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Redox behaviour of copper mordenite zeolite

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Fourier transform–infrared photoacoustic spectroscopy (FT–IR/PAS) and X-ray diffraction (XRD) techniques have been used to study the reduction of copper (II) oxide supported on mordenite zeolite, through the adsorption of carbon monoxide and hydrogen gases at 723 K. It was found that bands due to the bridged hydroxyl groups (3614–3630 cm^{-1}) and the Al–OH groups (3780–3787 cm^{-1}) show significant changes upon carbon monoxide and hydrogen adsorption whereas the Si–OH band did not change after the adsorption. Two further bands were detected at 2156 and 2297 cm^{-1}, assigned to carbon monoxide adsorbed on Cu^+ species and on the copper–aluminate species, respectively. XRD patterns have demonstrated the proposed interaction between Cu^{2+} with aluminium mordenite, to form aluminate, whereas FT–IR spectra have established an interaction between carbon monoxide molecules and the aluminate species.

1. Introduction

Copper-exchanged zeolites have been extensively studied as oxidation and isomerization catalysts where the intrazeolitic copper centres are the active sites [1]. Therefore, there has been an upsurge of interest in the reduction of these divalent copper ions, as part of the oxidation process.

Different zeolites have been employed to study the process of intra-framework Cu^{2+} reduction. In particular, extensive studies using Cu^{2+} zeolite have recently been reported [1, 2]. These studies have shown that the degree of cation reduction and the resultant dispersion of the active metal would have a direct influence on the catalytic behaviour.

It is a well-known phenomenon that the reducibility of transition ions increases in the sequence $Y < X < A$ zeolite [3–6]. Mordenite zeolite has shown a high accessibility towards metal-ion exchange [7, 8] if it is compared with some other zeolites, such as natrolite and analcime [9]. Extensive studies of mordenite containing metal ions are essential in order to shed more light on its reduction behaviour and to rationalize it with other types of zeolite from the view point of reduction feasibility.

To date, detailed studies concerning the reduction behaviour of Cu^{2+}-mordenite have not yet been carried out. This paper reports the results of a Fourier transform-infrared photoacoustic (FT–IR/PA) investigation of the reduction properties of Cu^{2+}-exchanged zeolite mordenite with particular emphasis on the probability of interaction of the reducing gases with mobile Cu^{2+} ions inside the mordenite framework.

2. Experimental procedure

Sodium small-port mordenite (SPM, supplied by La Grand Pavoisse, Montoir-France), was converted to the Na^+/Cu^{2+} form by a conventional ion-exchange procedure [7]. The concentration was chosen on the basis that the exchange procedure was about 80%. Further experimental details can be found elsewhere [1].

The samples were heated in vacuum (10^{-4} torr) to 723 K in a volumetric adsorption apparatus (5 °C min^{-1}) for 4 h before the adsorption of the reducing gases takes place *in situ* at 723 K. Carbon monoxide and hydrogen (purity 99%) are admitted at the respective saturation vapour pressures on the sample for 3 h and evacuated at the same temperature (723 K) for 0.5 h.

The samples were then placed in a dry-nitrogen purged glovebox before recording the IR measurement on a Nicolet 5-DXB FT–IR spectrometer equipped with the METC-100 photoacoustic cell. Further information about the FT–IR/PA can be found elsewhere [10]. Diffraction patterns were taken with a General Electric reflection diffractometer (model XRD-5) using CuK_α radiation. The data were recorded from $2\theta = 6°–80°$ at 2° min^{-1}.

3. Results and discussion

3.1. Frequencies in the 2800–450 cm^{-1} region

Fig. 1 shows the IR spectra of degassed Na^+-SPM and Cu^{2+}-SPM at 723 K and their interactions with carbon monoxide and hydrogen gases, at the same

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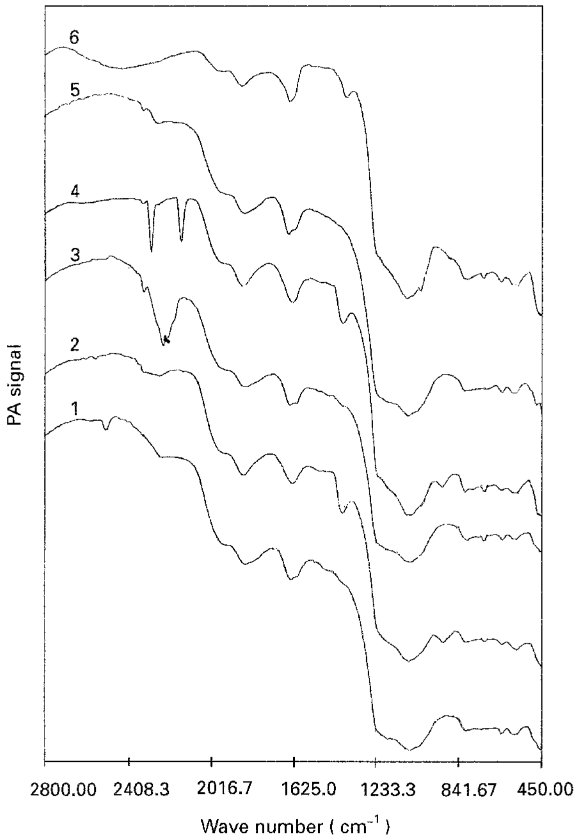

Figure 1 PAS-IR spectra of Na$^+$-mordenite (SPM) and Cu^{2+} -mordenite catalysts interacted with carbon monoxide and hydrogen gases at 723 K in the 450–2800 cm^{-1} region. 1, SPM (parent sample); 2, Cu^{2+}-SPM; 3, SPM interacted with carbon monoxide gas; 4, Cu^{2+}-SPM interacted with carbon monoxide gas; 5, SPM interacted with hydrogen gas; 6, Cu^{2+}-SPM interacted with hydrogen gas.

temperature (723 K). These spectra were recorded after cooling the sample to 298 K.

The IR spectrum of Na$^+$-SPM shows the charactertistic two bands, at 1800–1900 and 1630 cm^{-1}, assigned to lattice overtone vibrations. The deformation vibration of water can also contribute to the band at 1630 cm^{-1} [11].

The T–O symmetric stretching (AlO$_4$-tetrahedra in four rings [12]) is observed at 730 cm^{-1} and the more specific mordenite lattice vibrations are located at 645 and 580 cm^{-1}. The Si–O tetrahedral asymmetric stretching vibration is always near the limit of photoacoustic saturation.

It also appears that the spectral variation within the Na$^+$-SPM framework in the 450–1233 cm^{-1} range, is less sensitive to any change, irrespective of the presence of cations or the interaction with the reducing gases, except for the appearance of the cation-framework band at 930 cm^{-1}. This spectrum also exhibits a small band at 2515 cm^{-1} and this could be a consequence of the non-desorbed water molecules interacting with the acidic hydroxyls [13].

The Cu^{2+}-SPM spectrum shows a band at 930 cm^{-1}, assigned to CuO species, which is very close to the absorption band measured by Mohamed *et al.* [14].

The band at 1398 cm^{-1}, which cannot be related to the intensity of either the oxide band or the zeolite framework and only associated with the presence of copper, can be attributed to nitrate anion in the copper (II) nitrate solution [15]. However, the permanent existence of this band even after heating to 723 K confirms that a readsorption of the nitrate anion on the catalyst surface must have occurred [16].

The IR spectrum obtained from the adsorption of carbon monoxide on Na$^+$-SPM shows an unresolved band at 2245 cm^{-1} and a small shoulder at 2334 cm^{-1}. The former band can be attributed to the formation of carbon dioxide as a result of heating the sample at high temperatures, while the band at 2334 cm^{-1} could be related to the interaction of CO with Na$^+$-SPM.

In a previous study [7], sodium mordenite was found to exhibit an incomplete exchange of Na$^+$ by Cu^{2+} ions. Because sodium is the smaller of the two ions, a stronger ion-dipole interaction lies at the origin of this difference. Therefore, the very small shoulder at 2334 cm^{-1} (compared with that for copper, which will be mentioned later, and is very weak) is also detected in spectra 4 and 5, confirming the prominent existence of CO–Na$^+$-SPM species even after the exhaustive exchange with copper.

Na$^+$ ions, which may be found in different sites because of their small size, can take part in such an interaction (CO–Na$^+$ SPM) especially after removal of the last water molecules, which can be desorbed at such high temperatures (723 K) [7]. Therefore, the ions try to compensate for the loss in solvation by moving closer to the walls of the structure in search of coordination with structural oxygen atoms or with the incoming guest carbon monoxide molecules.

When Cu^{2+}-SPM is exposed to carbon monoxide adsorption at 723 K, two bands at 2297 and 2156 cm^{-1} are clearly detected. The band at 2156 cm^{-1} is assigned to carbon monoxide adsorbed on Cu$^+$ species, and this is in agreement with the findings of Huang [17]. The band observed at 2297 cm^{-1}, which can be explained in terms of electrostatic interaction with the cations, is due to carbon monoxide adsorbed on isolated Cu^{2+} ions incorporated in the zeolite framework. It was reported earlier that an adsorption band near 2200 cm^{-1} has been observed for carbon monoxide adsorbed on X and Y zeolites containing bivalent cations [18].

The 2297 cm^{-1} band, which reflects the increase of surface coverage by carbon monoxide, can be attributed to carbon monoxide adsorption on the Cu^{2+}-exchanged mordenite. More specifically, because the intensity of the 930 cm^{-1} band reflects the possible interactions of Cu^{2+} with the framework aluminium [8] (i.e. aluminate formation) we may assign the 2297 cm^{-1} band to the carbon monoxide adsorbed on the framework aluminium interacted with Cu^{2+} ions. Further evidence can be adduced as follows.

The strongly physisorbed water liberated from the adsorption sites at high temperatures can hydrolyse Si–O–Al bonds thus freeing the aluminium from the structure and depositing it in the channel system (i.e. a self-steaming process). This process has been associated with so-called deep-bed conditions [19], i.e. due to an increase in the dimensions of the zeolite bed, and consequently also a decrease in evacuation efficiency from the bed, the interaction probability is enlarged and structural dealumination is enhanced. Such an effect (dealumination) can be minimized or avoided through outgassing in progressive steps (± 30 °C) up to 723 K over a period of 48 h [20] (instead of 4 h used in this work).

As a comparison, the IR spectra of adsorbed carbon monoxide on Al_2O_3/SiO_2 show a band at 2229 cm^{-1} [21]. Flanigen *et al.* [11] mentions that the relative concentration of silicon and aluminium in site T affects the frequency of the band.

Further evidence for establishing the above proposed interaction can be visualized from the following sequence. During the ion-exchange and drying steps, copper ions are anchored as aquo complexes to the mordenite OH groups; however, on degassing, all water molecules are removed while the oxide forms are obtained which, in turn, can react with aluminium resulting from the self-steaming process. Furthermore, according to the high loadings of copper, a more covalent oxide is obtained whose sintering seems to occur [22] with short Cu–O distances. It is then possible to correlate the band at 2297 cm^{-1} with the interaction of aluminium, sintered with much of the copper oxide at the surface, with the carbon monoxide adsorbing species.

The large probability of the sintering process occurring is evinced through the removal of oxygen from the mordenite lattice when carbon monoxide is introduced on to an oxygen-covered surface and carbon dioxide appears readily in the gas phase; accordingly the presence of bridged bonds (Al–O–Cu, Si–O–Cu) will be depleted.

On applying hydrogen to SPM, no change in the spectrum could be obtained if it is compared with the parent sample (non-reduced). The adsorption of hydrogen on Cu^{2+}-SPM exhibits a broad band at 2500 cm^{-1}, attributed to water desorption. The small changes in the 450–1000 cm^{-1} region confirm the reduction of the oxide forms of copper.

It is obvious that copper exhibits no strong chemisorption with the molecular hydrogen but does so with carbon monoxide because of increasing dipolar interactions of carbon monoxide molecules.

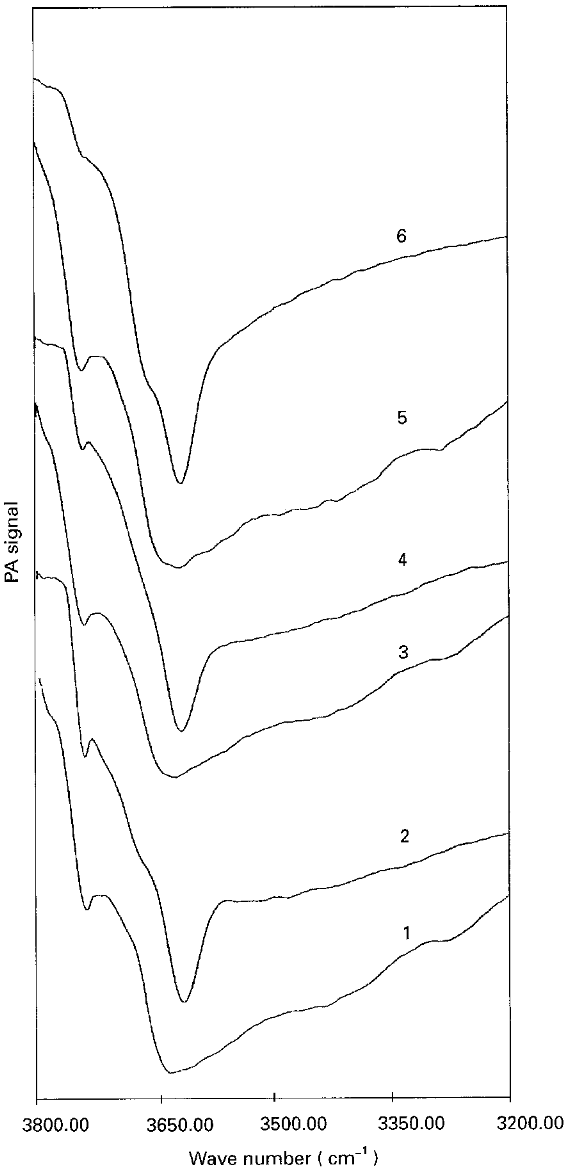

Figure 2 PAS–IR spectra of Na^+-mordenite and Cu^{2+}-mordenite treated with carbon monoxide and hydrogen at 723 K in the 3800–3200 cm^{-1} range. 1, SPM (parent sample); 2, Cu^{2+}-SPM; 3, SPM treated with carbon monoxide gas; 4, Cu^{2+}-mordenite treated with carbon monoxide gas; 5, SPM treated with hydrogen gas; 6, Cu^{2+}-mordenite treated with hydrogen gas.

3.2. Hydroxyl groups region

Fig. 2 shows the IR spectra of carbon monoxide and hydrogen adsorption on Na^+-SPM and Cu^{2+}-SPM catalysts in the 3800–3200 cm^{-1} region.

The IR spectrum of Na^+-SPM shows four types of hydroxyls of relatively different intensities: 3748 cm^{-1} of the terminal OH group; 3643 cm^{-1} of the bridged OH group, which is associated with acid centres; 3400–3200 cm^{-1} of water bridging vibrations; and a shoulder at 3780 cm^{-1} attributed to Al–OH groups [23].

The IR spectrum of Cu^{2+}-SPM reveals two bands at 3748 and 3618 cm^{-1}. It is obvious that the bridged OH group is shifted to lower wave numbers from 3643 cm^{-1} to 3618 cm^{-1} as a result of Cu^{2+} addition. As already pointed out, this site is very active. Because the bridged OH group is assigned by many authors [24] to the Bronsted site, the shift to lower wave numbers is expected upon copper-ion exchange because of the nature of the copper ions which only create Lewis acid centres.

The shoulder at 3780 cm^{-1} shifted to 3787 cm^{-1} upon copper addition, confirming the interaction of copper with Al–OH species, whereas the band of the free hydroxyl group shows no appreciable decrease in intensity or a shift in frequency to establish the reactivity of Al–OH groups compared with those of Si–OH groups.

Indeed, establishing copper aluminate formation rather than the corresponding copper silicate, is dependent on copper concentration (high) and calcination temperature (high, vacuum 10^{-4} torr); thus favouring the aluminate formation rather than the silicate one is a necessity.

The Cu^{2+}-SPM spectrum exposed to carbon monoxide adsorption depicts the same bands as in the Na^+-SPM sample (also exposed to carbon monoxide) with a significant shift to lower wave numbers for the bridged hydroxyl group of the former sample. It is obvious that the increase in copper content produces a significant shift to lower frequency for the 3643 cm^{-1} band as a result of decreasing surface coverage of carbon monoxide caused by replacing the ν (OH–CO) mode by the Cu–CO mode. This significant shift to lower wave numbers for the bridged OH groups upon carbon monoxide adsorption can be attributed to the formation of copper (I) aluminate species. This conclusion was in agreement with the findings of Lambert and Eysel [25].

The broad band at 3433 cm^{-1} in spectrum 3 cannot be accounted for by the ν (OH–CO) mode, but can be assigned to the perturbation of ν (OH–) modes due to the interaction with the terminal hydroxyls. As a result of this H.B. (Hydrogen Bonding), the terminal OH group band showed a shift from 3748 cm^{-1} to 3744 cm^{-1}.

It is also obvious that the intensity of the sharp bands of Cu-SPM and CO–Cu–SPM, of identical positions at 3618 cm^{-1}, are nearly the same. This can be attributed to the blocking of the one-dimensional channel system in zeolite by copper atoms, i.e. copper phases on the external zeolite surface are predominant. This will lead to a decrease of the surface coverage of carbon monoxide. This constant behaviour of the band after carbon monoxide adsorption indicates that the amount of active phase is proportional to that site. Thus some idea of the catalytic activity can be obtained by measuring the number of active sites through the chemisorbed carbon monoxide molecules.

On applying hydrogen to Cu^{2+}-SPM, an appreciable shift to lower wave numbers for the free vibrational silanol groups at $3745\text{–}3735 \text{ cm}^{-1}$ is obtained. This is a consequence of the water liberated from the surface hydroxyl groups. The behaviour of the bridged hydroxyl groups when carbon monoxide is adsorbed on Cu-SPM is very similar in intensity to Cu-SPM exposed to hydrogen adsorption, and a small shift to lower wave numbers for the latter band, to 3614 cm^{-1}, is observed. The main reasons for this peak shift ($3643\text{–}3614 \text{ cm}^{-1}$) are probably the effect of Cu(I) aluminate or metallic copper formations as a result of the high temperature and the frequent decrease in the framework oxygen, and the significant increase in the diameter of the copper clusters as a result of the high copper content.

Furthermore, the $3780\text{–}3787 \text{ cm}^{-1}$ band has disappeared from spectrum 5 (Na-SPM + H_2) while it is retained in spectrum 6 (Cu-SPM + H_2) as a result of the interaction of aluminium hydroxyls with copper ions or the retaining of some hydrogen as lattice OH groups [26]. Generally, one can suggest that there is a relationship between the bridged OH group (more acidic) interacted with copper ions, and the significant alterations concerning the $3787\text{–}3780 \text{ cm}^{-1}$ band obtained upon carbon monoxide and hydrogen adsorption. However, this is manifested in the direct interaction between copper aluminate species and the guest gases.

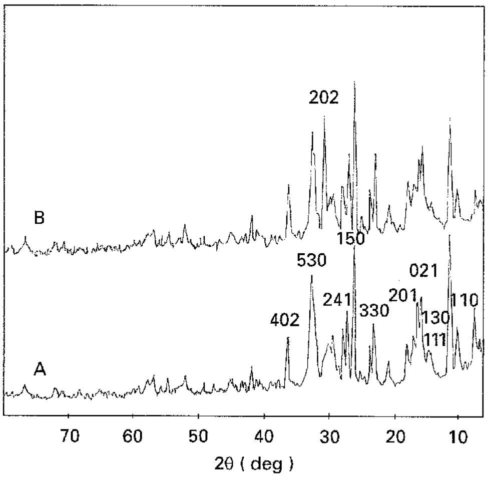

Figure 3 X-ray diffraction patterns for 723 K heated samples. (A) Na^+-mordenite, (B) Cu^{2+}-mordenite.

3.3. X-ray patterns

Extensive research has been done on the localization of cationic sites in both hydrated and dehydrated mordenites [27–30]. Only minute changes are perceived in the lattice and channel dimensions, despite wide variations in cation occupancies. Mordenite has an orthorhombic unit cell and a *Cmcm* space group. It is observed that the peaks due to the mordenite framework of $2\theta = 7°$, $10°$ and $11.5°$) showed a significant decrease in intensity upon copper addition (Fig. 3). This reflects the decrease of crystallinity upon copper modification. The general decrease in crystallinity usually confirms a decrease in aluminium content [31]. Some other peaks at $2\theta = 23°$, $26°$ and $31°$, showed a significant increase in intensity.

The changes in distribution of intensity of diffraction maxima upon the introduction of copper into Na^+-SPM may indicate some distortion inside the zeolite framework. Furthermore, the peak at $2\theta = 30.5°$ is never seen in the mordenite sample and it reflects the possible interaction of copper with the mordenite framework. Very small peaks at $2\theta = 28°$ and $35°$ are also detected. Furthermore, no drastic changes in the mordenite structure are observed upon copper addition as inferred, for example, from the intensities of (1 1 1), (2 0 1), (4 0 2), (2 4 1) and (5 3 0) reflections in the X-ray diffraction patterns. This could be a result of the precalcination step which seems to inhibit particle growth. These results are in agreement with the IR data obtained for the internal tetrahedral vibrations near 1050 and 730 cm^{-1} which reflect no significant changes in breadth and position after the copper addition.

The peak at $2\theta = 30.5°$, which agrees with the ASTM file, can be attributed to Cu (II) aluminate species.

4. Conclusion

The vibrational spectra of copper when interacting with mordenite zeolite were studied; however, the formation of aluminate species was obtained which in turn formed strong bonds when subjected to carbon monoxide and hydrogen gases.

Large discrepancies were displayed between the interactions of the aluminate species with carbon monoxide and hydrogen molecules. Stronger interactions were favoured with carbon monoxide molecules than with hydrogen molecules.

Similar bands of bridged hydroxyl were detected during the adsorption of carbon monoxide and hydrogen over Cu^{2+}-SPM, however, a shift to lower wave numbers for the latter band (H_2–Cu^{2+}-SPM) was obtained, suggesting that the formation of metallic copper, as well as an increase in copper thickness, must have occurred.

Considerable attention has been paid to the 2297 cm^{-1} band, which is attributed to the interaction between copper aluminate species and carbon monoxide molecules. This assignment was evinced by the following observations.

(i) The formation of copper aluminate species was confirmed from shifting of the shoulder at 3780 cm^{-1}, of Al–OH groups, to 3787 cm^{-1} upon copper addition.

(ii) XRD patterns reflect a new peak, never seen in the mordenite sample, at $2\theta = 30.5°$, which was in agreement with ASTM files, and attributed to Cu^{2+}-aluminate species. Furthermore, the general decrease in aluminium content, resulting from the significant decrease in crystallinity, reflects the possible interactions of copper with the aluminium species.

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