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FT-IR study of the adsorption of carbon monoxide and of some nitriles on Na-faujasites: Additional insight on the formation of complex interactions

Pawel Kozyra[a,b], Isabel Salla[a,c], Tania Montanari[a], Jerzy Datka[b,1], Pilar Salagre[c,2], Guido Busca[a,*]

[a] DICheP, Università di Genova, P.le J.F. Kennedy 1, I-16129, Genova, Italy
[b] Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060, Kraków, Poland
[c] Dept. de Química Física I Inorgànica, Marcel·lí Domingo s/n, 43007, Tarragona, Spain

Abstract

The low temperature adsorption of CO and the room temperature adsorption of propionitrile (PrN), isobutyronitrile (IBN) and pivalonitrile (2,2-dimethyl-propionitrile, PN) have been investigated on NaX (Si/Al atomic ratio = 1.3) and NaY (Si/Al atomic ratio = 2.4) zeolites by FT-IR spectroscopy. The bands of CO adsorbed on NaY have been reassigned. The relevance of Na^+ ions at S_{III} or $S_{III'}$ positions also on NaY has been emphasized. Evidence is provided for the formation of complex interactions where nitrile molecules interact with more than one site, likely more than one Na ion, as previously observed on alkali metal containing MOR zeolites. The possible relevance of this interaction is briefly discussed.

Keywords: Na-faujasite; Low-temperature adsorption; Sodium site; Carbon monoxide; Nitriles

1. Introduction

Sodium-faujasites, in the form of either NaX or NaY, and other alkali-metal exchanged faujasites are widely applied in the industry [1] as selective adsorbants for gas mixture separation and gas purification, and as catalyst supports and catalyst components [2] as well.

Either in the form of powder packed beds or of membranes, alkali metal zeolites may allow the drying of air [3], the separation of air components (N_2/O_2) by pressure/vacuum swing adsorption procedures [4], the separation of CO_2 from different gaseous streams [5], the alkene/alkane [6], the benzene/cyclohexane [7] and the xylene isomers separations [8].

The faujasite structure is formed by quite wide supercages accessed through 12-membered silicate rings with 0.74 nm diameter, much smaller sodalite cages accessed through 6-membered silicate rings and hexagonal prisms connecting the sodalite cages. Cations are located in different positions in the cavities depending on hydration–dehydration states or upon adsorption of different molecules [9,10]. The medium Lewis acidity of the alkali and alkali earth cations, increased by the loss of ligands in dry zeolites, is the key feature for the use of these materials as regenerable adsorbants. According to Davis [11], that recently reviewed the perspectives of their use as catalysts, alkali-exchanged zeolites are considered to be solid base catalysts but their active sites should be envisioned as a combination of a Lewis acid and a Lewis base sites.

The low temperature adsorption of CO is today, perhaps, the most popular technique for Lewis acidity characterization but is also used for characterizing Brønsted sites of protonic zeolites by applying the H-bonding method [12–15]. The position of νCO of adsorbed CO is shifted upwards on Lewis acidic d_0 cations and on protonic sites as the result of a σ-type donation of the lone pair at the carbon atom, or of a simple polarization of the molecule. However, it has been shown that also the O atom lone pair can be involved in a very weak O-bond interaction, which shifts down the CO stretching frequency [16]. CO as a

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* Corresponding author. Tel.: +39 010 353 6024; fax: +39 010 353 6028.
E-mail addresses: datka@chemia.uj.edu.pl (J. Datka), salagre@quimica.urv.es (P. Salagre), Guido.Busca@unige.it (G. Busca).
[1] Tel.:+48 12 633 637; fax: +48 12 633 0515.
[2] Tel.:+34 977559571; fax: +34 977559563.

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probe actually allows a very detailed analysis of the surface sites as they appear at low temperature without strong perturbations of the surface, having also free access to even very small cavities and avoiding steric hindrances. This is a good opportunity to evaluate ‘‘pure acidity’’ [17] but, at the same time, it is a drawback, because it does not provide information on the location of the sites in or out the different cavities of microporous materials. On the contrary, the use of sets of differently hindered nitriles may allow to discriminate between adsorption sites located in differently hindered sites or at the external surface in protonic [18,19] and cationic zeolites [20].

The interaction of basic molecules with the active sites in zeolites is generally modeled as being due to ‘‘one site–one molecule’’ interactions, or sometimes as ‘‘one site–two molecules’’ interactions. In the case of the adsorption of diatomic molecules on cationic zeolites, such as CO [21] and N_2 [22,23] but also concerning the adsorption of nitriles, end-on σ-bonding interactions only are usually considered. In contrast, for olefins such as butenes [24,25] and pentenes [26] side-on π-bonding is very likely to occur.

Low temperature CO adsorption and hindered nitriles adsorption have been used recently to reexamine the adsorption sites of Na-mordenite [27], and of other alkali-metal mordenites [28] and in these cases the formation of strongly adsorbed species interacting with more than one cation, possibly with a π-bonding additional to usual σ-bonding, or with a cation and an oxide ion has been proposed. The existence of complex interactions involving both cations and oxide species has also been proposed for ammonia adsorption on alkali-metal faujasites [29].

Low temperature [30–35] and room temperature [36] IR studies of CO adsorption on alkali-metal faujasites have been published. In this paper we report on our re-examination of the CO-NaFAU system and on a new study on the adsorption of hindered nitriles on NaX and NaY samples, in order to check if interactions similar to those observed on NaMOR are detectable on these systems.

2. Experimental

Zeolite NaY (Si/Al = 2.56) has been synthesized in the Institute of Industrial Chemistry of the Warsaw University while NaX zeolite (Si/Al = 1.31) has been synthesized in the Institute of Chemical Technology of the Jagellonian University in Krakow. The structures have been confirmed by the analysis of the XRD patterns and of the skeletal IR spectrum. CO cylinders were purchased from SIAD while the nitriles, propionitrile (PrN), isobutyronitrile (IBN), pivalonitrile (PN), were pure products purchased from Aldrich.

Self-supporting pressed disks of pure zeolite powders were activated ‘‘in situ’’ in the IR cell by outgassing at 723 K before the adsorption experiments. A conventional gas manipulation/outgassing ramp was connected to a IR cell which allowed cooling by liquid nitrogen in an external jacket.

The adsorption/desorption process has been studied by transmission FT-IR. For nitriles, the adsorption procedure involves contact of the activated sample disk with vapors at room temperature at a pressure not higher than 2.5 kPa. The desorption process at increasing temperatures in the range 273–573 K was performed in dynamic vacuum. CO adsorption was performed at 130 K (real sample temperature measured by a thermocouple) by the introduction of a known dose of CO gas. IR spectra were collected evacuating at increasing temperatures between 130 and 273 K.

3. Results

3.1. Low temperature CO adsorption on NaX and NaY

The overall spectrum of the activated NaX sample shows, in the OH stretching region, a weak sharp band at 3684 cm^{-1} that does not correspond to the OH stretching of the bridging hydroxy groups of NaHX zeolite [37]. This weak feature, observed frequently on NaX samples [26], is likely associated to traces of residual water molecules [38]. In the case of the NaY, the spectrum shows a sharp band at 3739 cm^{-1}. This band can be assigned to the OH stretching of terminal silanol Si–OH groups located at the external crystal surface or in structural defects. In both cases no evidence is found for bridging OHs (typically found in the range of 3650–3550 cm^{-1} in proton-containing faujasites) showing that cation exchange is complete.

Fig. 1 shows the IR bands of CO adsorbed at low temperature on NaX zeolite. At temperatures lower than 163 K, mainly one asymmetric and very intense (maximum out of scale) band is observed in the CO stretching range. With outgassing at increasing temperatures, the intensity of this band diminishes the main maximum being found at 2165 cm^{-1} with a second pronounced component at 2176 cm^{-1}. Additionally, other two bands with very weak intensity, located at 2138 and 2115 cm^{-1} are present. By progressively increasing temperature upon outgassing, the main band, together with its shoulder (that at low surface coverage shifts up to 2182 cm^{-1}) parallelly decrease their intensity, while the two lower frequency components disappear even earlier.

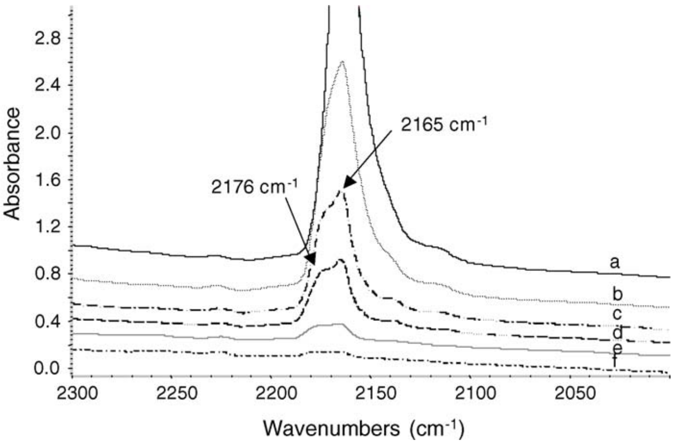

Fig. 1. FT-IR spectra of activated NaX in the presence of CO gas under evacuation at 163 K (a), 173 K (b), 183 K (c), 193 K (d), 203 K (e), and 213 K (f) in the CO stretching range.

Our spectra look very similar to those reported by Martra et al. [35] whereas they seem distinctly different from that reported by Hüber and Knözinger [33] on a NaX sample at 88 K and at 0.1 hPa CO pressure. As it is well known, four predominant locations have been found for Na^+ ions in the faujasite structure. The S_I and $S_{I'}$ sites, that are, respectively, in the center of the hexagonal prisms and near the 6-membered mouth in the interior of the sodalite cages, are considered to be not accessible to CO. The S_{II} and S_{III} sites are, respectively, near the walls of the supercage, at the center of 6-membered and 4-membered mouths. Martra et al. [35] assigned the main band they found at 2164–2167 cm^{-1} to CO C-bonded to S_{II} site cations, whereas the shoulder they report at 2175–2177 cm^{-1} was assigned to CO C-bonded to S_{III} site cations. In contrast, Hüber and Knözinger [33] assigned the most intense band, found at 2166 cm^{-1}, to CO C-bonded to S_{III} site cations, with a shoulder at 2157 cm^{-1} assigned to CO C-bonded to S_{II} site cations.

The band at 2139 cm^{-1} disappears completely quite fast in vacuum and therefore it can be attributed with confidence to pseudo-liquid (physisorbed) CO inside the zeolite pores. The band at 2115 cm^{-1} can be attributed to O-bonded CO species ($Na^+\cdots OC$) although, as noted by Martra et al. [35], C-bonded ^{13}CO and a component of sodium-dicarbonyl species may contribute to it.

The spectra of the IR bands of adsorbed CO on NaY zeolite are shown in Fig. 2. We observe an intense and asymmetric band with the main maximum at 2172 cm^{-1} and a weak band at 2123 cm^{-1}. Only by expanding the weak spectra recorded after outgassing at 193 and 203 K (see Fig. 2, inset) two additional components in the main peak become evident, one at higher frequency, the other at lower frequency with respect to the main maximum, namely at 2182 and near 2155 cm^{-1}. Hüber and Knözinger [33] found a similar spectrum with four components and attributed them to CO C-bonded on S_{II} sites near 6-membered ring having one, two (meta), two (para) and three Al ions. The approach of Hüber and Knözinger [33], which is also based on the Na and Al distribution between the different sites as deduced from NMR and XRD data, seems questionable to us, because of the exceeding intensity of the band at 2172 cm^{-1}. In fact, as it is well evident in the spectrum observed at saturation, the band at 2172 cm^{-1} is by far the most intense, the other being only observable at very low CO coverage. This band is attributed to CO C-bonded to Na ions on S_{II} sites near two Al-containing 6-membered rings, but this species should not be so more likely than the others. Also in this case, the band at 2121 cm^{-1} can be attributed to very weakly bonded CO possibly as $Na^+\cdots OC$.

As a conclusion, neither on NaX nor on NaY we can find low frequency but strongly adsorbed CO species. We could conclude that multiply-bonded CO species like those observed on alkali mordenites cannot be formed on NaFAU possibly because of the larger dimension of the supercages of the FAU structure which prevents the ‘‘multiple’’ sites to be near enough to establish this interaction.

3.2. Adsorption of propionitrile on NaX and NaY

Propionitrile (PrN) adsorption can be used for characterizing adsorbing sites in zeolites. Such molecule do not have relevant steric hindrance and can interact with all adsorption sites in the case of mordenite samples [19,20,27].

The spectra of PrN adsorbed on NaX and NaY samples, and after outgassing at different temperatures, are shown in Figs. 3 and 4, respectively. The nitrile spectrum in CCl_4 solution, used as a reference, is also shown. From the subtracted spectra of PrN adsorbed on NaX after evacuation at room temperature (Fig. 3b) a broad band is observed at 2250 cm^{-1} in the CN stretching region. By heating at 373 K under vacuum, this band starts to resolve into two with maxima at 2256 and 2246 cm^{-1}. Finally, after the desorption process at 423 and 473 K (Fig. 3d and e), two bands are observed with the maxima at 2262 and 2228 cm^{-1}. The main band at the lowest coverages is found at wavenumbers similar to that found on NaMOR [27], but it is

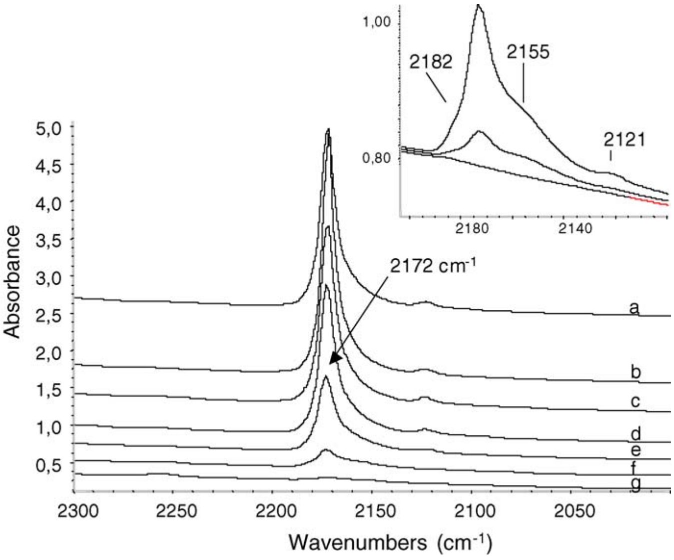

Fig. 2. FT-IR spectra of activated NaY in the presence of CO gas under evacuation at 133 K (a), 143 K (b), 153 K (c), 163 K (d), 173 K (e), 193 K (f), and 203 K (g) in the CO stretching range.

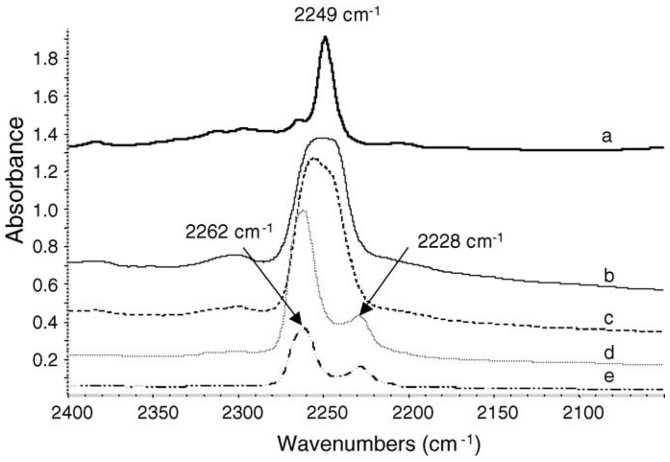

Fig. 3. FT-IR spectra of PrN in CCl_4 solution (a), NaX in the presence of PrN vapors after evacuation at room temperature (b), at 373 K (c), 423 K (d), and 473 K (e).

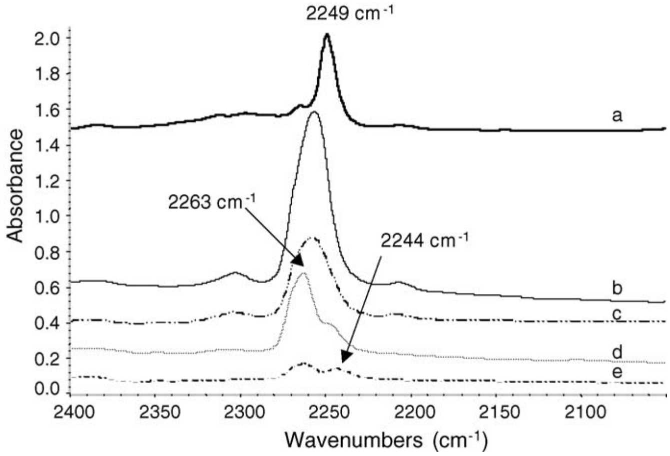

Fig. 4. FT-IR spectra of PrN in CCl_4 solution (a), NaY in the presence of PrN vapors after evacuation at room temperature (b), at 373 K (c), 423 K (d), and 473 K (e).

indicative of the PrN interaction with Na ions through the N lone pair. The lower frequency band, instead, is at a definitely lower wavenumber with respect to that found on NaMOR [27], and assigned to a ‘‘multiply bonded’’ species.

A more detailed analysis of the CN stretching region can be made by analyzing the spectra obtained by subtracting from the band obtained in every step, the spectrum of the step before (Fig. 5). This shows that the main band, that shifts upwards with respect to that of the same compound in solution, actually contains at the lowest coverages at least two components (2269 and 2263 cm^{-1}). The main feature, still present after outgassing at 373 K, is still located near 2247 cm^{-1} with a fourth component near 2252 cm^{-1}. Interestingly, upon outgassing at 373 K the absorption at 2245–2253 cm^{-1} decreases in intensity while that at 2262 and 2268 cm^{-1} increases in intensity. In practice it seems clear that some propionitrile molecules displace from weaker to stronger adsorption sites, and that the two families (weaker and stronger sites, possibly due to Na^+ ions at S_{II} and S_{III} or $S_{III'}$ respectively) are both double (i.e. composed by two different species). This shift may be associated to the slight heating performed, that may allow the nitrile molecule to reach more easily quite hindered sites.

A parallel situation is found for PrN on NaY (Fig. 4). From the subtracted spectra of PrN adsorbed on NaY after evacuation at room temperature and at 373 K (Fig. 4b and c) a broad band with the main maximum at 2258 cm^{-1} is observed on the CN stretching region. By heating at 423 and 473 K under vacuum (Fig. 4d and e), also in that case a new band at lower frequencies appears. Thus two bands at 2263 and 2244 cm^{-1} are observed again. On NaY however, the lower frequency band is relatively less intense and significantly less shifted down than on NaX.

The analysis of the subtraction spectra (Fig. 5B) shows that at the lowest coverages the bands on NaY and on NaX are very similar, for both position and relative intensity. Instead, at higher coverages, the main band on NaY is at higher frequencies than on NaX (2255 cm^{-1} with respect to 2245–2253 cm^{-1}). All features are actually shifted a little bit upwards on NaY than on NaX. This parallelism supports the assignment of the two features to the nitrile adsorbed on Na^+ ions at S_{II} and S_{III} or $S_{III'}$ respectively. If this is true, the existence and activity of well-defined Na^+ sites at S_{III} or $S_{III'}$ also in the case of NaY should be confirmed.

3.3. Adsorption of isobutyronitrile and pivalonitrile on NaX and NaY

Isobutyronitrile (IBN) and pivalonitrile (PN) are more hindered nitriles, whose access to the mordenite ‘‘side pockets’’ was found to be partially forbidden [19,20,27]. They will be used here to check if hindering of the access to Na ions in faujasites can be found.

The subtracted spectra obtained for NaX sample using IBN and PN vapors as probe molecules are shown in Figs. 6 and 7, respectively.

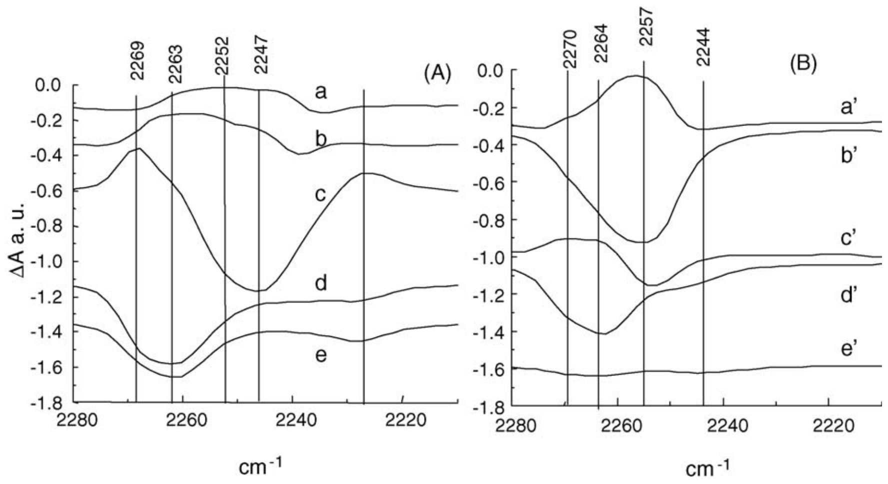

Fig. 5. Subtraction spectra relative to Fig. 3 (A left, PrN adsorbed on NaX) and to Fig. 4 (B right, PrN adsorbed on NaY). a and a′, evacuated at r.t.—in presence of the vapour; b and b′, evacuated at 373 K—evacuated at r.t.; c and c′, evacuated at 423 K—evacuated at 373 K; d and d′, evacuated at 473 K—evacuated at 423 K; e and e′, evacuated at 523 K—evacuated at 473 K.

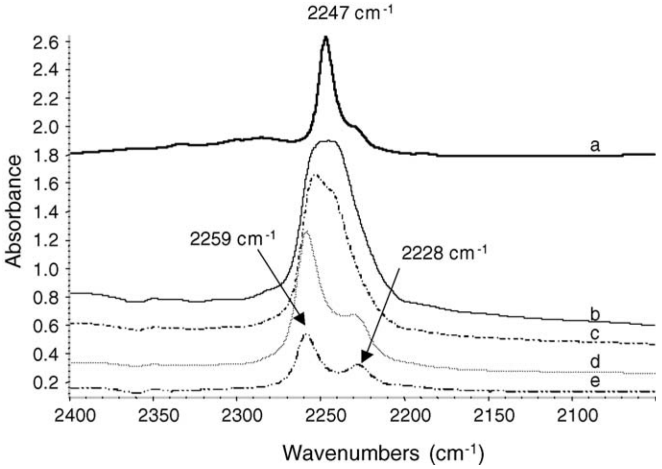

Fig. 6. FT-IR spectra of IBN in CCl_4 solution (a), NaX in the presence of IBN vapors after evacuation at room temperature (b), at 373 K (c), 423 K (d), and 473 K (e).

In the spectra of IBN adsorbed on NaX and evacuated at room temperature a broad band centered at 2247 cm^{-1} can be observed (Fig. 6b). When increasing the outgassing temperature to 373 K, this band becomes narrower with the maximum at 2253 cm^{-1} and a shoulder at 2244 cm^{-1} (Fig. 6c). By further increasing temperature the intensity of the band diminishes and two bands are observed at 2259 and 2228 cm^{-1} (Fig. 6d and e).

The behavior observed for the spectra of PN adsorbed on NaX is similar to that observed for IBN on the same zeolite.

After PN adsorption on NaX a broad band centered at 2239 cm^{-1} is observed when evacuating at room temperature (Fig. 7b). When increasing the outgassing temperature to 373 K, a shoulder at 2234 cm^{-1} starts to appear (Fig. 7c), and finally, at the desorption temperature of 473 K, the spectrum shows two bands with the maxima at 2250 and 2223 cm^{-1} (Fig. 7d). Thus, after both IBN and PN adsorption/desorption on NaX, a band at frequencies lower than the frequency of the corresponding nitrile solution spectra is observed (Figs. 6a and 7a), and these bands show a higher resistance to the desorption process.

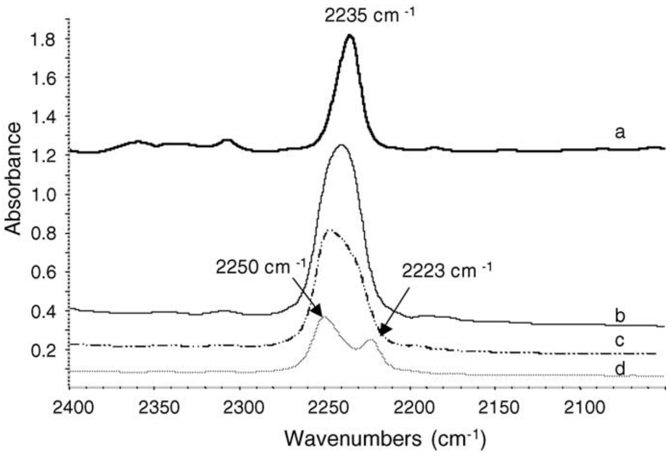

Fig. 7. FT-IR spectra of PN in CCl_4 solution (a), NaX in the presence of PN vapors after evacuation at room temperature (b), at 373 K (c), and 473 K (d).

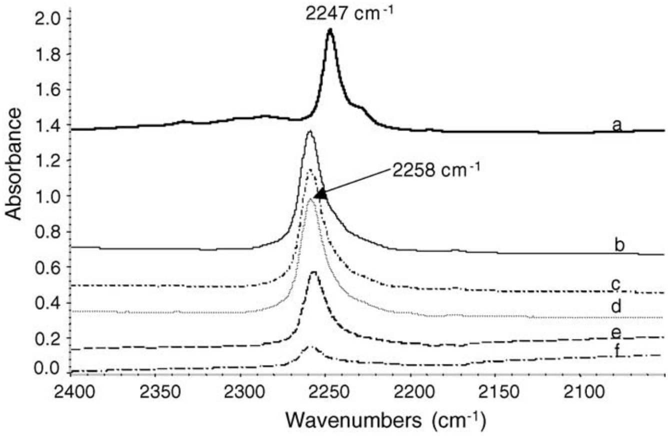

Fig. 8. FT-IR spectra of IBN in CCl_4 solution (a), NaY in the presence of IBN vapors after evacuation at room temperature (b), at 373 K (c), 423 K (d), 473 K (e), and 523 (f).

The spectra relative to the adsorption of IBN and PN on NaY are shown in Figs. 8 and 9, respectively. In both cases the spectra obtained are similar: one asymmetric band with a tail at lower frequencies is observed, well shifted above the band for the free nitrile. In the case of IBN this band is centered at 2258 cm^{-1} and in the case of PN this band is centered at 2251 cm^{-1}. These bands decrease in intensity and become narrower when temperature increases during evacuation. So, in the case of IBN and PN adsorption on NaY we have not observed the band at lower frequencies than the liquid nitrile spectrum.

An analysis of the subtraction spectra relative to the adsorption of the most hindered nitrile, PN, on NaX and NaY (Fig. 10) can give some further information on the multiplicity and distribution of Na^+ sites. It seems that this hindered nitrile gives rise to less resolved bands but the maximum shifts more continuously from near 2240 to 2250 cm^{-1} on NaX and that the position is nearly the same also on NaY.

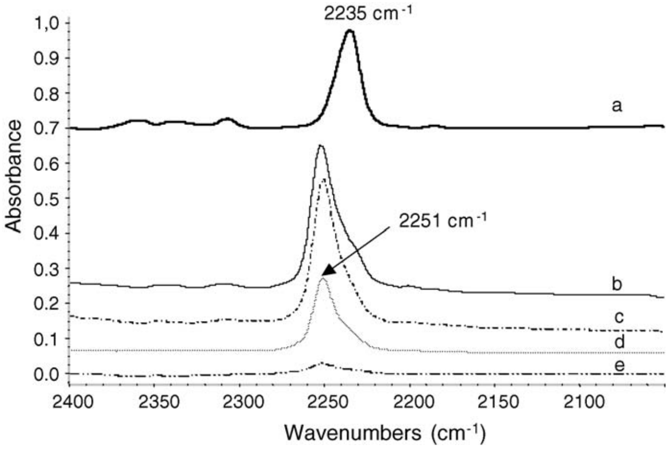

Fig. 9. FT-IR spectra of PN in CCl_4 solution (a), NaY in the presence of PN vapors after evacuation at room temperature (b), at 373 K (c), 423 K (d), and 473 K (e).

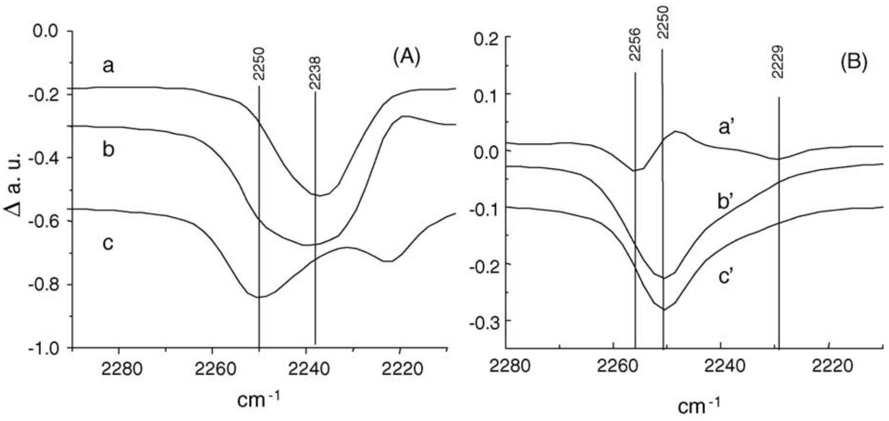

Fig. 10. Subtraction spectra relative to Fig. 7 (A left, PN adsorbed on NaX) and to Fig. 9 (B right, PN adsorbed on NaY). a and a′, evacuated at r.t.—in presence of the vapor; b and b′, evacuated at 373 K—evacuated at r.t.; c and c′, evacuated at 423 K—evacuated at 373 K.

4. Discussion

4.1. Adsorption sites and σ-bonded CO adsorbed species

The sodium distribution in anhydrous NaX and NaY has been the object of several studies [8,9,39,40]. Although other possible locations have been considered by different authors, an idealised (and slightly simplified) model for NaX faujasite with a Si/Al ratio of 1, having for the unit cell the formula $Na_{96}Si_{96}Al_{96}O_{384}$, implies a 100% occupation of the 32 so-called $S_{I'}$ sites which are located in the interior of the sodalite cage in front of the 6-membered ring window connected to the hexagonal prism, the 100% occupation of the 32 S_{II} sites which are located in the middle of the 6-membered ring window connecting the supercage and the sodalite cage, and the 66% occupation of the 48 S_{III} sites, which are a little displaced towards the interior of the supercage, near the middle of the 4-membered rings separating them from the sodalite cage [9]. Other authors [8] put 32 Na^+ ions in one-third of the $S_{III'}$ sites (instead of the S_{III} sites), located in the 12-membered ring windows of the supercage. By decreasing the Al and the sodium contents [9] (so shifting from NaX to NaY) the occupancy of sites $S_{I'}$ and S_{III} decreases while sites I (located just in the middle of the hexagonal prisms) become populated. For a Si/Al of 3 (i.e. with a formula $Na_{48}Si_{144}Al_{48}O_{384}$) sites S_I and S_{II} are fully populated, while $S_{I'}$ and S_{III} are now empty.

According to most authors, sites I and I′, which are in the interior of the sodalite cage and of the hexagonal prisms, respectively, should be inaccessible to adsorbates. So adsorption is expected to occur in the supercage only. Every supercage may contain up to eight Na ions: four cations at S_{II} and four cations at S_{III} (or $S_{III'}$) for Si/Al = 1, while only the four cations at S_{II} for Si/Al = 3. In the case of our samples, characterized by Si/Al ratios of 1.31 and 2.56, the Na cation distribution should be not very different from those considered for the ratios Si/Al = 1 and 3, respectively.

In NaX, Na^+ ions in S_{III} sites are expected to have a higher positive charge than those at S_{II}, so the Lewis acidity of cations at S_{III} is expected to be the greatest [33]. Also cations located in $S_{III'}$ sites [8], if any, should be more Lewis acidic than those in S_{II}. In agreement with this, and with previous authors, we assign the bands at 2176 and 2165 cm^{-1} observed after low temperature CO adsorption on NaX to carbonyls on Na^+ S_{III} (or $S_{III'}$) and S_{II} cations, respectively. This also agrees with the relative intensity of the observed bands: the band attributed to carbonyls on S_{III} ions is less intense at saturation than that attributed to carbonyls on S_{II}, in agreement with a S_{III}/S_{II} well lower than 1 in our sample whose composition is near $Na_{55}Si_{137}Al_{55}O_{384}$.

As for the assignment of the bands associated to CO adsorbed on NaY, the main band observed at 2172 cm^{-1} is quite easily attributed to carbonyls on Na^+ ions located in site S_{II}, which is expected to be largely predominant. The shift to higher frequency of this species on NaY with respect to NaX (for sites at S_{II}) should indicate that oxygen species in the 6-membered ring windows near S_{II} are a little less basic on NaY than on NaX, according to the lower Al content in the framework. The expansion of the spectra recorded at very low coverages allows to evidence two other components, very weak though, at 2182 and at 2155 cm^{-1}. In their previous work, Marra et al. [31] found only the main band. Hüber and Knözinger [33] and Vayssilov et al. [32] instead, found, besides the main one at 2172 cm^{-1}, three more at 2182, 2165, and 2155 cm^{-1}. They assigned those four bands to Na^+-carbonyls on four different S_{II} sites associated to different Al contents and positions. This assignment has also been given by Tsyganenko et al. [34]. This assignment seems however to be inconsistent, in our opinion, with the exceedingly stronger intensity of the component at 2172 cm^{-1} observed at saturation, with respect to the other components assigned to species having virtually a similar probability. On the other hand, the composition of our sample (which is actually the same of the sample used in [31] and [32]) that corresponds to a formula near $Na_{55}Si_{137}Al_{55}O_{384}$, is such that occupancy of site III should be still nil. So, the band at 2182 cm^{-1} is reasonably due to Na^+ carbonyls on residual S_{III} sites. Consequently, the band assigned to CO on S_{II} cations should be almost insensitive to the number of Al ions in the 6-membered rings. As for the feature observed at 2155 cm^{-1}, it seems evident that it is due to a species which is in very small amounts but that is more strongly bonded than that characterized by the band at 2172 cm^{-1}. In fact, outgassing tend to cause the disappearance of the band at 2172 cm^{-1} but leaves more evident the band at 2155 cm^{-1}. Here we found a species that appears to be less shifted upwards but more resistant to outgassing than the usual Na^+ carbonyls. This may be due either to diffusion effects (the desorption is hindered in some way) or to the existence of a different interaction. From these consideration, we can propose two different assignments for this species, either to terminal carbonyls on Na^+ ions located in the interior of the sodalite cage or in the hexagonal prisms, whose desorption could be hindered by the small dimensions of the cavity windows, or, alternatively, to multiply bonded species in the supercage. However, the lack of detection of this species on NaX (in whose supercage much more Na^+ ions are present) allows us to rule out this second possibility. It seems to us possible that a few CO molecules, whose van der Waals radius is not far from the half of the diameter of 6-membered ring windows, could find the way to enter the sodalite cavities (perhaps through defective sites) and to produce carbonyls on Na^+ located at $S_{I'}$ sites.

4.2. *"Usual" σ-bonded nitrile adsorbed species*

As shown in Table 1 and in Figs. 2–10, the adsorption of all nitriles gives rise to bands located well above the frequency of the free molecule, that may be assigned to "usual" σ-bonded nitrile adsorbed species on Na^+ ions. The analysis of the behavior of these bands allows us actually to observe several components that are certainly in relation to a remarkable heterogeneity of the available Na^+ ions. For PrN, IBN, and PN three or four different adsorbed species may be observed. The comparison allows to suggest that the bands at higher frequencies can be assigned to nitrile molecules adsorbed on the most electron withdrawing Na^+ cations located at S_{III} or $S_{III'}$ sites, while the less perturbed nitrile species should be due to the more abundant Na^+ cations located at S_{II} sites. This means that the existence and relative importance of Na^+ cations located at S_{III} or $S_{III'}$ sites should be not negligible, in agreement with the most recent data concerning the distribution of Na ions in NaY zeolite.

A rough evaluation of the amount of adsorbed nitriles on NaX and NaY shows that adsorbed species are definitely more abundant on NaX than on NaY, while that there is not much difference between the different nitriles adsorbed in the same solid. So the amount of adsorbed species depends on the amount of Na^+ ions in the supercage, while steric hindrance is not so important, due to the sufficiently large size of this cage.

4.3. *"Unusual" low frequency nitrile adsorbed species*

The data reported here may be discussed in parallel with the recently published ones concerning the adsorption of CO and several nitriles on alkali-MOR zeolites in the same conditions [27,28]. Over alkali-MOR we found in the spectral region of both, CO and CN stretchings, the unusual formation of bands at lower frequencies with respect to the free molecule but resisting outgassing more than the "usual" species characterized by the bands at higher frequencies than those of the free molecules. This behavior was interpreted assuming that these "unusual" species are involved in multiple or complex interactions, involving either more than one cation or one cation and one framework oxygen atom.

The possibility of the formation of these strongly bonded species also on NaX and NaY is determined here and, finally, this confirms that this is potentially a very relevant kind of interaction. A few papers in the literature mentioned the possibility of similar "complex" interactions with simple molecules like, e.g. acetylene [13,41]. The spectroscopic evidence of the formation of such species actually gives a quite unusual light to the chemistry of cationic zeolites, where the formation of "two sites–one molecule" adsorbate–adsorbant interaction (usually not taken into account) must be considered possibly as the more determinant one.

In [27] the low frequency–strong interaction species were supposed to be due either to interaction with more than one cation or to a complex interaction involving one cation and one basic oxygen. In the case of NaX samples with Si/Al atomic ratio = 1, every supercage, which is near a sphere with 13 Å diameter, contains eight Na^+ ions, four at S_{II} and four at S_{III} or $S_{III'}$. The data of Buttefey et al. [42] indicate that most Na ions should actually be significantly displaced from the S_{III}

Table 1
Position of the IR bands (cm^{-1}) of adsorbed nitriles and CO on NaMOR [27,28], NaY, and NaX

Adsorbed molecule	NaMOR	NaX	NaY	Free molecule
CO			2182	
	2175	2176	2172	
	2164	2165	2155	
	2138	–	–	2143 (gas)
Propionitrile	2267	2269–2263	2270–2264	
		2252–2247	2255–2253	2249
	2241	2228	2244	
Isobutyronitrile	2260	2265–2245	2265–2252	2247
	2235	2228	–	
Pivalonitrile	2253	2250–2237	2256–2250	2235
	2221	2223	–	

crystallographic position (∼1 Å), and that some of them are very much displaced until occupying the $S_{III'}$ crystallographic position.

The distance between two S_{II} sites is 7.69 Å [42], while the distance between a S_{II} and a S_{III} or $S_{III'}$ crystallographic site may be as low as 4.5–5.5 Å [43].

The possibility of forming species where interaction involves both the Na cation and the oxygen to which the same ion is also bonded, like proposed to occur with ammonia on NaX [29], seems unlikely for the much larger nitrile molecules. On the other hand, the possibility of weak interactions of the C–H bonds of nitriles with other oxygen atoms exposed in the cavity (like proposed to occur for hydrocholorocarbons in Na-faujasites [44]), should not cause a decrease in the CN stretching frequency. Taking into account that the cations may displace a little bit upon adsorption of different molecules, the possibility of the formation of adsorbed species where two different cations interact with the N lone pair and with a π-type orbital seems to be possible on NaX. The more difficult detection of such species on NaY, where we can find it for the unhindered nitrile, PrN, unlike the hindered nitriles IBN and PN, is logically due to the much lower occupancy of $S_{III'}$ and/or S_{III} sites in this case, and to the less easy accommodation of the hindered and rigid nitrile molecules PN and IBN, with respect to PrN.

Another interesting feature is that the shift down of the CN stretching frequency is definitely stronger on NaX (∼20 cm^{-1}) than on NaY and NaMOR (∼5–12 cm^{-1}) for PrN and IBN, while it is similar on NaX and NaMOR for PN (∼13 cm^{-1}). Because of the lower Al and sodium contents on NaMOR (Si/Al 6.5) and NaY than on NaX, we may conclude that the predominant Na–Na distance of the nearest cations is definitely larger on NaMOR (and NaY) than on NaX, so in the last solid this interaction may be stronger at least for the less sterically demanding nitriles.

The abundance of this ‘‘unusual’’ interaction may be measured by using the ratio (*R*) of the bands of ‘‘unusual strongly bonded species’’/‘‘usual σ-bonded species’’. This ratio is definitely larger on NaMOR when hindered nitriles are considered (like PN, or also benzonitrile and orthotoluonitrile) than when unhindered nitriles (like PrN) are taken into account, just in contrast with what happens on NaY. Consequently, it seems very likely that these interactions mostly occur in or at the mouth of the main channels in the case of NaMOR, where the most hindered nitrile should not penetrate. The above defined ratio (*R*) is definitely larger for NaMOR [27] than for NaX at least for PN and IBN, and this may be related to the larger size of the faujasite supercage windows with respect to the mordenite main channels. Thus this interaction should be limited at the pore mouths for NaMOR but should occur in the supercages for NaFAU, where the ‘‘usual’’ interactions also occur and are very abundant.

This ‘‘unusual’’ interaction is observed on NaX and NaY for nitriles but not for CO. This may be associated to the exceeding weakness of the basicity of CO with respect to that of the nitrile molecules (proton affinity 598 versus 783 kJ/mol for acetonitrile). Alternatively, it may be due to the quadrupolar nature of CO (where the oxygen is formally positively charged) with respect to the polar nature of the C≡N triple bond, which finally results in a lower availability of π-type full orbitals of CO and of its lone pair at oxygen to interact to a further Na^+ ion with respect to nitriles.

In any case, this result evidences one of the limits in the use of CO as a probe molecule for zeolite adsorption sites, as discussed elsewhere [45]. Also in this case CO, because of its weakness as a base and its very low dimension fails in giving information on effects, which are more or less cooperative and spatially demanding.

5. Conclusions

The study of CO adsorbed at low temperature and of a set of differently hindered nitriles adsorbed on NaX and NaY zeolites allows to obtain some new information on the sites available for these materials which are relevant in industrial adsorption and catalytic processes. In particular we modified the assignments given in the literature to the features of CO adsorbed on NaY zeolite.

Our data show that two types of adsorbed species are well evident: (i) simply coordinated species via a Lewis acid–base interaction and (ii) multiply bonded species.

The typical single coordination of CO through the C atom lone pair to Na^+ cations is well evident and it has been the object of several previous investigations. However, the data reported here allow to significantly modify the previous assignments for CO adsorbed on NaY. The data in fact can be satisfactorily interpreted considering the existence and the role of Na^+ cations at S_{III} or $S_{III'}$ sites (not negligible for Si/Al well lower than 3), in addition to the predominant cations at S_{II}. Nitrile adsorbed species allow us to conclude that both families of sites, at S_{II} and at S_{III} or $S_{III'}$ positions, are actually heterogeneous, possibly due to the different number of Al ions present in the neighbourhood.

O-bonded adsorbed CO species are also observed, as emphasized in previous studies. They give rise to very weakly adsorbed species that should not be very relevant in practice just because of their weakness.

On the other hand, nitrile adsorptions allows to show the formation on NaX and NaY, like previously on alkali MOR, of multiply bonded species. They are formed with nitriles, unlike CO, on NaX and NaY. One of the reasons may be the stronger basicity of nitriles, although these molecules differ for many other aspects like electronic and steric features. Although we still cannot produce a model for them, it seems to us that the ‘‘multiply bonded species’’ should primarily involve two cations, just because in the zeolite channels the more basic oxygens are actually shielded by the cations and this should hinder their direct interactions with CO and the CN bonds of nitriles. Nevertheless, additional stabilizing interactions by basic oxygen atoms on the hydrocarbon chain of nitriles, that very likely occur, should not have a determining effect on the lowering of the CN stretching frequency.

On the other hand, the evidence of the formation of this ‘‘multiply bonded species’’, that, when observed, are the most strongly adsorbed and the most resisting outgassing, tends to propose a partially new view of the chemistry of adsorption in zeolites. In fact, in previous studies one site–one molecule or one site–two molecules interactions have been mostly considered to occur and modeled in theoretical studies. In contrast, we show here that two sites–one molecule interactions may be very relevant. Adsorption on zeolites may appear as a cooperative action where the cavity plays a role not only as a host of the adsorption sites, but as a unique environment where complex adsorption phenomena may occur.

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