

Low Temperature CO Adsorption on Na-ZSM-5 Zeolites: An FTIR Investigation

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CO was adsorbed at 77 K on two Na-ZSM-5 zeolites which had Si/Al = 14 and Si/Al = 35, respectively. IR spectra in the OH-stretching region showed absorption bands at 3747 and 3673 cm^{-1} assigned, respectively, to terminal silanols and to hydroxyls located on extraframework aluminium species. These OH groups were more strongly perturbed than silanols by adsorbed CO, thus suggesting a more pronounced Brønsted acidity. The major features of the spectra in the CO-stretching region are two intense absorptions centered, respectively, at 2178 and 2138 cm^{-1} . Neither of them, however, is a single-peak band. The 2178- cm^{-1} band was assigned to CO molecules polarized by Na^+ ions. It could be resolved into two components, revealing coordination of Na^+ ions by one molecule (high-frequency component) or by more than one (low-frequency component). The high-frequency component showed an asymmetric profile which was assigned to the presence of Na^+ ions in slightly different environments. The 2138- cm^{-1} band corresponds to liquid-like CO inside the zeolite channels where the molecule behaves as a hindered rotor, thus explaining the fine structure observed. A weak IR absorption was also observed at 2112 cm^{-1} and assigned to CO simultaneously interacting through both ends with two Lewis acid centres. Finally, a combination mode observed at 2305–2315 cm^{-1} allowed assignment of a value of ca. 140 cm^{-1} to the Na^+ -CO stretching vibration. © 1992 Academic Press, Inc.

INTRODUCTION

ZSM-5 is a representative member of a series of silicon-rich zeolites with medium pore-size dimensions (about 0.55 nm in diameter) which find extensive application as acid-type catalysts. Acid-catalyzed reactions involving high-silica zeolites include selective paraffin cracking (1, 2), olefin oligomerization (3, 4), methanol to gasoline conversion (5–7), and alkylation of arenes (8, 9).

The acidic properties of silicon-rich zeolites arise mainly from bridged structural hydroxyls inside the channels (Brønsted acid sites), but some Lewis acidity is usually present as well. Brønsted acidity can be regulated through changes in the Si/Al ratio, which can be made to vary from 7.5 to infinity without alteration of the basic structural features (10, 11). Values from 250 upwards

are shown by silicalite, the high-silica end member of the series. Lewis acidity is generated when zeolites are activated by thermal dehydroxylation. During activation, some aluminium is released which gives rise to extraframework $\text{Al}(\text{OH})_x$ species (12–15). These can be further dehydroxylated to generate an aluminium oxide phase with Lewis acid sites (coordinatively unsaturated Al^{3+} ions) similar to those exhibited by active aluminas. Trigonal framework species (Al and Si^+) could also be generated during activation, and act as Lewis acid sites in ZSM-5 zeolites (12, 16–19). A different source of Lewis acidity is provided by metal ions in cation-exchanged zeolites. Cations, being electron acceptors, are able to act as Lewis acid centres in the broad sense.

Detailed characterization of the internal surface of zeolites is much needed for a deep understanding of the prominent catalytic

properties exhibited by these materials. However, the simultaneous presence of different acid centres along with possible structural heterogeneities often make this task a difficult one to accomplish. IR spectroscopy, using suitable probe molecules, is a powerful means to analyse surface active centres. However, the complexity of the adsorbate–adsorbent and adsorbate–adsorbate interactions along with some intrinsic limitations of the technique often call for a very precise analysis of the spectra in order to extract all the information available. We offer here a careful IR spectroscopic investigation of CO adsorption on two Na-ZSM-5 zeolites, at Si/Al = 14 and Si/Al = 35, respectively. The full power of the technique is illustrated through a detailed analysis not only of the major features of the spectra, but also of the minor details experimentally observed.

EXPERIMENTAL

Na-ZSM-5 samples with Si/Al = 14, and Si/Al = 35 were supplied by Enichem ANIC Laboratories (Bollate, Milano); they are hereafter called Na-ZSM-5 (14) and Na-ZSM-5 (35), respectively. Thin self-supporting wafers were activated in vacuum at 623 K for 1 hr, inside the IR cell.

Infrared spectra were taken using a vacuum-purged Bruker FS 113v spectrometer operated at 2 cm^{-1} resolution, and following an *in situ* procedure. All of the spectra shown were taken at liquid-nitrogen temperature.

RESULTS AND DISCUSSION

OH-Stretching Region

Figure 1 shows the IR absorption spectra of Na-ZSM-5 (14) in the OH-stretching region. Spectrum 1, taken before dosing with CO, displays two bands centred at 3747(s) and 3673(w) cm^{-1} , respectively. The 3747- cm^{-1} band corresponds to terminal silanol groups mainly located in the outer surface of the zeolite crystals (12, 20–22). The 3673- cm^{-1} band has been assigned (16, 23) to ex-

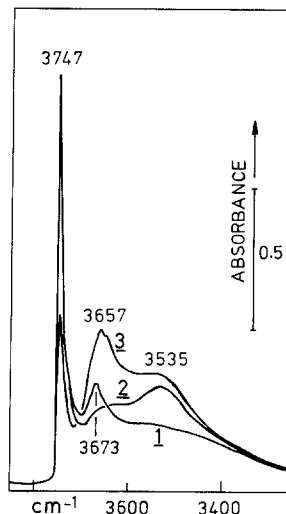


FIG. 1. IR spectra in the OH-stretching region of Na-ZSM-5(14): (1). Effect of an increasing equilibrium pressure of adsorbed CO; (2, 3). Curves (1) and (2) are coincident in the 3747 cm^{-1} region.

traframework Al–OH species formed during thermal activation. Bridging structural hydroxyl groups of the Si(OH)Al type are known to give IR absorption at 3625–3615 cm^{-1} (12, 16, 22, 24). Pure Na-ZSM-5 would not exhibit such a feature; however, the asymmetry observed in the low-frequency side of the 3673- cm^{-1} band suggests that the actual sample investigated might have a small proportion of bridging OH groups.

A broad background absorption is also observed in the whole 3700–3400 cm^{-1} region. Several authors (25–27) have pointed out that during partial dealumination (which generates extraframework species) small hydroxylated cavities (nests) are created. Hydrogen-bonded silanols present at these nests are probably the species responsible for the broad structureless absorption in the 3700–3400- cm^{-1} region. These OH-groups are not easily accessible to CO; consequently no effect on them is observed upon CO dosing.

The effect of dosing with CO is shown by spectrum 2 (which corresponds to the most intense spectrum in Fig. 2) and spectrum 3. Hydroxyls located on extraframework alu-

minium species are the first ones to be disturbed by CO. This results in a decrease of the absorption band at 3673 cm^{-1} and parallel growth of a new band centred at 3535 cm^{-1} , which corresponds to CO-perturbed hydroxyls. Silanol groups are not significantly altered at this stage. Admission of a further dose of CO (spectrum 3) results in a substantial decrease of the 3747-cm^{-1} band, and consequent appearance of a new IR absorption at 3657 cm^{-1} due to perturbed silanols. This experiment strongly suggests that extraframework hydroxyls exhibit a more pronounced Brønsted acidity than terminal silanols. This is why the former show a more pronounced shift, and broadening, of the CO-perturbed absorption band.

CO-Stretching Region

IR spectra in the CO-stretching region are shown in Fig. 2 for Na-ZSM-5 (14) and Fig. 3 for Na-ZSM-5 (35). The most intense feature of these spectra is band A which at low CO equilibrium pressure displays a maximum at 2178 cm^{-1} , thus showing a hypsochromic shift of 35 cm^{-1} with respect to the free CO molecule (2143 cm^{-1}). This band can readily be assigned to CO polarized by Na^+ ions. On NaCl the corresponding band of adsorbed CO appears at 2160 cm^{-1} (30); the larger hypsochromic shift observed for Na-ZSM-5 is likely to reflect more coordinative unsaturation of the Na^+ ion in the zeolite, as compared to the NaCl surface. We note that, in agreement with the above assignment, the corresponding relative intensity of the 2178 cm^{-1} band is higher in the case of Na-ZSM-5 (14), which has the larger sodium content. When the equilibrium pressure of CO is increased, band A shows a small downward shift which reaches 10 cm^{-1} for the last dose in Fig. 3. Because of signal saturation, this displacement is more difficult to quantify in the case of Na-ZSM-5 (14), but qualitatively it can also be observed in Fig. 2. The origin of this downward shift must be assigned to "solvation" of the intrazeolite Na^+ ions by CO. At high equilibrium pressure, more than one

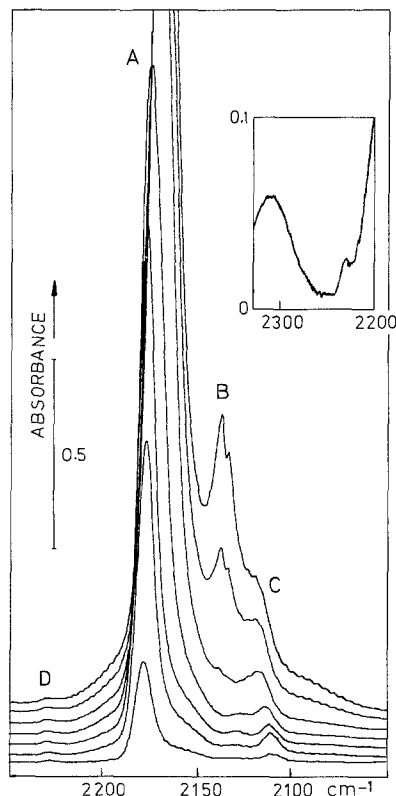


FIG. 2. IR spectra in the CO-stretching region of Na-ZSM-5(14) at increasing CO equilibrium pressure: 10^{-2} , 10^{-1} , 6×10^{-1} , 1, 2, 4, and 7 Torr (1 Torr = 133.3 Pa). Inset shows a combination mode *ca.* 2300 cm^{-1} . The zeolite blank has been subtracted from each spectrum.

CO molecule will be coordinated to each Na^+ ion. The individual interaction is thus lowered, and the corresponding CO-stretching frequency is less altered (with respect to free CO). This hypothesis can be further substantiated. Careful inspection of the band profile revealed that A is not a single absorption band. Using a home-developed deconvolution program (28) resolution into two components A_1 and A_2 was achieved, as shown in Fig. 4. These components are centred at 2178 and 2170 cm^{-1} , respectively. The intensity of the peak at higher frequency (A_1) increases up to a maximum value (spectrum b in Figure 4) and then decreases. The component at lower frequency (A_2) increases continuously, as shown in Figure

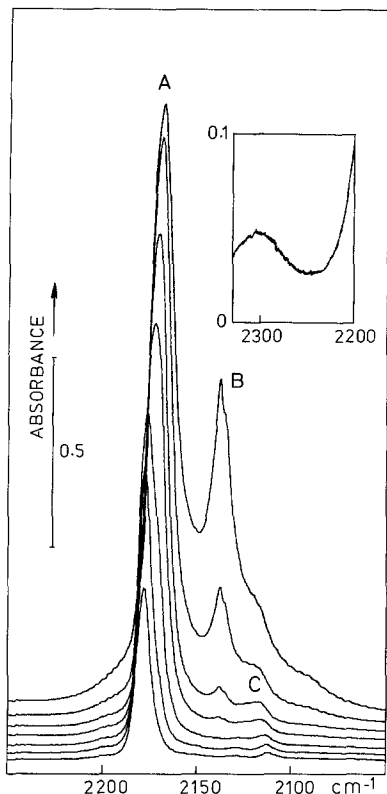
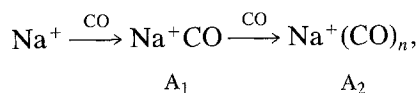


FIG. 3. IR spectra in the CO-stretching region of Na-ZSM-5(35) at increasing CO equilibrium pressure: 7×10^{-2} , 10^{-1} , 5×10^{-1} , 1, 2.5, 5, and 10 Torr. Remaining comments as in Figure 2.

4e. This is precisely the behaviour to be expected from the stepwise process,



where an Na^+ ion initially coordinated to a CO ligand is progressively coordinated (solvated) by more CO molecules, thus increasing the intensity of component A_2 at the expense of A_1 .

It should be noted that the shape of the A_1 component is clearly asymmetric (Fig. 4a). This indicates that we are dealing with a family of similar, but slightly heterogeneous, $\text{Na}^+ \cdots \text{CO}$ species. The observed

heterogeneity is probably associated with the presence of Na^+ ions in slightly different environments within the zeolite framework (for instance, Na^+ ions at channel intersections, and inside the channels). Proton-perturbed CO molecules (i.e., CO interacting with Brønsted acid sites) would also produce IR absorption at about 2165 cm^{-1} , but at the low CO coverage implied in spectrum 4a this is not likely to be the main source of asymmetry of band A_1 .

Band B (Figs. 2 and 3) appearing at 2138 cm^{-1} is readily assigned to physisorbed CO in a liquid-like state inside the pores of the zeolite. It only develops at high equilibrium pressures, and the observed frequency compares well with that of CO in a condensed phase (29), or physically adsorbed on oxides and halides (30–32). We note that inside the zeolite channels the CO molecule should behave as a hindered rotor, and this explains the complex structure exhibited by band B.

A weak band (C) is also observed in the low frequency region of Figs. 2 and 3. This band appears at 2112 cm^{-1} and gradually moves to higher frequencies (up to 2118 cm^{-1}) as the equilibrium pressure of CO is increased. A similar band, at 2121 cm^{-1} , has also been observed (33) for CO adsorbed on zeolite Na-Y. We assign this band to CO molecules already interacting with Na^+ ions through the carbon atom, and which interact *via* the oxygen end with another Lewis centre. The nature of this (second) Lewis acid centre cannot be fully discerned at this stage. A nearby Na^+ ion could act as such, but some other singularities such as coordinatively unsaturated Al^{3+} ions in the extra-framework phase, or trigonal framework Al or Si, are also possible candidates. It is worthwhile to note, in this context, that the low intensity of band C shows that only a very small fraction of CO molecules find themselves in a situation apt for double coordination. This is especially the case when due consideration is taken of the fact that extinction coefficients become increased when the CO-stretching frequency falls be-

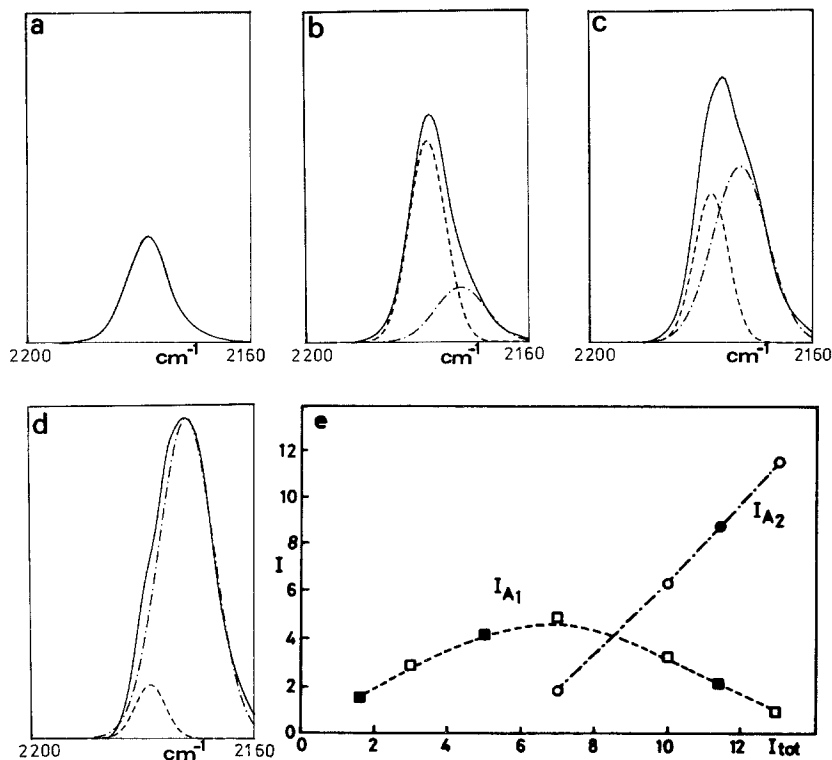


FIG. 4. Parts (a–d). Deconvolution using two Gaussian functions of band A from the first four spectra in Fig. 3 (increasing CO doses). In part (e) the intensity of each deconvoluted component is plotted vs. the overall intensity. Besides the points corresponding to 4a–d (open symbols) others were added (filled symbols) which correspond to spectra at CO doses not shown (for clarity) in Fig. 3. Note that, at the CO equilibrium pressures implied in the corresponding spectra, gas-phase CO is not contributing.

low the gas-phase value (34). The observed upward shift of band C with increasing CO pressure is readily assigned to coordination of the second Lewis acid centre by CO molecules.

Another very weak band (D) is observed, at 2230 cm^{-1} , in the IR spectra of Fig. 2. A similar weak band (at 2238 cm^{-1}) has also been reported for CO adsorbed onto γ -alumina, and assigned (32) to CO σ -bonded to strong cationic Lewis acid sites. In the present case such sites are likely to be furnished by highly unsaturated Al^{3+} ions located in the extraframework species. This would be consistent with the fact that band D was not observed for Na-ZSM-5 (35) (Fig. 3), which has a higher Si/Al ratio and therefore contains a considerably smaller proportion of aluminium.

Acidity

The IR study on CO adsorption can be used to evaluate the Brønsted and Lewis acidity of Na-ZSM-5. Proton-donor sites can be investigated in the OH-stretching region, where the IR band shifts to lower frequency when hydrogen-bonded CO complexes are formed. Electron-acceptor sites can be monitored in the CO-stretching region, where the band frequency increases with increasing Lewis acidity (or polarization power) of the acceptor sites. A summary of the present results is given in Table 1, where data for related materials is also presented for comparison. It is readily seen that silanol groups in Na-ZSM-5 show about the same $\Delta\nu_{\text{OH}}$ as silanols in (hydroxylated) SiO_2 . They can thus be

TABLE 1
Frequency Shifts (cm^{-1}) Caused by Interaction of CO with OH-Groups and L-sites (L = Lewis acid)

Material	ν_{OH}	$\Delta\nu_{\text{OH}}$ after CO adsorption (downward shift)	ν_{CO}	$\Delta\nu_{\text{CO}}$ (upward shift) from CO gas ($\nu_{\text{CO}} = 2143 \text{ cm}^{-1}$)	Reference
SiO ₂ (Aerosil)	3748–3751	78–108			(35, 36)
H-ZSM-5 (Si(OH)Al)	3615–3620	310–320			(16)
HNa-Y (Si(OH)Al)	3652	275			(17)
Na-ZSM-5 (silanols)	3747	90			Present work
Na-ZSM-5 (Extraframework)	3673	138			Present work
γ -Al ₂ O ₃ (Al _{tet})			2190–2210	47–67	(32)
γ -Al ₂ O ₃ (Al _{oct})			2165	22	(32)
γ -Al ₂ O ₃ (strong L-sites)			2238	95	(32)
Na-ZSM-5 (Na ⁺)			2178	35	Present work
Na-ZSM-5 (strong L-sites in extraframe- work species)			2230	87	Present work

considered as non-acidic. OH-groups in extraframework Al(OH)_x species are slightly acidic. Note, however, that the corresponding frequency shift (138 cm^{-1}) is significantly smaller than the reported values for bridged OH groups in either HNa-Y (275 cm^{-1}) or H-ZSM-5 ($310\text{--}320 \text{ cm}^{-1}$), which reflects the weak Brønsted-acid character of extraframework species.

The Na⁺ ion in Na-ZSM-5 provides Lewis acidity comparable to that shown by coordinatively unsaturated Al³⁺ ions at the γ -Al₂O₃ surface. The observed $\Delta\nu_{\text{CO}}$ value (35 cm^{-1}) falls between those corresponding to Al_{tet} ($47\text{--}67 \text{ cm}^{-1}$) and Al_{oct} (22 cm^{-1}) in γ -Al₂O₃. For the zeolite with smaller Si/Al ratio (Na-ZSM5(14)) a stronger Lewis-acid site ($\Delta\nu_{\text{CO}} = 87 \text{ cm}^{-1}$) was also found, and already discussed (band D in Fig. 2).

Metal–Carbon Bond Vibration

Coordination of CO to Na⁺ ions, as previously discussed, should also result in the appearance of IR absorption at a frequency corresponding to the metal–carbon bond. For organometallics and for CO adsorbed on metals, the metal–carbon stretching vibration was found at about $500\text{--}380 \text{ cm}^{-1}$ (37, 38). A rather smaller value is expected for the Na⁺–CO bond, where CO is polarized by the Na⁺ ion. The zeolite wafer is not IR transparent in the far IR, thus precluding direct observation of the Na⁺–CO stretching mode. However, the inset of Figs. 2 and 3 shows a weak band at $2305\text{--}2315 \text{ cm}^{-1}$ which was observed to disappear upon outgassing the adsorbed CO. We believe this band to be the combination mode of the metal–carbon vibration with the intense CO mode giving rise to band A. Consequently,

a value of about 140 cm^{-1} is inferred for the Na^+ -CO stretching vibration. It should be borne in mind that we are dealing with high CO equilibrium pressure, whereby the peak frequency of band A is 2168 cm^{-1} . To the best of our knowledge, this is the first time that this Na^+ -CO vibration frequency has been experimentally determined.

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