at 1872 cm^{-1} . A marked change is obtained when pyridine is adsorbed on the 9 wt.% copper sample, producing partly resolved bands at 3745, 3670 and 3550 cm^{-1} , and a shoulder at 3710 cm^{-1} (Fig. 3).

The high frequency 3710 cm^{-1} (free OH) and 3550 cm^{-1} (OH...OH) bands can be explained by the formation of a hydrogen bond with the pyridine molecules, the bands having different intensities with increasing temperature. These bands, which also depend on the nature of the cation, are largely eliminated during the thermal evacuation. It is known that the free hydroxyl groups at 3745 cm^{-1} have little acidic character, whereas the band at 3670 cm^{-1} has some intrinsic acidity implying that protons are more easily released [18]. Therefore it is possible to assign the latter band to the Lewis acid site originating via the coordinate bonds LPY. Further evacuation of the sample at successively

Table 2
Integrated band intensities for the bands near 1450 and 1609 cm^{-1} and their ratios, as a function of evacuation temperature for the 9 wt.% Cu sample (spectra given in Fig. 2)

Pyridine desorption temperature (K)	Area under the peaks		Ratio
	1450 cm^{-1}	1609 cm^{-1}	
373	2.36	0.94	2.5
410	1.57	0.83	1.9
450	1.10	0.37	2.97
523	0.62	0.15	4.13
663	0.35	0.05	7.00

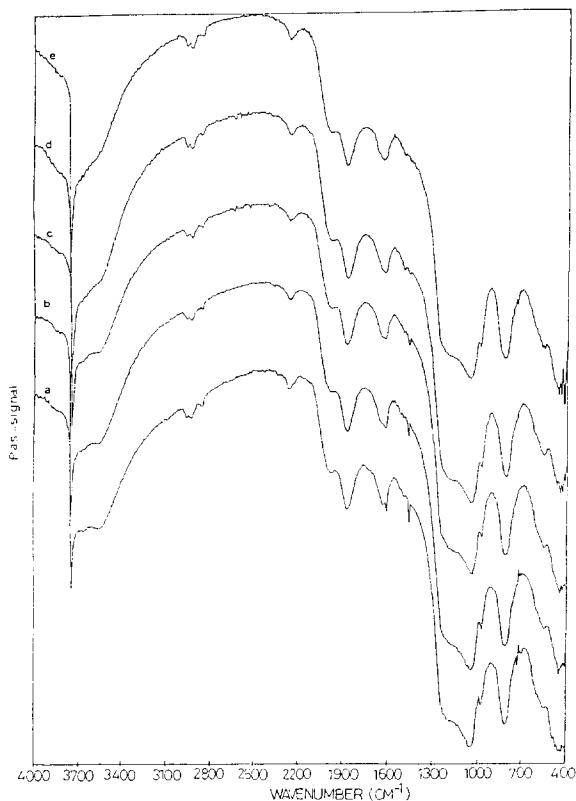


Fig. 3. FT-IR/PA spectra of pyridine desorbed from silica gel 60 containing 9 wt.% Cu, in the 4000–400 cm^{-1} range, at the following temperatures: spectrum a, 373 K; spectrum b, 410 K; spectrum c, 450 K; spectrum d, 523 K; spectrum e, 663 K.

higher temperatures permits the elimination of the 3670 cm^{-1} band at 523 K, reflecting the fairly weak Lewis acidity of this band. Therefore, the behaviour of the Lewis acid sites is not likely to be correlated with the behaviour of hydroxyl groups.

More evidence can be obtained by observing the weakening of the bridged hydroxyl group of silica, which showed a change in the frequency of its bending vibration (795–760 cm^{-1}) that can be correlated with the strength of the coordination of copper to silicon atoms, i.e. the bending frequency would decrease with the weakness of coordination.

In the low wavenumber spectral region (1300–400 cm^{-1}), an intense band at 795 cm^{-1} due to the silica substrate is observed beside a band near 980 cm^{-1} , which is known to be due to

the Si–OH stretching mode of isolated silanol groups [19]. However, a clearer picture about the surface structure of copper cannot be obtained in that region because of the strong absorption by the skeletal modes of silica gel, i.e. it is difficult to describe exactly the appearance of the copper species on the silica support. The significant shift to lower wavenumbers of the deformation band (795–760 cm^{-1}) can be attributed to the probability of coupling with the substrate mode.

In view of the above, a relationship is found between the behaviour of the DSC scans in the medium temperature range (140–240 °C) and the band at 1450 cm^{-1} , since both show a decrease in temperature (shift) and in wavenumber, upon increasing the temperature. However, the high temperature peak in the DSC thermograms (360–400 °C), which represents the more stable Lewis acid site, is correlated with the band at 1609 cm^{-1} which shows a degree of stability toward the successive increase in temperatures.

The amount of pyridine molecules irreversibly adsorbed at 423 K on Cu–SiO₂ catalysts as a function of the different amounts (wt.%) of copper is illustrated in Fig. 4. The amount of pyridine adsorbed per gram of adsorbent is significantly increased from 3 wt.% Cu to 9 wt.% Cu to give values of 0.11 mmol g^{-1} and 0.15 mmol g^{-1} respectively. This is in agreement with the findings of Taniguchi et al. [20].

For the 15 wt.% Cu sample, no significant

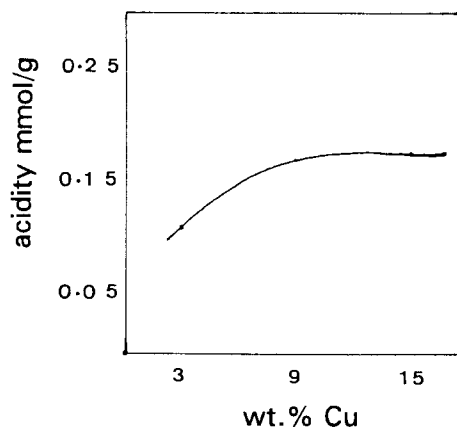


Fig. 4. Acidity variation of Cu–SiO₂ catalysts as a function of different amounts (wt.%) of copper cations.

increase of pyridine adsorption is observed. This is due to the blocking of the small pores of silica [21] at such a high amount of copper, since the accessibility of these pores to pyridine diffusion may have been restricted.

Therefore, pyridine will only be adsorbed on the surface and not inside the pores, reflecting the constant behaviour observed for the last two samples.

3.4. State of copper oxide supported on silica

The adsorption of CO on precalcined and degassed 3, 9 and 15 wt.% Cu–SiO₂ catalysts at 723 K is depicted in Fig. 5. The IR spectra of all catalyst samples, obtained at room temperature [21], showed three absorption bands at 2128, 2173 and 2248–2259 cm⁻¹. The major band at 2128 cm⁻¹ is due to CO adsorbed on small CuO

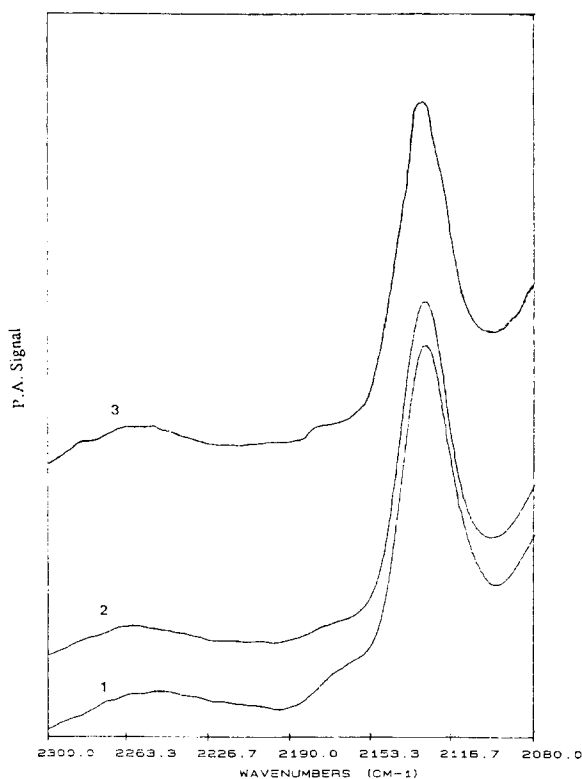


Fig. 5. FT-IR/PA spectra of CO adsorbed on the following catalysts at 723 K: spectrum 1, 3 wt.% Cu–SiO₂; spectrum 2, 9 wt.% Cu–SiO₂; spectrum 3, 15 wt.% Cu–SiO₂.

particles [11]. The absorbance of this band does not show any sharp decrease or increase revealing that the CO molecules are strongly adsorbed on the CuO surface. More interesting is the behaviour of this band, which does not show any shift whatever the adsorption or desorption time.

The formation of free CuO at such low loadings (3 wt.%) may be explained by the weakness of the Cu–SiO₂ interaction, and possibly a high heterogeneity of the SiO₂ support is obtained, i.e. the adsorption sites are able to adsorb Cu^{II} oxide strongly at the very beginning; however, these sites may participate in a monolayer formation of CuO.

The relatively lower frequency of the 2128 cm⁻¹ band compared with the 2146 cm⁻¹ band observed by other workers [22] confirms that very small copper particles must be assumed. Furthermore, typical half-widths of this band for all the different copper loadings can be connected with the homogeneity of the copper particle sizes on these catalysts.

The weak band at 2173 cm⁻¹, which matches the broad band described by other workers [23], is due to carbon monoxide bound to Cu^I sites distributed uniformly on the silica surface. This band showed a significant enhancement at higher loadings (spectrum 3) i.e. CO adsorption on Cu^{II} species is not equal for all samples. The broad band at 2248 cm⁻¹, obtained for the 3 wt.% Cu sample, is shifted to 2259 cm⁻¹ for both the 9 and 15 wt.% Cu samples. This band showed a significant dependence on metal loading and hence mean copper particle size. Furthermore, when the loading increases, the oxide obtained cannot be the same because there may be some CuO particle interactions. Therefore this band can be attributed to the CO adsorbed on agglomerated copper clusters.

One cannot attribute this band to copper silicate species, since the amount of silicate produced beyond the 4 wt.% Cu loading is minute [16]. In fact, the crystalline phase of cupric oxide increases as the total loading is increased; however, this is dependent on the calcination temperature (high), copper concentration (high) and the surface area of the support, which is also very high. This situation can easily favour cluster formation on increasing the copper content on the heterogeneous

surface. No evidence for this band could be found in the ion-exchange prepared copper–silica catalysts.

The relatively similar behaviour of the 2128 and 2259 cm^{-1} bands for both the 9 and 15 wt.% Cu catalysts may indicate blocking of the small pores earlier at the 9 wt.% Cu loading. The same behaviour is also found with pyridine adsorption.

Furthermore, the accessibility of copper species to CO molecules suggests that the dispersion of the active phase remains constant when the copper oxide exceeds a certain coverage.

Generally, one can conclude that, when the copper loading is beyond the saturation concentration, the excess CuO aggregates to form a particulate or bulk phase and, accordingly, the CO adsorption is reduced.

4. Conclusions

DSC is employed to show the influence of the thermal desorption of pyridine from the different Lewis acid sites in order to relate the structural changes and strength of these sites to pyridine desorption.

FT-IR/PAS spectra were obtained at different evacuation temperatures in order to gain more specific information concerning the strengths of the different Lewis sites and their stabilities. As a result of these investigations, evidence for the strength of the 1609–1612 cm^{-1} band over the 1450–1443 cm^{-1} band is detected. Moreover, the existence of split bands give an indication of the presence of two distinct types of coordinatively unsaturated copper cations.

The quantitative adsorption of pyridine on the Cu–SiO₂ catalysts was shown to display a constant behaviour with the high Cu loadings (9 and 15 wt.%), because of the blocking of the small pores of silica earlier at the 9 wt.% Cu loading. This agrees with the similar behaviour of the 2128 and

2259 cm^{-1} bands, obtained for both the 9 and 15 wt.% Cu catalysts, upon CO adsorption.

The final achievement was to identify the surface structure of copper on silica, which shows a relatively high reduction rate; this was found to be formed from CuO, Cu^{II} and Cu^I species when CO adsorption takes place.

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