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Nature and reactivity of Co species in a cobalt-containing beta zeolite: an FTIR study

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Abstract

Co–Al–BEA samples have been prepared in an attempt to introduce Co at tetrahedral lattice sites. No positive evidence of insertion has been gained, and no new Brønsted acidity is developed. The sample, instead, contains at least three families of Co^{2+} surface sites, CoA, CoB and CoC. CoA ions, the dominating species, are at extraframework positions (carbonyl species at 2208 cm^{-1}; mononitrosyl at 1939 cm^{-1}: a large fraction forms dinitrosyl species). CoB and CoC are two types of Co^{2+} ions grafted to the surface in defective situations (hydroxyl nests or stacking faults) and similar to Co species grafted to amorphous silica (carbonyl species at 2196 and 2184 cm^{-1}; mononitrosyl species at 1915 and 1895 cm^{-1}, respectively, form dinitrosyl species readily). Co^{3+} is also present in small amounts only after NO contact, and is responsible for a mononitrosylic species at 1954 cm^{-1}. Dinitrosyl species for CoA, CoB and CoC share the same modes at 1815 and 1900 cm^{-1}: $Co^{3+}(NO)_2$ probably has the asymmetric mode at 1850 cm^{-1}. Interaction with ammonia of irreversibly adsorbed NO species suggests the possible occurrence of cation pairs. The availability of two coordinative unsaturations on most Co species (or the occurrence of cation pairs) allows a reversible disproportionation of NO_2, consisting in the simultaneous adsorption of two molecules with a partial electron transfer from one ligand to the other, with formation of ${NO_2}^{\delta+}$ and ${NO_2}^{\delta-}$ species: at a later stage of interaction, a proper disproportionation yielding nitrate species is observed. The presence of Co^{2+} ions at extraframework positions together with some dealumination of the samples accounts for the negligible presence of Brønsted acidity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt; Beta zeolites; FTIR spectroscopy; Adsorption

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1. Introduction

With increasing concerns over air pollution caused by nitrogen oxides, improved methods for controlling NO_x emission have been recently sought. At present, selective catalytic reduction (SCR) by ammonia is the only well-established method available for lean NO_x reduction: its use, however, is limited to large-scale facilities, and application to e.g. automotive exhaust is considered to be impractical [1]. SCR of NO_x by hydrocarbons may provide a convenient and inexpensive process for such case if unburned hydrocarbons act as reductants [2,3].

An important stage in the development of SCR reaction was the discovery by Li and Armor [4,5] that the NO_x reduction on Co-ZSM5 can be performed with methane. Under the spur of this finding, attempts have been made to prepare new Co-containing zeolites

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(or zeotypes) more and more efficient in the SCR of NO_x by hydrocarbons. Traditional ion-exchange techniques [6–8] yield active samples: e.g., Co-containing ZSM-5 samples display high catalytic activity in the conversion of hydrocarbon to light olefins [9]. The synthesis of Co-substituted zeolites and zeotypes has also been attempted [10–14], as transition-metal ions incorporated into the framework of molecular sieves, besides acting as redox centres, may lead to the modulation of Brønsted and Lewis acidic properties, as documented for Me-APOs [11,12]. Insertion of Co ions into the lattice has been claimed [10]; convincing evidence, however, has not been given, in contrast with the case of tri- and tetravalent cations in zeolites or with Co-APOs [11,15,16].

In the present contribution, we report on a Co-containing beta zeolite where Co species have been introduced during the synthesis, and consider the valence and coordinative state of the Co cations. The specimens are mainly studied by FTIR spectroscopy of adsorbed molecules, namely CO, NO and NO_2. The results are compared, on the one hand, with literature data on Co-exchanged zeolites [17–22], and, on the other hand, with similar data for silica-supported Co ions [23]. The reason is that zeolite Beta, characterised by the intergrowth of two polymorphs, shows a remarkable presence of stacking faults at which surface-like SiOH groups are found. In some cases, results concerning these related systems have been reported.

2. Experimental

Co containing beta zeolites (hereafter referred to as Co–Al–BEA) have been synthesised hydrothermally at 400 K under static conditions starting from a gel with the composition 99.9 SiO_2 (Ludox Hs-40)–1.0 Al_2O_3–4.5 Na_2O–26.2 TEA–1054 H_2O. Cobalt was added as $Co(NO_3)_2{\cdot}6H_2O$ salt. The obtained material has been characterised by XRD that shows the presence of a monophasic system with the BEA structure. The AAS measurement on the dissolved Co–Al–BEA shows a ratio Si/Al of 27 and a cobalt content of 1.4 wt.%.

Template was removed by first calcining the as-synthesised sample at 823 K under dynamic vacuum (10^{-4} Torr) for 2 h, then treating in O_2 (150 Torr) at 823 K for 2 h and finally outgassing at the same temperature for 30 min: this is the standard sample, which will be referred to as outgassed sample. Oxidised samples were obtained by the same procedure, but the sample was cooled down in oxygen instead of evacuating. Reduced samples were obtained by treating for 1 h the outgassed sample in H_2 (150 Torr) at 823 K. Boron containing samples, indicated hereafter as Co–B–BEA, taken as reference for some experiments, have been synthesised and activated following the same route. The Co-containing faujasite has been obtained following a standard exchange procedure starting from the sodium form of zeolites and a cobalt nitrate solution: the extent of exchange was 14%.

For IR measurements, self-supporting wafers were prepared and activated under dynamic vacuum (10^{-4} Torr) for 2 h at 673 K in an IR cell allowing in situ thermal treatments, gas dosage and measurements both at room and at low temperature are to be made. The FTIR spectra were collected on a Bruker IFS 55 Equinox instrument equipped with an MCT cryodetector working with 2 cm^{-1} resolution.

3. Results and discussion

3.1. The OH stretching region

Fig. 1 reports the spectra of Co–Al–BEA after outgassing (spectrum a), oxidation (b), reduction (c) and subsequent re-oxidation (d). All spectra show as common features: (i) a broad band centred at 3738 cm^{-1}, markedly tailed on the low frequency side; (ii) a weak absorption at 3618 cm^{-1}; (iii) a broad absorption centred at about 3500 cm^{-1}. Spectra a and c show a new feature at 3628 cm^{-1}, absent in the spectra of oxidised samples (spectra b and d), hardly distinguishable because it is heavily superimposed to the band at 3618 cm^{-1}, and therefore marked in the figure by a dashed vertical line.

As it concerns features (i) and (iii), these are assigned to the O–H stretching vibrations of terminal silanols (3738 cm^{-1}) and interacting silanols (3500 cm^{-1}) located in defects like hydroxyl nests or in stacking faults. The 3618 cm^{-1} band is due to the OH stretching mode of Si(OH)Al groups (Brønsted groups). Its intensity is much smaller than what is usually found [23], i.e. in the samples under study

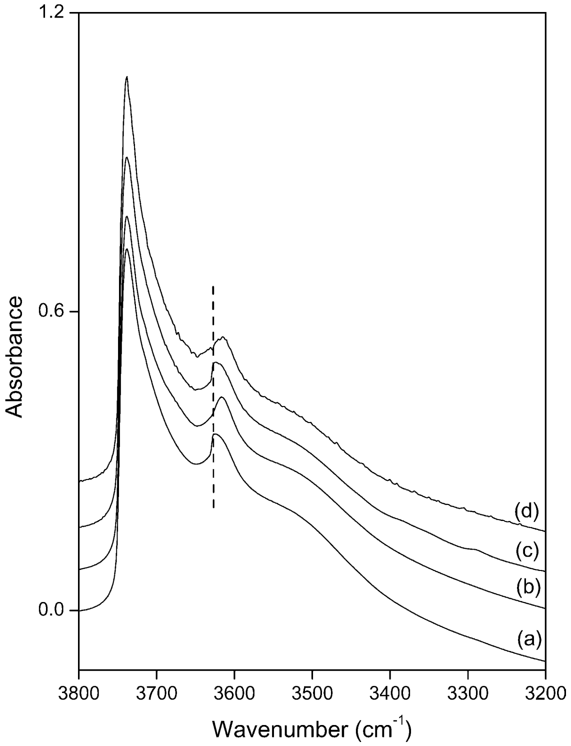
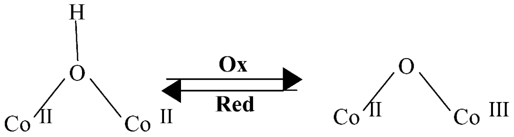


Fig. 1. IR spectra in the hydroxyl stretch region of the sample Co–Al–BEA after: (a) outgassing; (b) oxidation; (c) reduction; (d) further oxidation.

Brønsted acidity is a minor feature. This is perhaps evidence of dealumination; a major cause is the presence of Co cations in extraframework positions discussed below.

The presence of the 3628 cm^{-1} component depends on the oxidation or reduction treatments of the sample, i.e. this band is due to the stretching vibration of some CoOH species (Co ions being the sole redox species present in the system), the nature of which is discussed later.

Adsorption of CO at 77 K (not shown), carried out on outgassed samples in order to measure their Brønsted acidity, shows that the weak 3618 cm^{-1} band is eroded, with the parallel formation of a band centred at 3315 cm^{-1}, due to the O–H stretching vibration of Brønsted acid sites interacting via hydrogen bond with CO. The observed shift (-300 cm^{-1}) is close to that observed on pure beta samples [23], i.e. the presence of Co does not seem to modify the Brønsted acidity of the zeolite. The 3628 cm^{-1} component is not affected by CO adsorption, i.e. the related hydroxyl species do not show any Brønsted acidity. This feature, together with the observed redox behaviour, suggests that these are sitting on CoO clusters in which a bridged hydroxyl group may reversibly be transformed into a bridging oxo group in redox processes (Scheme 1).



Scheme 1.

The 3628 cm^{-1} component is also observed with the sample before template elimination: this suggests a possible location of CoO clusters at the external surface of the zeolite crystals. This being a minor feature of the system, it will not be considered any further.

3.2. CO adsorption

Fig. 2 reports the spectra of the outgassed Co–Al–BEA after adsorption at room temperature with increasing doses of CO. Corresponding spectra of both oxidised and reduced samples do not differ appreciably from those of the outgassed sample. We take this as evidence that the vast majority of Co species has a valence state constant with respect to treatments with either O_2 or H_2. The whole body of evidence shows that the valence state is +2. Diffuse reflectance spectra in the UV–Vis (not reported) do support this conclusion [22]. Exceptions are the clustered species outside the zeolite crystals to which Scheme 1 refers, and a small fraction of Co^{2+} ions which are able to bind reversibly dioxygen molecules, probably through the reaction:

$$Co^{2+} + O_2 \leftrightarrow Co^{3+} + O_2^{-}$$

documented by changes in the UV–visible spectra (not reported). A different situation is encountered with NO (see below) which seems to act as oxidant to some extent.

At low coverages, a weak absorption at about 2238 cm^{-1} is seen, together with a more intense band at 2208 cm^{-1}. This band shows a composite tail on the low frequency side, in which two components at about 2196 and 2184 cm^{-1} are seen. Increasing

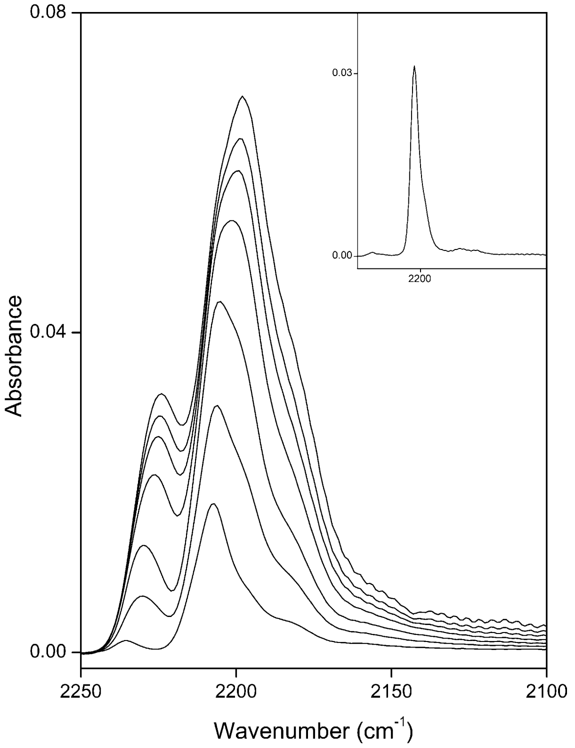


Fig. 2. Room temperature IR spectra in the CO stretch region for CO adsorbed on the reduced sample Co–Al–BEA at various pressures in the range 0–4.5 Torr. Inset: room temperature spectrum of 0.1 Torr CO adsorbed on Co–Na–Y.

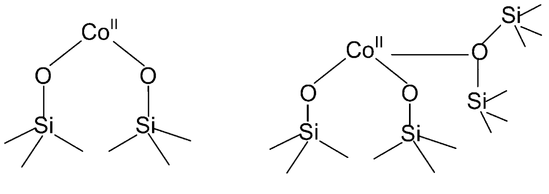
the CO pressure causes, together with an increase of the overall intensity, a marked bathochromic shift of the 2238 cm^{-1} band. The shoulders at 2196 and 2184 cm^{-1} are now evident, and the 2196 cm^{-1} component has increased its relative intensity with respect to the other absorptions. For higher pressures, the 2238 cm^{-1} band is definitively shifted to about 2225 cm^{-1} and the 2196 cm^{-1} one is the main absorption of the whole spectrum. No absorption is seen in the range 2140–2050 cm^{-1}, where the frequencies of CO adsorbed on bulk CoO are known to fall [25,26].

A band at about 2225 cm^{-1} is typical of CO interacting with isolated Al^{3+} centres [24,27] coming from incipient dealumination. The rather marked bathochromic shift of the band with coverage, together with its sizeable intensity, is probably an evidence of dealumination, yielding small particles of Al$_2$O$_3$, in which heterogeneity in the Al^{3+} Lewis centres occurs.

The other absorptions at 2208, 2196 and 2184 cm^{-1} are due to Lewis centres not involving Al^{3+}, i.e. Co centres in different coordinations. The high frequency value of the 2208 cm^{-1} band suggests that the corresponding Co^{2+} cations are in a low coordination state like that of cations in counterion positions. Indeed, the inset in Fig. 2, concerning a parallel experiment carried out on Co–Na–Y, indicates the presence of only one absorption at 2205 cm^{-1}. This comparison allows the assignment of the 2208 cm^{-1} band to CO interacting with Co^{2+} ions in exchange position (site CoA). Experiments (not reported) carried out on Co–B–BEA lend support to the interpretation. As boron atoms prefer trigonal to tetrahedral coordination [28,29], no acidity is developed when B atoms are inserted into the lattice, and “regular” silanols are only required to terminate the network: consequently counterions are not required, and the 2208 cm^{-1} band is absent, whereas the other two CO absorptions do survive. Further evidence comes from outgassing at higher temperature (also not reported): when dealumination is beginning to take place, Co–Al–BEA samples show a marked decrease of the intensity of the 2208 cm^{-1} absorption band.

As the Co–B–BEA sample does show both the 2196 and the 2184 cm^{-1} bands, these are not related to cations in exchange position, i.e. to the presence of Al in the lattice. CO adsorbed on silica supported Co^{2+} [23] shows instead a band at 2180 cm^{-1} close in frequency to that observed here at 2184 cm^{-1}. Accordingly, the 2184 cm^{-1} band is assigned to CO interacting with Co^{2+} ions in internal defects of the lattice (hydroxyl nests) or stacking faults, which may provide surfaces close in nature to those of silica.

Transition metal cations supported on silica (like Co^{2+} [23] or Cr^{2+} [30]) may assume more than one configuration. In Scheme 2, the cation is shown both as linked only to two framework oxygen, and with a further ligand in its coordination sphere (siloxane bridge or a silanol).



Scheme 2.

The lower coordination number should cause a higher electric field at the cation site, and consequently a higher CO stretching frequency. Alternatively, as the siloxane moiety seems to act as an electron withdrawing ligand [30], the opposite assignment can be proposed. The presence of both the 2184 and 2196 cm^{-1} bands is so accounted for. The corresponding Co^{2+} species are designated as CoB and CoC, respectively.

Spectra of CO adsorbed at 77 K (not reported) do not bring any further information as it concerns bands assigned to Co^{2+} species. The main difference with respect to the spectra collected at room temperature is that a rather weak band is visible at about 2174 cm^{-1} due to CO interacting with the residual Brønsted sites. We note the absence of components at about 2176 cm^{-1}, which is usually indicative of the presence of Na^{+} ions ([15,16] and references therein).

3.3. NO adsorption

Fig. 3 reports the spectra of the Co–Al–BEA sample outgassed at 823 K for pressures up to 0.2 Torr and Fig. 4 those for higher NO pressures. The spectrum corresponding to the first gas admission is reported as spectrum (a) both in Fig. 3 and in the inset. A complex absorption is seen, with components at 1954, 1939, 1915 and 1895 cm^{-1}. This last component is not to be mistaken for the band developing at nearly the same frequency (≈1900 cm^{-1}) later in the experiment when dinitrosylic species are formed, because in this case the band at 1900 cm^{-1} is accompanied by a three times more intense companion at 1815 cm^{-1}.

Subsequent NO dosage (spectrum b) markedly increases the overall intensity and, in particular, that of the 1939 cm^{-1} band; new absorptions appear at 1815 and 1850 cm^{-1} (shoulder). In spectrum c, the intensity of the 1939 cm^{-1} band is not basically changed, while the intensities of all other bands increase, with the exception of the component at 1954 cm^{-1}, no more present; a definite band grows at 1900 cm^{-1}. At higher frequencies, a broad absorption appears at 2124 cm^{-1}, together with a tiny band at 2252 cm^{-1}.

Spectrum c in Fig. 4 is the same as in Fig. 3. With increasing pressure, the intensity of both the 1939 and 1915 cm^{-1} bands is progressively reduced, while the intensities of all other bands increase. At about 1908 cm^{-1} an isosbestic point is seen, which gives clear evidence of chemical transformation.

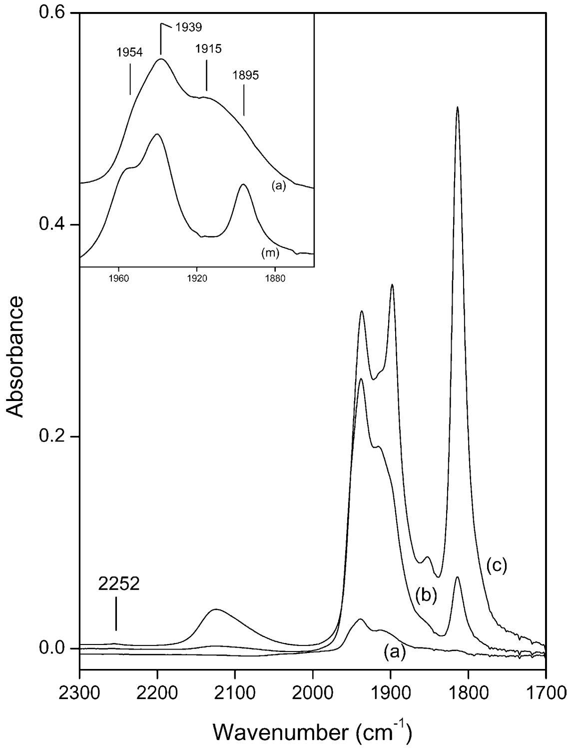


Fig. 3. IR spectra of the reduced sample Co–Al–BEA after contact with NO: (a) 0.01 Torr; (b) 0.04 Torr; (c) 0.15 Torr. The inset compares the first spectrum with the last one of the experiment (spectrum m in Fig. 5).

Fig. 5 describes the effect of outgassing the sample at increasing temperatures: adsorbed species are strongly held, so that the absorptions markedly decrease only for temperatures higher than 373 K. The last spectrum (curve m), taken after outgassing at 423 K, shows again the 1954 cm^{-1} band, which was already present in the adsorption run at low coverages. The inset in Fig. 3 compares this last spectrum m with the first spectrum of this experiment (curve a in Fig. 3) of similar overall intensity: contact with NO has definitely increased the intensity of the 1954 cm^{-1} band.

Bands in the 2000–1800 cm^{-1} range have been observed for NO adsorption on Co-zeolites [18,20,21,31,32], Co–APO [33] and Co/SiO_2 [23] and assigned to mono and dinitrosylic species. On this basis, the absorptions at 1954, 1939, 1915 and 1895 cm^{-1} present at the very beginning of the adsorption experiment are assigned to the mononitrosyl species. The assign-

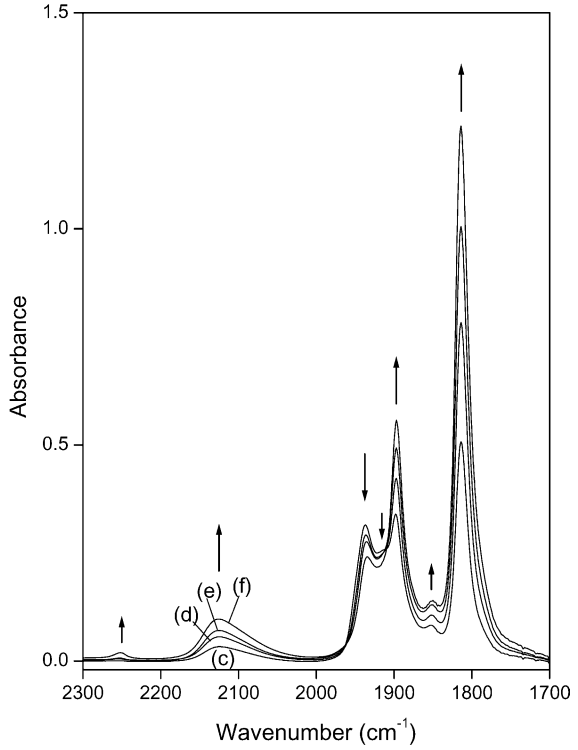


Fig. 4. IR spectra of the reduced sample Co–Al–BEA after contact with NO: (c) as the last one in Fig. 3; (d) 0.4 Torr; (e) 1.5 Torr; (f) 5.5 Torr.

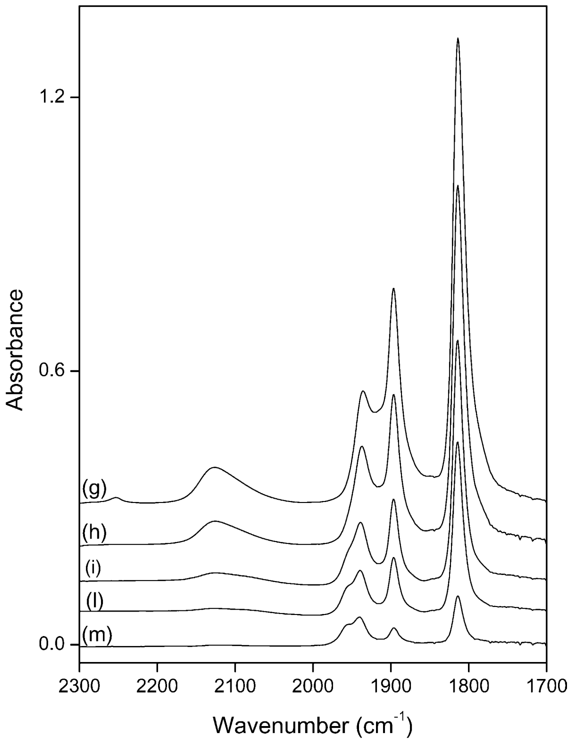


Fig. 5. IR spectra of the reduced sample Co–Al–BEA after contact with NO and outgassing at: (g) room temperature; (h) 323 K; (i) 373 K; (l) 403 K; (m) 423 K. This last spectrum is compared with the first one of the experiment (spectrum a) in the inset to Fig. 3.

ment to specific Co ions is as follows. Literature data [31,32] indicate that the 1939 cm^{-1} band is related to Co^{2+} ion in counterion position. This assignment is supported in the present case by NO adsorption on the same Co–Al–BEA sample outgassed at higher temperature (and therefore partially dealuminated), as on such sample the 1939 cm^{-1} absorption shows a low intensity. The two bands at lower frequencies (1915 and 1895 cm^{-1}) correspond to mononitrosyls on sites CoB and CoC, respectively. The band at 1954 cm^{-1} is assigned to Co^{3+} because its frequency is higher than that of counterionic Co in site A, which is likely to show the highest degree of coordinative unsaturation. Moreover, its intensity is observed to increase after NO contact, most probably because of some oxidation of divalent Co to trivalent species. It appears that NO acts as a better oxidating agent than O$_2$, which does not alter basically the valence state of cobalt ions (see above).

A parabolic correlation exists between the shifts in stretching frequencies of NO and CO adducts (Fig. 6) in the series CoA, CoB and CoC, of the form $\Delta\nu(\mathrm{NO}) = 0.0169\Delta\nu(\mathrm{CO})^2$. Note that in the case of alkaline cations, a similar correlation [34] was found to be linear: whereas in that case electrostatics dominates the interaction, in the present case covalence comes into play. If the parabolic trend in Fig. 6 is extrapolated up to 1954 cm^{-1}, the stretching frequency of Co^{3+}(NO), the corresponding frequency for the complex Co^{3+}(CO) is evaluated to be about 2216 cm^{-1}. To the best of our knowledge, CO adducts of Co^{3+} are not known: were they formed in the present case, i.e. were Co^{3+} species present even before NO contact, the corresponding CO band would be mixed to those arising from Al species.

The couple of bands at 1900 and 1815 cm^{-1} dominates the spectra at high coverages (Fig. 4), and is assigned accordingly to the symmetric and antisym-

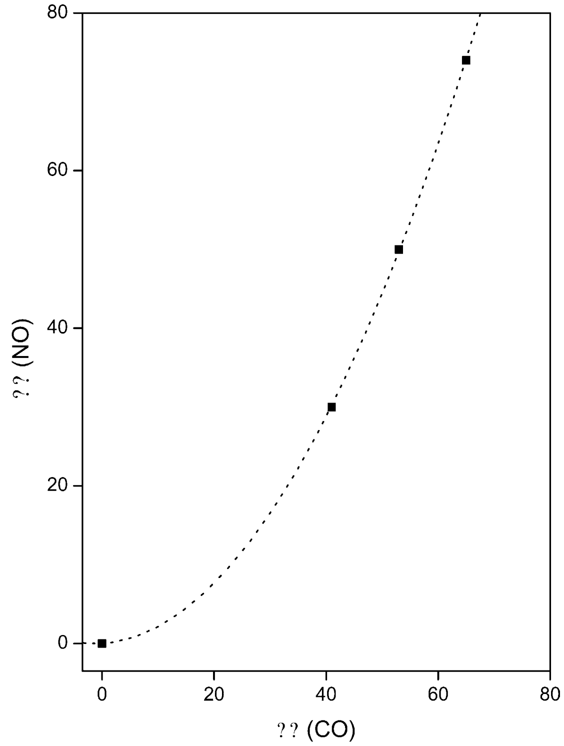
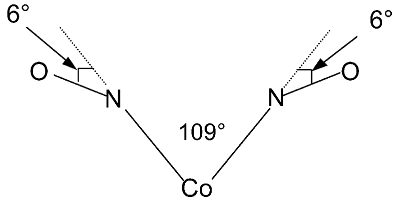


Fig. 6. Correlation between the shifts in NO and CO stretching frequency of mononitrosyl and monocarbonyl species formed on CoA, CoB and CoC with respect to the free molecules. The broken curve illustrates the parabolic dependence $\Delta\nu(\text{NO}) = 0.0169\Delta\nu(\text{CO})^2$.

metric stretching vibrations of a dinitrosylic species $Co^{2+}(NO)^2$, respectively. Apparently, all three types of Co^{2+} sites give rise to the same dinitrosylic species. The intensity of mononitrosyl bands at 1939 and 1915 cm^{-1} (the latter already at low pressures) decreases with the increase of the couple of bands at 1900 and 1815 cm^{-1}: accordingly, the isosbestic point at 1908 cm^{-1} is observed. No safe statement can be made concerning the 1895 cm^{-1} band, to which the symmetric mode of dinitrosyls at 1900 cm^{-1} superimposes. The coincidence of dinitrosylic species for CoA, CoB and CoC probably reflects the fact that dinitrosyls have the same geometry regardless of the starting configuration. The angle between the two NO oscillators may be evaluated as [36]:

$$\phi = 2\arctan\left(\frac{R_{\text{asym}}}{R_{\text{sym}}}\right)^{1/2}$$



Scheme 3.

where R are the intensities of the particular vibrational mode. In the present case, the ratio $R_{\text{asym}}/R_{\text{sym}}$ is about 3.22, which indicates that ϕ is ca. 122°. Note that a divalent cation is expected either to bind two ligands from the underlying solid or to carry an OH species for compensating the charge so that a reasonable minimal coordination number for dinitrosylic species is 4. As in other cases [30], the value of ϕ exceeds that expected for a tetrahedral coordination. Such excess can be interpreted as a consequence of the electron π-backdonation from the Co^{2+} to NO ligands in dinitrosyls, which is known to yield slightly bent Me–N–O moieties. In the present case, the Co–N–O angle would be about 6° assuming tetrahedral geometry (Scheme 3).

Since the mononitrosyl species at 1954 cm^{-1} is observed to disappear, also Co^{3+} ions are expected to form dinitrosylic species. These should have higher frequencies than those of Co^{2+} dinitrosyls. The assignment cannot be but tentative: as the band at 1850 cm^{-1} appears when the 1954 cm^{-1} band disappears, it is tempting to assign this band to the low-lying asymmetric mode of $Co^{3+}(NO)_2$ species; the corresponding less intense symmetric mode could easily be buried in the band envelope at around 1900 cm^{-1}.

At the highest coverages in Fig. 4 the 1939 cm^{-1} band is still present, probably indicating that a fraction CoA is reluctant to add a second NO molecule. This is probably connected to the heterogeneity of exchange positions characteristic of the BEA structure [35]; it is also to be recalled that Co ions in counterion location in low-Al zeolites may carry an OH group as charge-compensating moiety, which occupies one coordinative position, and may render difficult the further insertion of a ligand.

A point worth of comment is the position of the bands of Co^{2+} mononitrosylic species with respect to those of dinitrosylic ones. The frequencies of the former are rather high when compared to other systems not involving Co^{2+} [37]: for example, with Cu(I)-zeolites [37], the band of mononitrosyl species is intermediate between the two dinitrosyl bands. NO seems to give rise with Co^{2+} to partially charged mononitrosylic species, usually referred to for simplicity as NO^+ complexes [38–41]. A possible reason is that Co^{2+} cations (which have a d^7 configuration) complete the d shell by the donation of both the electron pair of the N atom and the extra unpaired electron. Consequently, mononitrosyl species do not show appreciable back-donation whereas sizeable backdonation occurs when two ligands are on the same cation, and the density of charge would be too high on the cation. As a consequence, the average of the symmetric and asymmetric frequencies is about 1850 cm^{-1}, i.e. definitely below those of mononitrosylic species.

A band in the neighbourhood of 2125 cm^{-1} has been observed repeatedly after the adsorption of NO or NO_2. Lavalley and coworkers [42] have assigned this band when formed on H-ZSM-5 to NO^+ species acting as counterion to the negative zeolitic oxygen. This is probably not the case in the present system because Brønsted acidity is negligible. We are inclined to assign this band to a nitrogen dioxide molecule with partial positive charge, usually referred to as $NO_2{}^+$, coming from disproportionation of nitrogen monoxide. Two mechanisms are possible, either $2NO \rightarrow NO_2 + \frac{1}{2}N_2$ or $3NO \rightarrow NO_2 + N_2O$: the latter envisages formation of N_2O. Note that a peak at 2252 cm^{-1}, due to adsorbed N_2O, is observed since the very beginning of the experiment (curve c in Fig. 3 and curves c–f in Fig. 4). NO_2 formed does not give rise to any band below 1700 cm^{-1} in contrast with what is reported below for the adsorption of NO_2 alone. This is probably due to the oxidised nature of the surface as discussed above. A candidate surface species for the formation of $NO_2{}^+$ is Co^{3+}, according to the equation:

$$Co^{3+} + NO_2 \Leftrightarrow Co^{3-\delta} \cdots NO_2{}^{\delta+}$$

3.4. Room temperature interaction of other molecules with irreversibly adsorbed NO

Fig. 7 reports the adsorption of ammonia on NO irreversibly held at r.t. Spectrum a is that before NH_3 contact and shows the mononitrosylic species CoA(NO) at 1939 cm^{-1} and the dinitrosylic species at 1815–1900 cm^{-1}. When dosing ammonia (spectrum b) the intensity of the 1939 cm^{-1} band decreases somewhat, while the couple of bands of the dinitrosylic species undergo a slight bathochromic shift. Raising the ammonia pressure (spectrum c and d) progressively decreases the intensity of the 1939 cm^{-1} band, which appears depleted in the last spectrum (e). The dinitrosylic species are instead still present, retaining the original intensities and only showing a bathochromic shift of about 8 cm^{-1}.

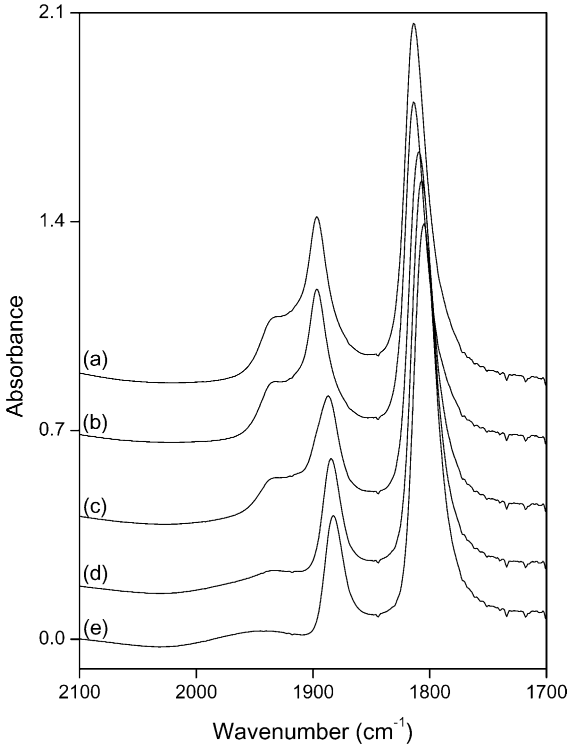


Fig. 7. IR spectra concerning the adsorption of ammonia on the reduced sample Co–Al–BEA after contact with NO and room temperature outgassing: (a) starting spectrum; spectra (b)–(e): increasing ammonia pressures from 0.02 to 1.5 Torr.

Mononitrosylic species clearly undergo a ligand displacement reaction. The perturbation of dinitrosilylic modes is far less easy to interpret. A ligand insertion leading to a mixed $Co(NO)_2NH_3$ complex could be invoked. Corresponding literature data do not match, however, with the features observed. Insertion of ammonia on silica-supported Cr(II) dinitrosyls [43] causes a remarkable bathochromic shift of both dinitrosylic modes, definitively larger than what was observed in the present case: the shift is larger for the low-lying mode, and the ratio of intensities is decreased because the geometry of the complex has changed. Neither feature is observed in the present case. Lunsford and coworkers [31,32] showed that on a Co/Y sample mixed $Co(NO)_2NH_3$ are formed, with a shift of both bands of about 30 cm^{-1} with respect to $Co(NO)_2$ species. In both literature cases, bathochromic shifts are due to the fact that NH_3 increases the electronic density at the metal ion, and consequently a higher backdonation to the NO ligands takes place, which lowers the related stretching frequencies.

In the present case, the observed shifts are too small to correspond to the insertion of an ammonia ligand. The shift, though small, does not correspond to a weak interaction, because it is not markedly pressure-dependent, and is instead partially irreversible at room temperature. It seems therefore that the shift in NO stretching modes of dinitrosyls are a second-order effect due to a rather energetic process on a nearby cation, i.e. the adsorption of a single ammonia molecule on a site either empty or carrying one NO ligand which is displaced. If so, it is necessary to admit that all cations bearing two NO ligands have at least a nearby Co companion. Similar conclusions were drawn, although on a different basis, by Ohtsuka et al. [1]. Another possibility is that Co^{2+} cations carrying two nitrosyl ligands are adjacent to Al^{3+} centres, which also may coordinate strongly ammonia. In both cases, an electronic effect is transmitted from one cation to the adjacent one.

The stability of the irreversible nitrosyl complexes towards oxidising gases was checked. Contact with 50 Torr of oxygen did not cause any spectral changes even after 1 h. Contact with NO_2 is described below because the results are similar to what was observed with NO_2 alone. Changes in the spectra caused by the presence of a NO pressure, i.e. the self-interaction of NO leading to disproportionation, have been described above.

3.5. NO_2 adsorption, desorption and interaction with presorbed NO

Fig. 8 reports the spectra of Co–Al–BEA outgassed at 823 K for NO_2 pressures up to 0.2 Torr and Fig. 9 those for higher NO_2 pressures. NO_2 admission causes the formation of several bands in the 2300–1300 cm^{-1} range, growing simultaneously with pressure. A band is seen at 2133 cm^{-1} (tailed on the low frequency side); another at 1917 cm^{-1} with two pronounced shoulders at 1937 and 1900 cm^{-1}; two weak bands occur at 1816 and 1740 cm^{-1}; a complex envelope is observed in the 1650–1400 cm^{-1} range together with an absorption at 1327 cm^{-1}. When increasing the pressure of NO_2 (Fig. 9), the absorption at 2133 cm^{-1} is slightly shifted to high frequency and first increases in intensity and then decreases. In the meantime, a shoulder at about 2196 cm^{-1} is formed. The bands at 1937 and 1915 cm^{-1} are strongly decreased in intensity: that at 1816 cm^{-1} disappears, together with the component at 1900 cm^{-1}. Instead, all bands at lower frequencies grow, in particular the 1529 cm^{-1} band, which is now the most intense. Finally, new absorptions are found at 1642 and 1745 cm^{-1}.

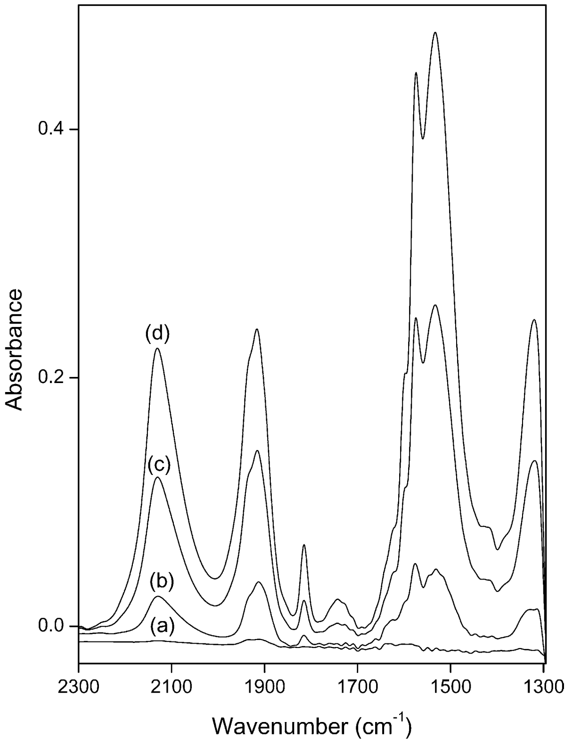


Fig. 8. IR spectra of the reduced sample Co–Al–BEA after contact with NO_2. Low pressure region: (a) 1.5×10^{-3} Torr; (b) 0.03 Torr; (c) 0.10 Torr; (d) 0.15 Torr.

As before, the absorptions at 1937 and 1917 cm^{-1} are due to mononitrosyl species, whereas the 1900 and

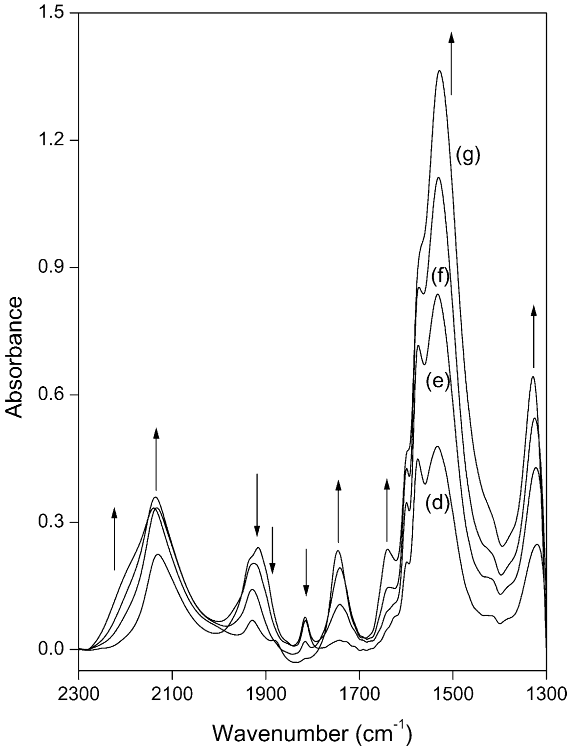


Fig. 9. IR spectra of the reduced sample Co–Al–BEA after contact with NO_2. High pressure region: (d) 0.15 Torr; (e) 0.25 Torr; (f) 0.30 Torr; (g) 1.5 Torr.

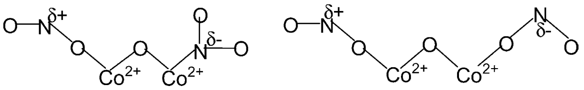
1815 cm^{-1} pair is assigned to dinitrosyls. The band at 1745 cm^{-1} is assigned to the dimer N_2O_4, probably adsorbed on sites not involving the Co cations: evidence for this comes from the perturbation of hydroxyl groups observed (not reported). The 1327 cm^{-1} band is assigned [23,39] to symmetric nitrite ion. The envelope of bands in the 1650–1400 cm^{-1} is attributed by many authors [23,39] to nitrate ions. An alternative possible assignment is to asymmetric nitrite species NO_2^-, interacting with the Co centre via the O end. The 2133 cm^{-1} band is assigned to the stretching frequency of the $NO_2^{\delta+}$ species [44–47], which were found at 2125 cm^{-1} in the previous case.

The first stages of adsorption are characterised by the formation of small amounts of mononitrosyl and dinitrosyl species. Chemical analysis of the NO_2 gas rules out the substantial presence of NO impurities. NO_2 is probably acting as oxidant in the first stages of contact, and NO is the product. The population of dinitrosyl species is remarkably small with respect to that of mononitrosyls: the corresponding Co sites seem to be engaged in phenomena other than the formation of dinitrosyls. Due to the absence of Brønsted sites, also in the present case, we are inclined to rule out the occurrence of NO^+ species as the source of the band at 2133 cm^{-1}. Instead, we favour the assignment of this band to $NO_2^{\delta+}$ species. Some components in the complex envelope at around 1500 cm^{-1} are probably ascribable to nitrite species NO_2^- or nitrito-like $NO_2^{\delta-}$. The simultaneous presence of partially oxidised and reduced species, the limited extent of formation of dinitrosylic species, and, above all, the reversible nature of the species assigned to $NO_2^{\delta+}$ and $NO_2^{\delta-}$ (see below) strongly suggests that electron transfer has taken place, without actual exchange of oxygen atoms, on the same Co centre or on adjacent ones. Taking into account that many Co sites have two coordinative unsaturations, a tentative structure (Scheme 4) is envisaging the simultaneous presence of an $NO_2^{\delta+}$ moiety and of a NO_2^- group, either with symmetric or asymmetric structure. A different possibility, though similar, involving a pair of Co^{2+} cations is shown in Scheme 5.

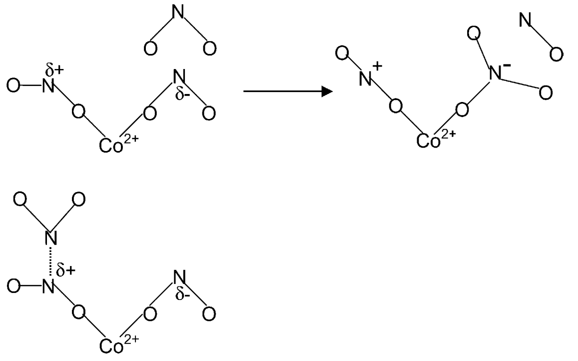
Scheme 4.

A positive partial charge straightens the NO_2 moiety (NO_2^+ is linear), and the opposite does a negative partial charge. In Schemes 4 and 5, accordingly, the $NO_2^{\delta+}$ moiety is represented as nearly linear, and the $NO_2^{\delta-}$ ligand has a O–N–O angle smaller than 134°, that of gaseous NO_2.

On sites with only one coordinative unsaturation, adsorption of NO_2 probably involves electron transfer. With divalent cations the electron is probably transferred from the cationic centre, giving rise to a nitrito-like species ($Co^{2+} + NO_2 \rightarrow Co^{3+}–NO_2^-$), because of the large electron affinity of NO_2. Co^{3+}



Scheme 5.



Scheme 6.

cations probably give rise, as proposed above, to $Co^{3-\delta} \cdots NO_2{}^{\delta+}$ species.

Changes at higher pressure are probably related to the reaction of gaseous NO_2 with adsorbed species. Ultimate evidence on surface processes is however lacking, and the following considerations have to be taken as rather speculative. The nitrito-like reduced species depicted in Schemes 4 and 5 may undergo reaction transforming the nitrite moiety into a nitrate one (upper part of Scheme 6), via the reduction of NO_2 to NO.

The species responsible for the band at 2196 cm^{-1} is formed under a substantial pressure of NO_2 and only in the presence of the 2133 cm^{-1} band. It has been noted [39,40] that the 2196 cm^{-1} band is accompanied by the band at 1745 cm^{-1}, typical of the adsorbed N_2O_4 dimer, which in turn requires a substantial NO_2 pressure. Szanyi and Paffett [48] have attributed the 2133 cm^{-1} band to the N_2O_4 species itself: this is surprising, because the gas-phase N_2O_4 species has no sizeable absorption in this region. We note that the species $NO_2{}^{\delta+}$ as in Schemes 4 and 5 carries the partial positive charge on the N atom, whereas the monomer NO_2 species has a lone pair on the N atom: the partially charged $NO_2{}^{\delta+}$ species and the neutral one NO_2 might thus engage in a weak Lewis adduct, where the two moieties are only slightly perturbed (lower part of Scheme 6), thus explaining the shift of the 2133 cm^{-1} band to 2136 cm^{-1} and the presence of the band at 1642 cm^{-1} due to NO_2 species in a state not to far from the gas-phase.

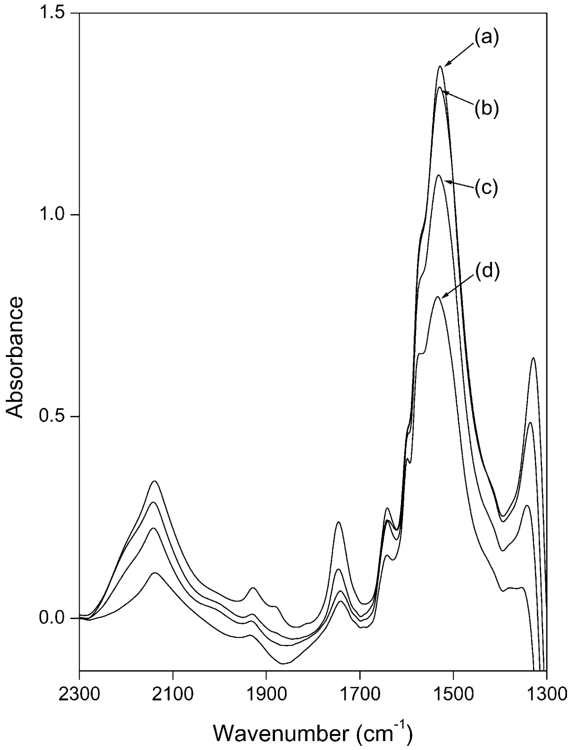


Fig. 10. IR spectra of the reduced sample Co–Al–BEA after contact with NO_2. Desorption experiment: (a) as spectrum (g) in Fig. 9; (b) equilibrium pressure: 0.5 Torr; (c) equilibrium pressure: 0.03 Torr; (d) outgassed 15'.

Fig. 10 describes the outgassing stage of the experiment with NO_2. By a decrease in pressure, both the bands related to oxidised species $NO_2{}^{\delta+}$ and those related to reduced species $NO_2{}^{\delta-}$ decrease their intensity, i.e. disproportionation of NO_2 is reversed by mere outgassing. This gives evidence in support of disproportionation occurring, in the early stages, as electron transfer within the same complex (a reversible process) instead of transfer of oxygen between species (a hardly reversible process). Species reluctant to desorption probably are nitrate groups.

The last spectrum of Fig. 9, more clearly reported also as the first spectrum in Fig. 10, show a weak band at 1876 cm^{-1}, already observed on a Co-ZSM5 sample by Lavalley and coworkers [42], assigned to adsorbed N_2O_3, formed by reaction of NO_2 with NO coming from the reduction of NO_2.

Interaction of irreversibly adsorbed NO with NO_2 follows a pattern rather close to adsorption of NO_2 alone (not reported).

4. Conclusions

No evidence has been gained concerning the presence of Co at tetrahedral lattice sites; no Brønsted acidity is developed, and the new hydroxyl band has been shown to be non-acidic. Co–Al–BEA sample contains at least three families of Co^{2+} sites, designated in the present work as CoA, CoB and CoC. CoA ions are at extraframework, counterionic positions, form a carbonyl species at $2208\,cm^{-1}$ and a mononitrosyl at $1939\,cm^{-1}$; a large fraction also forms a dinitrosyl species. On the basis of the intensities of adsorbed species, CoA seems to be the dominating species. This is one reason why the Brønsted acidity of the system is largely suppressed; the other is dealumination.

CoB and CoC are two versions of Co ions grafted to the surface in defective situations (hydroxyl nests or stacking faults), without any role of Al, and are therefore somewhat similar to Co species grafted to amorphous silica; carbonyl species are at 2196 and $2184\,cm^{-1}$, and mononitrosyl species at 1915 and $1895\,cm^{-1}$, respectively. CoB and CoC seem to form dinitrosyl species readily. Co^{3+} is present in small amounts, after NO contact, and is responsible for a mononitrosylic species at $1954\,cm^{-1}$.

Dinitrosyl species for CoA, CoB and CoC seem to share the same modes at 1815 and $1900\,cm^{-1}$: the corresponding species for Co^{3+} probably have the asymmetric mode at $1850\,cm^{-1}$, whereas the symmetric one is not buried by other absorptions. Interaction with ammonia of irreversibly adsorbed NO species suggests, on the one hand, that dinitrosyl species are reluctant to accept a third ligand, and on the other hand, the occurrence of cation pairs.

The availability of two coordinative unsaturations on most Co species (or the occurence of adjacent Co centres) allows a reversible disproportionation of NO_2, i.e. the simultaneous adsorption of two molecules on the same cation with a partial electron transfer from one ligand to the other, i.e. with formation of ${NO_2}^{\delta+}$ and ${NO_2}^{\delta-}$ species; at a later stage of interaction, a proper disproportionation yielding nitrate species is observed.

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