Adsorption of CO on NaZSM-5 zeolite under moderate temperature and pressure conditions: An FTIR investigation

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Adsorption of CO on NaZSM-5 zeolite was investigated at temperatures in the range 300–470 K and at pressures of 5–500 Torr using FTIR spectroscopy. The effect of exchanging the charge balancing cation in NaZSM-5 with a proton or calcium was evaluated. Data were also collected on NaY, CaY and CaX zeolites for comparison. We detected the development of six distinct C—O stretching bands with maxima at around 2111, 2130, 2146, 2160, 2176 and 2194 cm^{-1} during the adsorption of CO on NaZSM-5 zeolite at ambient temperatures. This was accompanied by the appearance of a prominent band at 2356 cm^{-1} and weak shoulder bands at frequencies around 2336, 2340, 2370 and 2380 cm^{-1} in the v_3 region of CO_2. All the $v(CO)$ bands and also the bands in the v_3 region of CO_2 exhibited similar behaviour as a function of adsorbate pressure, evacuation, rise in sample temperature, and the exchange of charge balancing cation. For instance, the intensity of all the C—O stretching bands showed a similar growth behaviour with increasing adsorbate pressure, though the extent of this growth was different for the individual IR bands. Similarly, these bands were removed simultaneously on evacuation. Furthermore, while all the vibrational bands in the $v(CO)$ region showed a uniform isotopic shift corresponding to a frequency ratio $v(^{13}C/^{12}C)$ of *ca.* 0.977 and $v(^{18}O/^{16}O)$ of 0.976 for the adsorption of $^{13}C^{16}O$ and $^{12}C^{18}O$, respectively, the bands in the $v_3(CO_2)$ region showed a red shift $v(^{13}C/^{12}C)$ of 0.972 with ^{13}CO and an isotopic shift corresponding to $^{16}O^{12}C^{18}O$ on $^{12}C^{18}O$ adsorption. No shift in $v(OH)$ bands was observed after CO adsorption under the conditions of this study. The results thus indicate that the individual zeolitic surface sites *e.g.*, the Al^{3+} sites, Bronsted acid sites or the charge balancing cations, may not participate directly in the bonding of CO molecules at room temperature or above. Instead, the cage effect of zeolites plays an important role. The data are interpreted to suggest the formation of weakly bonded clusters of CO and CO_2 molecules, occluded in the zeolitic cages and stabilized under the cationic field.

Introduction

Infrared spectroscopy of adsorbed carbon monoxide probe molecules has been widely employed for the investigation of acid sites and charge balancing cations in zeolites.[1-9] The development of C—O stretching bands in the 2135–2235 cm^{-1} region has been reported in these studies for adsorption of CO on ZSM-5 and other zeolites. There is, however, a controversy about the number of vibrational bands thus formed and also about their origin. For instance, a prominent band reported widely at a frequency in the 2173–2178 cm^{-1} range has been attributed differently to CO molecules interacting with the bridging hydroxy groups,[2] at surface Lewis sites[6] and with the charge balancing cations.[5,7,9] However, most of the studies mentioned above were performed at low sample temperatures (77–100 K) and at low pressures (5–20 Torr) and not much has been reported so far on the mode of CO adsorption/interaction on these zeolites under actual reaction conditions. In previous IR spectroscopy studies,[10,11] we have demonstrated the formation of $(CO)_n$ molecular clusters in the cavities of faujasite zeolites as a result of CO adsorption at room temperature. The charge balancing cations, temperature and the adsorbate pressure were found to have considerable influence on these clusters.

In the present study we report on the CO adsorption over NaZSM-5 zeolite at sample temperatures in the 300–475 K range and at adsorbate pressures of 10–500 Torr. The effect of exchanging the charge balancing cation in NaZSM-5 with a proton or with a calcium ion on its CO adsorption behaviour has been investigated. Data were also collected on NaY, CaY and NaX zeolites in addition to alumina and silica samples for comparison purposes. The effect of isotopic substitution in adsorbate CO on the frequency of vibrational bands developed in the process has also been monitored.

Experimental

Samples

A template free NaZSM-5 zeolite sample, having a Si/Al ratio of ~40 and a surface area of 280 m^2 g^{-1}, was provided by the Research and Consultancy Directorate of the Associated Cement Co. Ltd, Thane, India. The XRD pattern of this sample showed prominent bands at 2θ values of 24.41, 23.98, 23.32, 23.1, 8.95 and 8.03°, commensurate with the reported data on ZSM-5 zeolite.[12] ^{29}Si and ^{27}Al MAS NMR spectra were also recorded to characterize the zeolite used in this study. For this purpose, a Bruker-MSL-300 spectrometer operating at 59.62 MHz (for ^{29}Si) and 78.17 MHz (for ^{27}Al) was employed and the samples were spun at 2.3 kHz speed. A MAS NMR peak for ^{27}Al appeared at +56.3 ppm corresponding to the aluminium present in the tetrahedral position of the framework. No measurable signal due to octahedrally coordinated non-framework Al was observed. Similarly, the ^{29}Si MAS NMR spectrum showed a maximum at −113.1 ppm and weak bands at −106.3 and −115.1 ppm, characteristic of a high silica zeolite, such as ZSM-5 with Si/Al ≈ 40.[13] The HZSM-5 and CaZSM-5 samples were prepared by repeated contact of NaZSM-5 with 10% ammonium nitrate or calcium nitrate solution with intermediate centrifugation and

discard of the supernatant solution. The samples were washed thoroughly with demineralised water before filtration followed by drying at 370 K and calcination in pure nitrogen at 775 K for 16 h. The samples maintained their crystallinity and gave an XRD pattern similar to that of NaZSM-5 zeolite. Chemical analysis showed that about 70–80% of Na$^+$ ions were exchanged. The semiquantitative spectrographic analysis of NaZSM-5 and cation exchanged samples revealed that besides ∼500–1000 ppm of Fe, 100 ppm of Ti and 100 ppm of Mg, no other metal impurities were present beyond a detection limit of 10–20 ppm. The atomic absorption spectrophotometric analysis gave the Fe content as 400, 460 and 435 ppm in NaZSM5, CaZSM5 and HZSM5 samples, respectively.

For comparison, parallel studies were also performed on a high purity γ-alumina (surface area 150 m^2 g^{-1}) and a silica (surface area ∼175 m^2 g^{-1}) sample, obtained from ACC Ltd. Thane.

IR Spectroscopy

Self supporting sample wafers (∼80 mg) of 25 mm diameter were placed in a high-temperature, high-pressure stainless steel cell described earlier.[10,14] Samples were heated *in situ* for 25–30 h at a temperature of 600–625 K and under a vacuum of 1 × 10^{-4} Torr before exposure to carbon monoxide at the desired temperature and pressure. A Mattson model-Cygnus 100 FTIR equipped with a DTGS detector was employed and 300 scans were added at 4 cm^{-1} resolution for each spectrum. The spectra were recorded after an equilibration time of 30 min. The contribution of absorbance due to gas phase CO in the cell was compensated by independently recording CO gas IR spectra at different pressures and subtracting them suitably from the sample spectra.[10] All the IR data given in this text refer to such difference spectra, unless mentioned otherwise. The values given in parentheses in these figures refer to the absorbance of individual vibrational bands, which are taken as a measure of relative intensities for inter-comparison. The overlapping spectral bands were resolved using a Fourier self-deconvolution programme in the FTIR computer software which followed an apodization method developed by Kauppinen *et al.*[15] This helped in determining the number and the precise position of the component peaks. The deconvolution parameters employed for this purpose were: full width at half maximum (w) = 12–15, enhancement factor (k) = 1.1–1.3, Lorentzian fraction (f) = 3 and the apodization or smoothing function (a) = 3. The overlapping IR bands were also resolved computationally using the Microsoft-Windows 95 origin 4.1 package in order to estimate the relative integral area under individual peaks. A choice of multiple gaussian peaks gave an excellent fit for this purpose.

Carbon monoxide [99.9% purity, Airco (USA)] was used after trapping over solidified CO$_2$ in order to remove any carbonyl or moisture impurities. ^{13}C labelled (∼60%) carbon monoxide (Prochem Ltd., UK) and C^{18}O (99.8 atom% ^{18}O and 0.003% ^{17}O, from Johnson Matthey, USA) were used to record the isotopic shifts of different vibrational bands.

Results

CO adsorption

A typical IR spectrum of NaZSM-5 wafer outgassed at 600 K and exposed for 30 min to 100 Torr CO at ambient temperature is shown in Fig. 1(a). No IR bands were observed at frequencies lower than 2000 cm^{-1} in contrast to the case of NaX zeolite where two pairs of intense bands were observed in the 1300–1700 cm^{-1} region after CO adsorption under identical conditions.[10] Fig. 1(b) shows the difference spectrum obtained on subtracting the IR bands due to gaseous CO from the spectrum in Fig. 1(a). Fig. 1(b) thus presents the
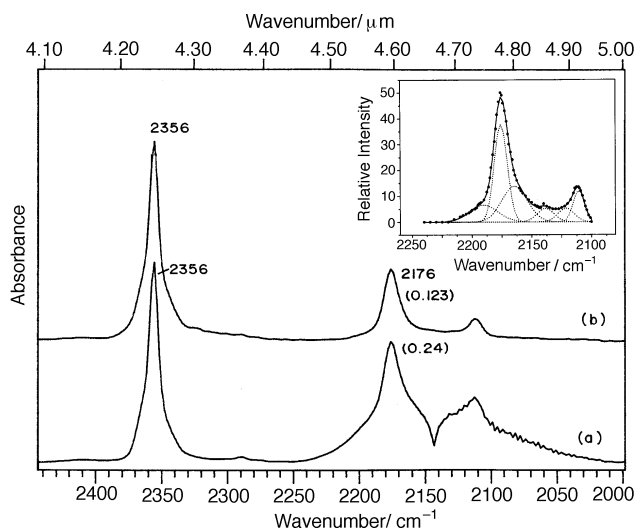
Fig. 1 (a) IR spectrum of NaZSM-5 zeolite exposed to 100 Torr CO at ambient temperature; (b) difference spectrum on subtracting gas phase IR bands of CO from spectrum (a). Inset: computer resolution of the C—O stretching bands in Fig. 1(b).

vibrational bands developed due to CO adsorption in zeolite. In addition to IR bands in the C—O stretching region, an intense and broad band in the v_3 region of CO$_2$ having a maximum at 2356 cm^{-1} and composed of some overlapping shoulder bands is also seen in Fig. 1(b).

Deconvolution and computational resolution

Fig. 2(a) and (b) give a deconvolution of the v(CO) and v_3(CO$_2$) region bands shown in Fig. 1(b). The presence of six distinct vibrational bands in the C—O stretching region with maxima at around 2111, 2130, 2146, 2160, 2176 and 2194 cm^{-1} can be observed in this figure. Similarly, the deconvolution of v_3(CO$_2$) region bands confirmed the presence of side bands at around 2326, 2340, 2370, and 2382 cm^{-1} in addition to a main band at 2356 cm^{-1} [Fig. 2(b)]. The position of the bands mentioned above was reproducible within ±0.5–1 cm^{-1} for the repeated experiments and for the different combinations of deconvolution parameters.

The nature of the constituent bands and their relative areas become clear from the computational resolution of IR bands shown in Fig. 1(b). A typical computational resolution of v(CO) bands in Fig. 1(b) is presented in the inset of Fig. 1. While the circles in this figure show the data points, the solid
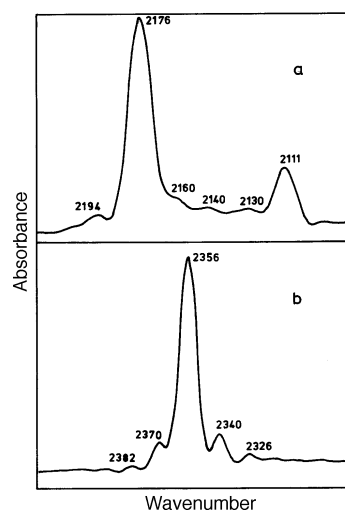

Fig. 2 Fourier self-deconvolution of (a) C—O stretching and (b) v_3(CO$_2$) region bands observed on NaZSM-5 zeolite after exposure at ambient temperature to 100 Torr CO.

curve represents the sum total of the component bands shown by dotted lines, indicating a close fit.

The intensity of both the v(CO) and the v_3 region CO_2 bands depended on the experimental parameters, such as contact time, sample temperature and adsorbate pressure, as described below.

Effect of contact time

While the frequency of different vibrational bands remained unchanged with increasing contact time of a sample with CO, the relative intensity of v(CO) bands showed marginal changes. Also, the intensity of v_3 vibrational bands of CO_2 increased progressively with time. An equilibrium state for both the v(CO) and v_3(CO_2) region bands was reached in about 30–40 min.

Effect of adsorbate pressure

Fig. 3(a)–(d) show the development of vibrational bands in v(CO) and v_3(CO_2) regions when CO was adsorbed on NaZSM-5 zeolite at ambient temperature but at different pressures. The vibrational bands in both the regions showed a progressive increase in intensity with a rise in adsorbate pressure, as is evident from the absorbance values given in these spectra. This is reflected clearly in the corresponding deconvoluted spectra shown in Fig. 4 for the two typical adsorbate pressures of 10 and 500 Torr.

When the pressure of carbon monoxide in the cell was reduced slowly by controlled pumping and IR spectra were recorded at different stages, a behaviour identical to that shown in Fig. 3 but in reverse order in terms of peak shape and intensity was observed. Fig. 5 presents some of these data for the v(CO) bands.

Almost all the vibrational bands, both in v(CO) and v_3(CO_2) regions, displayed a small but reproducible shift of about 2 cm^{-1} on a rise in adsorbate pressure from 10–500 Torr (Fig. 3 and 4). The integrated intensities of some of the prominent component bands in v(CO) and v_3(CO_2) regions, as evaluated from the computational resolution of overlapping bands, are presented in Fig. 6. These data show that all the bands followed a similar growth behaviour, $i.e.$, an initial near linear increase in intensity followed by an asymptotic growth, even though the extent of this growth was different for the different bands (Fig. 6).

Fig. 7 presents the fractional area covered by individual v(CO) IR bands [area under a band/sum of the area under different v(CO) bands at a particular pressure] as a function of

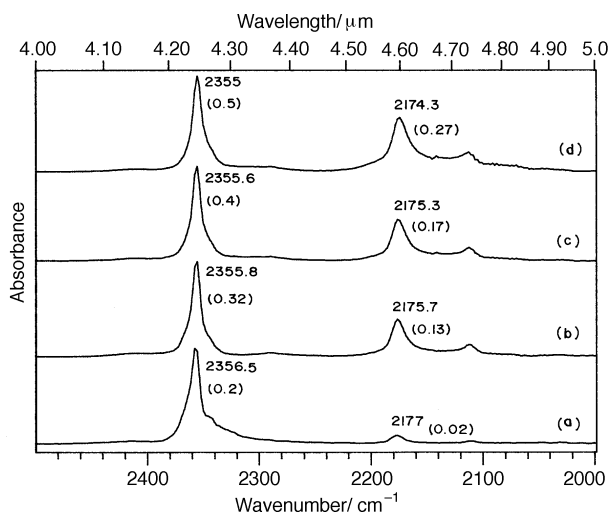**Fig. 4** Fourier self-deconvolution of v(CO) bands developed on NaZSM-5 zeolite after exposure at ambient temperature to (a) 10 Torr CO and (b) 500 Torr CO.

increasing adsorbate pressure. It is of interest to note that while the share of IR bands at 2160 and 2190 cm^{-1} increased, the fractional area covered by the bands at around 2175 and 2146 cm^{-1} decreased considerably. On the other hand, the fractional coverage of a band at 2111 cm^{-1} remained almost

Fig. 5 Some v(CO) region vibrational bands of NaZSM-5 zeolite developed after room temperature adsorption of CO at different pressures: (A) with increasing pressure, (B) with decreasing pressure. (a) 5, (b) 10, (c) 20 and (d) 50 Torr.

Fig. 3 Vibrational bands in v(CO) and v_3(CO_2) regions developed on NaZSM-5 zeolite after room temperature exposure to CO at different pressures. (a) 10, (b) 100, (c) 200 and (d) 500 Torr.
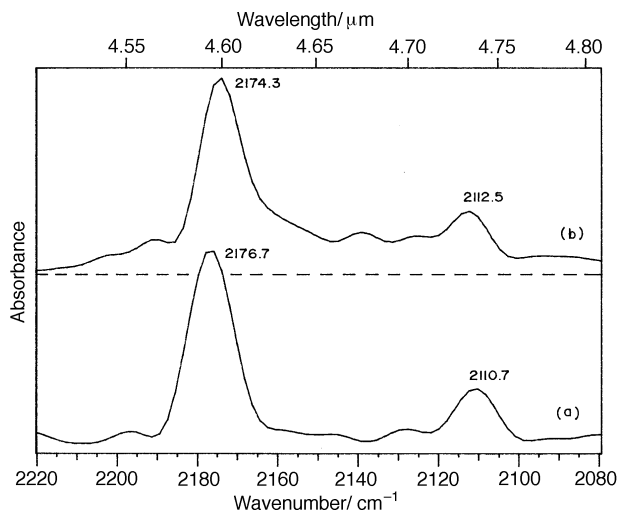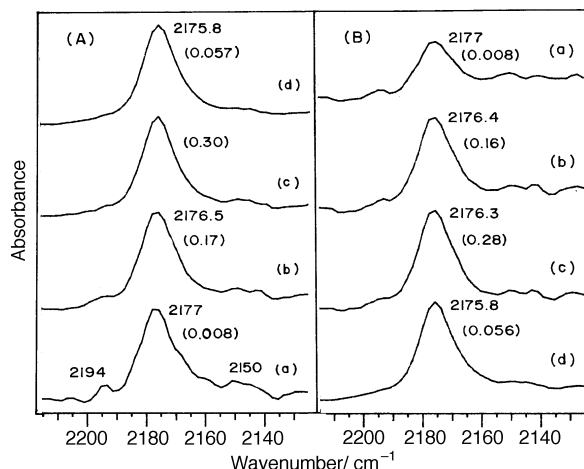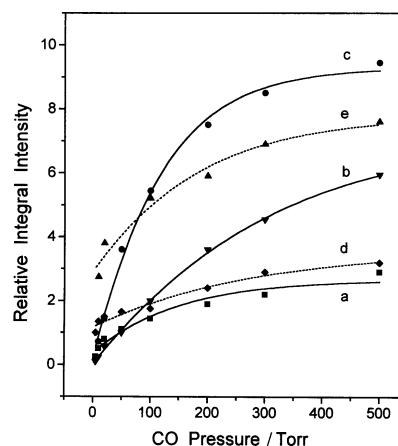

Fig. 6 Growth of some prominent v(CO) [spectra (a)–(c)] and v_3(CO_2) [(d), (e)] region IR bands after room temperature adsorption of CO on NaZSM-5 zeolite at different pressures. (a) 2111, (b) 2187, (c) 2175, (d) 2340, (e) 2356 cm^{-1}.
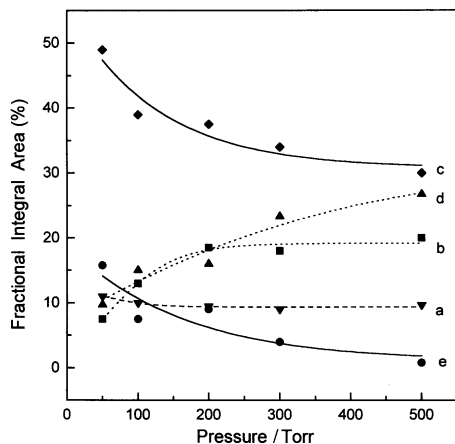
Fig. 7 Fractional area under individual IR bands developed on room temperature exposure of CO over NaZSM-5 at different pressures. (a) 2175, (b) 2160, (c) 2190, (d) 2111 and (e) 2146 cm^{-1}.

unchanged. A similar trend was also observed in the case of asymmetric stretching region bands of CO_2.

Effect of evacuation

Evacuation of the sample subsequent to CO exposure resulted in the quick removal of all the $v(CO)$ and $v_3(CO_2)$ region bands seen in Fig. 1.

Effect of temperature

The rise in sample temperature to 375 K resulted in the simultaneous removal of all the $v(CO)$ bands while the vibrational band with a maximum at 2356 cm^{-1} became more intense and broader [Fig. 8(a)–(c)]. With the further rise in sample temperature to 475 K, a broad band at around 2310 cm^{-1}, similar to that of gaseous CO_2, was also seen clearly [Fig. 8(d)].

Adsorption of labelled CO molecules

Spectra (a)–(c) in Fig. 9 present a comparison of the C—O stretching vibrational bands developed on NaZSM-5 zeolite after 30 min exposure at ambient temperature to $^{12}C^{16}O$ (20 Torr), $^{12}C^{16}O + ^{13}C^{16}O$ (2 : 3, 50 Torr) and $^{12}C^{18}O$ (20 Torr), respectively. These data, presented in a deconvoluted form for clarity of isotopic shifts, reveal a uniform red shift of 48 ± 1 cm^{-1} in all the $v(CO)$ adsorption bands of ^{13}CO [Fig.
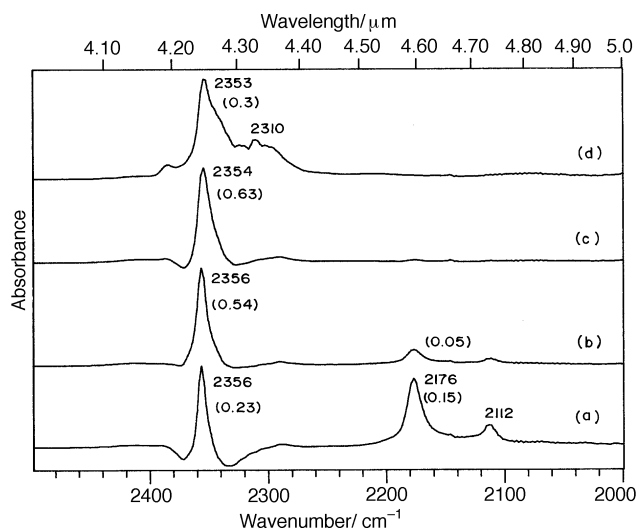

Fig. 8 Effect of sample temperature on the vibrational bands developed on NaZSM-5 zeolite after exposure to 100 Torr CO. (a) 300, (b) 340, (c) 375 and (d) 475 K.
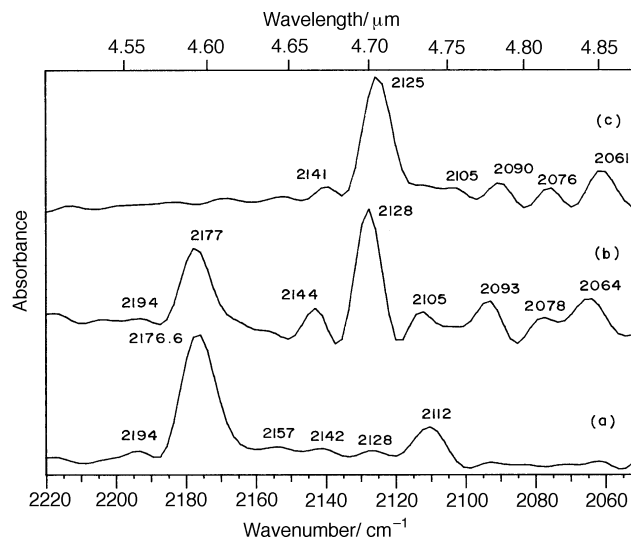
Fig. 9 Fourier self-deconvolution of $v(CO)$ region bands developed on NaZSM-5 zeolite after exposure to (a) 20 Torr $^{12}C^{16}O$, (b) 50 Torr $^{12}C^{16}O + ^{13}C^{16}O$ (2 : 3) and (c) 20 Torr $^{12}C^{18}O$.

9(b)]. The corresponding shift for the adsorption of $^{12}C^{18}O$ was found to be 52 ± 1 cm^{-1} [Fig. 9(c)]. The peak positions and the frequency shifts for individual bands are shown in Table 1.

Similarly, a uniform negative isotopic shift of 66–67 cm^{-1} was observed in all the v_3 bands of CO_2 on adsorption of $^{13}C^{16}O$. A deconvolution of these bands is given in Fig. 10 and the frequencies of individual bands are compiled in Table 2. When the $C^{18}O$ was exposed over ZSM-5 at ambient temperature, a pair of overlapping bands with maxima at 2356.7 and 2341 cm^{-1}, as shown in Fig. 10(c), was observed.

Adsorption over HZSM-5

Similar but very weak vibrational bands were observed when CO was adsorbed at ambient temperature on HZSM-5 zeolite, as shown in Fig. 11 for three different gas pressures. A comparison with the absorbance values given in Fig. 3 reveals that the intensities of $v(CO)$ bands in Fig. 11 were around 20–30% of the values observed for NaZSM-5 at a particular pressure. At the same time, negligibly small bands in the CO_2 stretch region were formed during CO adsorption over HZSM-5 (*cf.* Fig. 3). Also, the $v_3(CO_2)$ bands in Fig. 11 have a semblance with the IR bands of gaseous CO_2 at this pressure rather than with the bands in this region in Fig. 3.

Adsorption over other zeolites

Spectra (a)–(d) in Fig. 12 present comparative C—O stretching region IR bands of CaZSM-5, CaY, CaX and NaY zeolite samples, all recorded for 100 Torr CO exposure at room temperature. The extent of cation exchange in these samples was

Table 1 Isotopic shifts observed in various C—O stretch bands when $^{13}C^{16}O$ (3 : 2) and $^{12}C^{18}O$ were adsorbed over ZSM-5 zeolite at ambient temperature

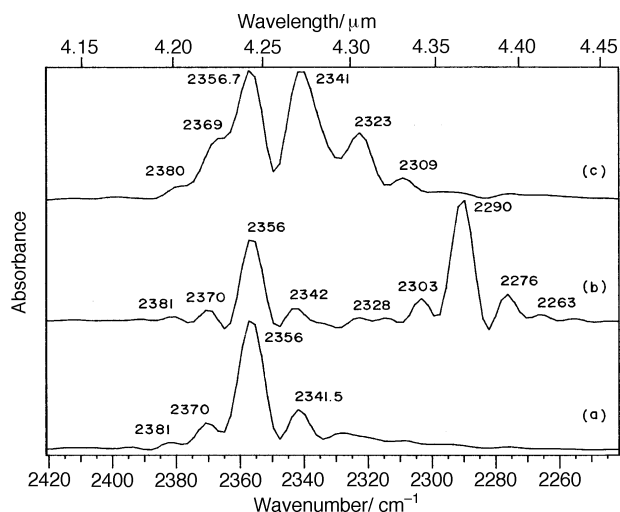| v on ^{12}CO adsorption/ cm^{-1}	$^{13}C^{16}O$		$^{12}C^{18}O$	
	v/cm^{-1}	$v(^{13}CO)/$ $v(^{12}CO)$	v/cm^{-1}	$v(C^{18}O)/$ $v(C^{16}O)$
2112	2064	0.978	2061	0.976
2127	2078	0.977	2076	0.976
2142	2093	0.977	2090	0.976
2157	2110	0.978	2105	0.976
2177	2128	0.977	2125	0.976
2194	2144	0.977	2141	0.976

Fig. 10 Fourier self-deconvolution of $v_3(CO_2)$ region bands developed on NaZSM-5 zeolite after exposure to (a) 20 Torr $^{12}C^{16}O$, (b) 50 Torr $^{12}C^{16}O + ^{13}C^{16}O$ (2 : 3) and (c) 20 Torr $^{12}C^{18}O$.

Fig. 12 Comparative $v(CO)$ bands of (a) NaY, (b) CaY, (c) CaX, and (d) CaZSM-5 zeolites, formed after 100 Torr CO adsorption at room temperature.

in the range of 70–80%. Data in these spectra show that in contrast to the results obtained for CaY zeolites where a blue shift of 16 ± 2 cm^{-1} as compared to that for NaY was observed in most of the $v(CO)$ bands[11] [Fig. 12(a) and (b)], no measurable shift in C—O stretching bands was observed for the adsorption of CO over CaZSM-5 zeolites under identical test conditions [Fig. 12(d), Fig. 1 and 2]. On the other hand, the effect of cation exchange on frequency of $v(CO)$ bands was identical in the cases of faujasite X- and Y-zeolites, having similar pore structure [Fig. 12(b) and (c)]. A similar trend was observed in the case of $v_3(CO_2)$ bands as well, and details of these aspects are given elsewhere.[16]

Table 2 Isotopic shift observed in various vibrational bands in the v_3 region of CO_2 when $^{13}C^{16}O + ^{12}C^{16}O$ (3 : 2) were adsorbed over ZSM-5 zeolites at ambient temperature

v on ^{12}CO adsorption/cm^{-1}	$^{13}C^{16}O$	
	v/cm^{-1}	$v(^{13}CO)/v(^{12}CO)$
2328.0	2263	0.9720
2342.0	2276	0.9718
2356.5	2290	0.9718
2370.0	2303	0.9717
2381.0	2314	0.9718

Effect of CO adsorption on hydroxy group bands

The frequency of the hydroxy group bands, in the case of both NaZSM-5 and HZSM-5 zeolites remained unchanged on CO adsorption under the experimental conditions of this study. In order to get better resolved vibrational bands in this region, a NaZSM-5 sample was deuteroxylated by heating it repeatedly *in situ* under D_2 atmosphere at 575 K. The effect of CO adsorption on the O—D stretching bands of a DZSM-5 sample is shown in Fig. 13. As mentioned above, no shift in any of the O—D stretching bands is noticeable in this figure. The absorbance values of the deuteroxyl bands reduced only marginally after CO adsorption [Fig. 13(b)], suggesting thereby no significant contribution of OH/OD bands in the development of $v_3(CO)_2$ bands reported in this study.

Adsorption of CO over alumina and silica

The vibrational bands with maxima at around 2170 and 2120 cm^{-1}, similar to the PR branches of gas phase CO, were observed on exposure at ambient temperature of 100 Torr CO on γ-alumina and silica samples, both pretreated for 24 h at 600 K under vacuum. Subtraction of vibrational bands due to gas phase CO from the spectra obtained for CO exposure over γ-alumina or silica gave rise to no detectable vibrational bands, indicating that no CO was adsorbed on these samples under the temperature and pressure conditions of this study.
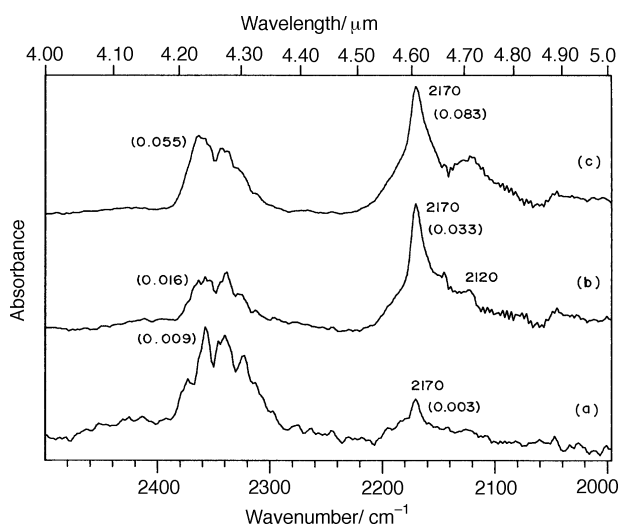

Fig. 11 IR bands developed on HZSM-5 zeolite after exposure at ambient temperature to different pressures of CO. (a) 20, (b) 100 and (c) 500 Torr.
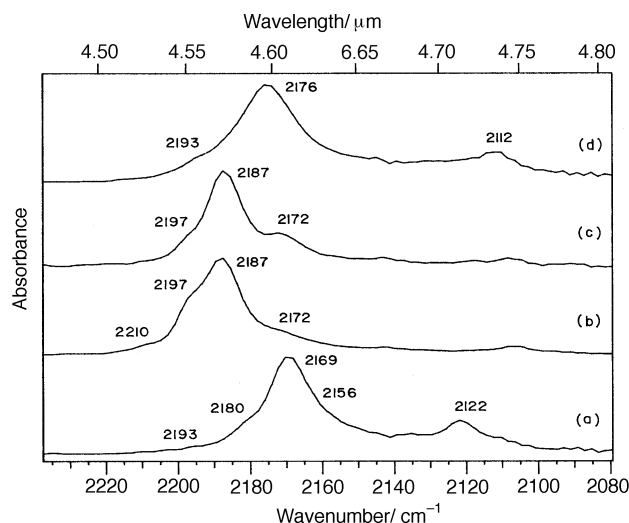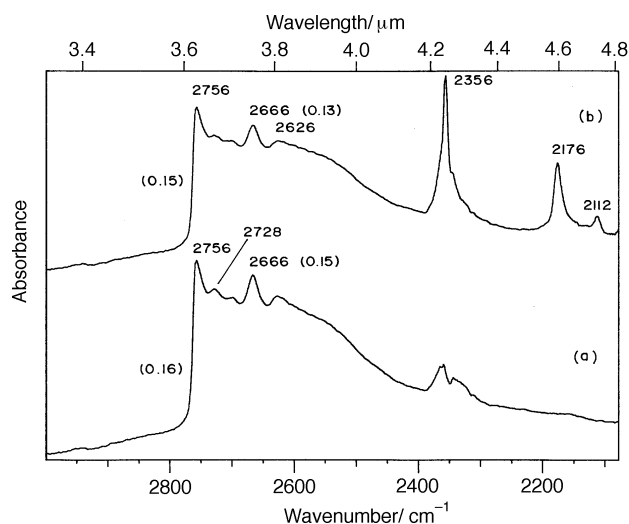

Fig. 13 FTIR spectra of a deuteroxylated NaZSM-5 zeolite before (a) and after (b) exposure to 100 Torr CO at ambient temperature.

Discussion

A number of studies have been devoted to the investigation of CO binding states on materials such as zeolites, alumina and silica *etc.*, though most of these studies were confined to measurements at low temperatures and low pressures. Also, contradictory assignments have been suggested for the observed $v(CO)$ bands, as is evident from the following brief summary of some of the previous studies concerning CO adsorption on ZSM-5 zeolites: (1) Bordiga *et al.*[5,7] observed two intense C—O stretching absorption bands at 2178 and 2138 cm^{-1} on adsorption of CO over NaZSM-5 at 77 K. The 2178 cm^{-1} band which could be resolved into two component bands centered at 2178 and 2170 cm^{-1} was assigned to CO molecules polarized by Na$^+$ ions in different environments.

(2) Out of the three strong bands at 2173, 2162 and 2138 cm^{-1} observed by Chen *et al.*[6] for CO adsorbed at 173 K on HZSM-5 zeolite, the band at 2162 cm^{-1} was attributed to interaction of CO with hydroxy groups, the 2173 cm^{-1} band was assigned to CO that interacted with the co-ordinatively unsaturated surface aluminium or silicon cations and the 2138 cm^{-1} band was associated with the weakly adsorbed or condensed CO on the surface or in the zeolite channels.

(3) Kustov *et al.*[2] reported a single intense IR band at 2172 cm^{-1} in the adsorption of CO over NaZSM-5 at 77 K which is attributed to interaction of CO with the Na$^+$ cations. However, CO adsorption over HZSM-5 under similar conditions gave rise to vibrational bands at 2138, 2175, 2195, 2222 and 2232 cm^{-1}. While the 2138 cm^{-1} band is ascribed to the physically adsorbed CO, the 2175 cm^{-1} band is attributed in this study to CO complexes with framework hydroxy groups as the intensity of this band decreased sharply after dehydroxylation of samples at temperatures above 870 K. The bands at 2232, 2222 and 2195 cm^{-1} are assigned to CO adsorbed on non-skeletal aluminium species. In addition, the OH band frequency was found to decrease by 310–320 cm^{-1} compared with that of free hydroxy groups and it was attributed to the formation of hydrogen bonded CO complexes with framework OH groups. CO adsorption induced red shift of the O—H frequency has also been reported by other research groups[8,9,17] and the extent of this shift is known to depend upon the nature of the hydroxy groups.

(4) Katoh *et al.*[18] reported the presence of three vibrational bands at around 2120, 2143 and 2170 cm^{-1} on CO adsorption over ZSM-5 zeolite at 226 K and the relative intensity of these bands depended upon the nature of the charge balancing alkali metal cation. These bands were assigned to the oriented species held on a cation, such as M$^+$—C—O and M$^+$—O—C, and the loosely adsorbed CO in ZSM-5 pores.

(5) Bands in the C—O stretching region have also been reported for CO adsorption at low temperatures over alumina and silica samples.[19–25] Thus, Zecchina *et al.*[19] reported the formation of four vibrational bands in the 2130–2240 cm^{-1} region on adsorption at 77 K of CO over an active alumina sample. The most intense band appearing at around 2190 cm^{-1} is assigned to CO molecules σ-bonded to bulk tetrahedral Al^{3+} ions generated on dehydroxylation of γ-Al$_2$O$_3$ surface and a weaker band observed at 2165 cm^{-1} is attributed to CO σ-bonded to octahedral Al^{3+} ions emerging on the surface. CO is similarly found to adsorb onto SiO$_2$ surfaces[24] where a band giving rise to $v_{CO} = 2158$ cm^{-1} is assigned to CO bound by hydrogen bonding to the SiOH$^{\delta+}$ groups to form a surface complex SiOH$^{\delta+}$—CO. The second mode of CO bonding gave rise to $v_{CO} = 2140$ cm^{-1} due to physisorbed CO species.

The possible assignments described above for low temperature adsorption of CO are not compatible to the data of the present study performed at higher temperatures, as becomes evident from the arguments detailed below.

(1) Though the σ-bonding with Lewis acid sites is known to

give rise to $v(CO)$ bands in the interval 2130–2240 cm^{-1} during the low temperature adsorption of CO over alumina,[6] these bands are found to be very weak for adsorption at room temperature or above.[22] This is consistent with the results of the present study and indeed we observed no measurable vibrational bands due to CO adsorption on γ-alumina at beam temperature. Furthermore, the intensity of the $v(CO)$ bands decreased drastically on exchanging Na$^+$ with protons (Fig. 11), when the number of aluminium sites remained almost unchanged. We may thus infer that the $v(CO)$ bands in Fig. 1, 2 and 8 may not arise from CO bonding with framework Al^{3+} sites.

(2) While discussion on the individual $v(O—D)$ bands is outside the scope of this study, on the basis of the fact that no shift is observed in the frequency of the $v(OD)$ bands after CO exposure (Fig. 13) we can rule out the possibility of CO bonding with the silanol or the bridge bonded hydroxy groups of ZSM-5 at room temperature or above. Very weak CO bands observed on HZSM-5 zeolite (Fig. 11), in spite of its higher acid strength than that of NaZSM-5, tend to support this inference.

(3) A progressive increase in the intensity of six distinct $v(CO)$ bands as a function of increasing adsorbate pressure and also its reversal with reducing pressure (Fig. 3–6) is expected only from some species of a gaseous nature, held weakly in zeolitic pores, and not from the CO molecules bonded strongly at specific zeolitic sites existing in limited numbers. The growth behavior of $v(CO)$ bands shown in Fig. 6 follows a trend similar to that reported by Rabo *et al.*[26] for the adsorption of CO in cation-exchanged Y-zeolites where the pressure-dependent variation of the intensites of $v(CO)$ bands is found to follow a Langmuir type equation implying the adsorption on non-interacting or only weakly interacting sites. This is in agreement with our inference.

(4) We now consider the possibility of CO bonding to charge balancing cations at different sites of ZSM-5. As is well known, the ZSM-5 zeolite has a three dimensional pore system consisting of two intersecting sets of tubular channels (*ca.* 0.55 nm in diameter) defined by ten membered rings of SiO$_4$ and AlO$_4$ tetrahedra. There are twelve crystallographically distinct 'T' sites in ZSM-5 zeolite which can be occupied by Si or Al. Energy minimization calculations by Catlow *et al.*[27] have shown that the energy of substitution of Al in place of Si in all these 12 crystallographic sites falls within a small energy range. Hence a random distribution of Al is predicted and therefore the charge compensating cation can occupy any of the 4 oxygen sites surrounding the Al. Thus, 48 possible cation sites exist in the pores of ZSM-5 zeolite, although their unequivocal occupancy has not been reported yet. However, it can be assumed that the extraframework cations are randomly distributed and are energetically indistinguishable *i.e.*, the binding energy of the extraframework cations with the zeolite framework is almost identical. We can thus arrive at a conclusion that the $v(CO)$ vibrational bands spread in a frequency interval of *ca.* 80 cm^{-1} [Fig. 2(a)] cannot have their origin in the bonding of CO molecules at the charge balancing cations of same mass but at different sites. Further evidence for this conclusion comes from an observation that no shift was detected in the frequency of $v(CO)$ bands for adsorption of CO over calcium exchanged ZSM-5 sample in contrast to the shifts observed in the case of a CaY or CaX zeolites under identical test conditions (Fig. 12). On the other hand, an identical behaviour is observed for the isostructural faujasite zeolites X and Y [Fig. 12(b) and (c)]. This clearly shows that the $v(CO)$ bands reported in this study are not cation specific but the pore structure plays a vital role in the mode of CO adsorption in zeolites.

(5) The possibility of a CO molecule bonded simultaneously at two different zeolite sites *via* its carbon and oxygen ends can also be ruled out since the expected isotopic shift in that

case will be different from that of gaseous CO, as observed in this study.

(6) The width of the different component bands at half maximum varied from 15–20 cm^{-1} (Fig. 1 and 2) as compared to a corresponding observed width of ~ 55 cm^{-1} for the P and R branches in the vibrational bands of gaseous CO at 100 Torr. Also, the rotationless structure as seen in Fig. 1(b) and Fig. 3, 4, and 8 clearly shows that these bands arise from the CO molecules entrapped under the ovarian conditions and not from the free CO gas molecules.

In the light of the points made above we may thus infer that the nature of CO bonding on zeolite surface at a temperature of 300 K or above is quite different than the modes reported in the literature for the lower temperature experiments. We may also conclude that the multiple C—O stretching bands shown in Fig. 1 and 2 may arise from some kind of adsorbate–adsorbate interaction rather than due to strong and direct binding of CO molecules at various possible zeolitic sites. A viable explanation for our observations may come from the formation of molecular clusters of CO, e.g. dimers, trimers etc. inside the zeolitic cages. This is in line with the conclusions reached in our earlier studies[10,11] where we demonstrated that CO was trapped in the form of $(CO)_n$ molecular clusters in the cages of X and Y zeolites, where they were stabilized under a cationic field.

As all the C—O stretching bands were removed quickly on pumping at room temperature and were not observed during high temperature exposure (Fig. 8), we reiterate that the CO molecules in the clusters mentioned above are held by dipole–dipole type weak forces. The mutual interaction of individual monomer components in these clusters will result in the multiple modes of vibrations and hence in the multiple IR absorption bands. Thus a dimer of CO molecules i.e. $(CO)_2$ may have the following two vibrational modes.

A dimer of carbon monoxide may thus give rise to two vibrational bands of different intensities, the band due to the antisymmetric (b_1) mode being more intense in the infrared. The splitting is caused by the weak interaction of the two identical frequencies of two monomer components. In the case of the adsorption of isotopic mixture (e.g., $^{13}CO + {}^{12}CO$), one in principle expects the appearance of three IR bands for each band of the dimer of a single isotopic system due to the existence of three possible species, i.e., $(^{12}CO)_2$, $(^{12}CO–^{13}CO)$ and $(^{13}CO)_2$. For a $^{12}CO + {}^{13}CO$ (1 : 1) mixture these species will exist in the proportions 1 : 2 : 1. But in the condensed phase spectra or spectra of adsorbed species, as in the present case where the bands are quite broad (15–20 cm^{-1}) and rotational structure is absent, observation of separate bands for mixed isotopic species is almost impossible. The situation is analogous to the symmetric and anti-symmetric stretches in the isotopic mixture of liquid water (i.e., $H_2O + D_2O$) where HDO bands always overlap the bands of the other two isotopic molecules and instead of the theoretically possible 6 bands we observe only 2 bands in a 1 : 1 mixture. In the present study, for a pair of antisymmetric (strong) and symmetric (weak) stretching bands in the 2200–2100 cm^{-1} region for a dimer of ^{12}CO (Scheme 1), we observe a corresponding pair of bands due to ^{13}CO in an isotopic mixture (Fig. 9). Obviously, the two bands of the $^{12}CO–^{13}CO$ dimer overlap with the bands of $(^{12}CO)_2$ and $(^{13}CO)_2$ and we therefore observe only four bands instead of the expected six in Fig. 9. An unambiguous assignment of the symmetric and assymmetric stretches of a dimer to the individual IR bands observed in our study is however not possible at present.

A trimer cluster of CO molecules is shown in Scheme 2. Being of C_{3v} symmetry, a trimer will similarly give rise to two IR bands, one due to a_1 (symmetric) and one due to e (doubly degenerate) modes of vibrations.

If the cluster size becomes too large, we may observe only a single vibrational band similar to liquid like systems.
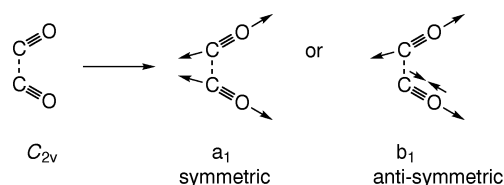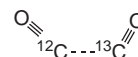

Scheme 1   Two possible modes of a dimer cluster of CO molecule
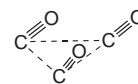
Scheme 2   A trimer of carbon monoxide

If the formation of clusters involves weak van der Waals' type bonding between monomers, the isotopic shifts may not be affected very much. Thus, in a mixed dimer, i.e.

each C≡O group will show its own shifted (or unshifted) band. Therefore, the changes in isotopic shifts due to coupling will be negligible, which is in agreement with the data given in Fig. 9.

The concept of molecular cluster formation is in harmony with the pressure effect data in Fig. 3–7 also. The referee has pointed out that the observed pressure dependencies are typical of CO adsorption on many cationic sites (Cr^{3+}, Al^{3+}, Ti^{4+}, Zr^{4+}, Ni^{2+} etc.). We may, however, mention again that adsorption of CO at energetically equivalent cation sites in NaZSM-5 or at impurity sites, such as Fe, may not give rise to multiple IR bands exhibiting pressure dependent growth behaviour shown in Fig. 6 and 7. Also the difference in adsorption behaviour as seen in Fig. 3, 11 and 12 for cation exchanged samples cannot be attributed to the presence of a metallic impurity since all the samples were of similar chemical purity. On the other hand, an initial near-linear and then asymptotic increase in the intensity of v(CO) bands in Fig. 6 may be well explained by the growth to different saturation concentration of individual CO clusters. Also, since a cluster is expected to show an intense and a weak band, as explained above, their intensities may also change differently as a function of pressure. The reducing fractional coverage under some of the IR bands (e.g. 2175 and 2146 cm^{-1} bands) as seen in Fig. 7 may thus be explained by the reduced concentration of some of the species (for example, a monomer or dimer) with the increase in CO pressure while the number of higher clusters (for example, a trimer) may increase, representing for example the behavior of IR bands at 2160 and 2190 cm^{-1}. The growth or decay of an individual molecular cluster will further be influenced by the zeolitic pore structure and also the electrostatic field associated with the cation, thus giving rise to a complex pressure dependent behaviour.

Data in Fig. 11 show that the intensity of the v(CO) bands in the case of HZSM-5 zeolite is about 20–30% of their intensity observed for NaZSM-5 under identical pressure conditions (Fig. 3). This is commensurate with the amount of residual Na^+ cations in HZSM-5 zeolite. Similar studies carried out with Y-zeolites[11,16] have demonstrated a strong correlation between the electrostatic field of the charge balancing cation and the relative intensity of the individual bands. This therefore supports our inference that the field associated with a balancing cation plays an important role in the formation and stabilization of the CO molecular clusters described above.

Data in Fig. 1 and 2 show that part of the adsorbed carbon monoxide is oxidised to CO_2 which gives rise to a prominent band at 2356 cm^{-1} along with four additional weak sidebands as shown in Fig. 2(b). Five vibrational bands with fre-

quencies at 2374, 2350, 2403, 2305 and 2290 cm^{-1} have been reported in the adsorption of CO_2 over X-type zeolites and the frequency and the relative intensity of these bands were found to depend upon the nature of the charge balancing cation and the pressure of the adsorbate.[28] These bands have been attributed to the linear species of carbon dioxide held in zeolite cages by an ion–dipole interaction.[28] However, as in the case of νCO bands, a uniform shift of 66 cm^{-1} is observed in the $\nu_3(CO_2)$ bands in our study (Table 2) which is similar to the isotopic shift expected for CO_2 gas molecules on ^{13}C substitution.[29] The spectra in Fig. 9(c) and 10(c) reveal that the ^{18}O shift in the CO_2 region is much smaller than the ^{13}C shift (Table 2). This can be accounted for by formation of only isotopically asymmetric CO_2; i.e. $^{16}OC^{18}O$ and not a symmetric $^{18}OC^{18}O$ species, irrespective of the extent of ^{18}O enrichment in adsorbed CO. The observed frequency shift of 16–17 cm^{-1} in vibrational bands of Fig. 9(c) is commensurate with the IR data reported for $C^{16}O^{18}O$ molecules.[30] The isotopic shifts thus lead to the conclusion that the CO_2 formation results from the CO interacting through C atoms to lattice oxygen sites. Other possible modes of CO_2 formation could be the reaction of CO with the zeolitic hydroxy groups and the reaction/disproportionation at the impurity sites. It is, however, of interest to note that no such $\nu_3(CO_2)$ bands were observed in our study on CO adsorption over HZSM-5 where very weak bands were formed in the C—O stretching region also (Fig. 11), thus indicating the negligible role of hydroxy groups. This is in agreement with the data of Fig. 13. The disproportionation route may also be ruled out, particularly in the case of data obtained at room temperature (Fig. 1 and 3). First, because it is known to be an activated process occurring only at elevated temperatures and secondly for CO disproportionation one should expect the formation of $C^{18}O_2$ in the data of Fig. 10(c) and not that of $C^{16}O^{18}O$. We may thus arrive at the conclusion that the polarised $(CO)_n$ species, formed only under cationic field, are more reactive than the CO molecules and are oxidised easily on interaction with the lattice oxygen.

Though an unequivocal assignment to the multiple vibrational bands observed in the asymmetric stretch region of CO_2 is difficult at this stage, the behaviour of these bands on evacuation, on rise in adsorbate pressure (Fig. 3) and on the isotopic substitutions (Fig. 10) provide ample evidence to suggest that they originate from certain species of a gaseous nature rather than from the CO_2 molecules bonded strongly at different zeolitic framework sites. In analogy with the arguments given above in favour of the existence of $(CO)_n$ clusters, we may attribute the $\nu_3 CO_2$ bands [Fig. 2(b)] to $(CO_2)_2$ type molecular clusters.

Our conclusions find support in the small angle neutron scattering studies of Renouprez et al.,[31,32] who demonstrated the existence of benzene clusters in zeolitic cages, the nature of which depended on the surface coverage. These benzene clusters are found to be bonded to sodium ions in super cages or held by van der Waals' forces in the circular windows linking neighbouring supercages. Computer simulation studies by Klein and coworkers[33,34] have similarly suggested that small molecular clusters, like that of methane, may form in the proximity of cations and at window sites in faujasite zeolites. It may also be mentioned here that the formation and the entrapment of the large noble metal based carbonyl clusters in the zeolitic cages has been demonstrated widely.[35−37]

Acknowledgements

References

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