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Cobalt on and in zeolites and silica–alumina: Spectroscopic characterization and reactivity

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Abstract

The adsorption of CO at 130 K has been studied on Co-H-FER, Co-H-MFI and Co-H-MOR, as well as on Co-silica–alumina and on Co-containing mesoporous materials. Over Co-H-MFI also the adsorption of NO and of ammonia and the coadsorption of *ortho*-toluonitrile and CO have been investigated. The data show that on all samples Lewis acidic isolated Co^{2+} species are predominant. However, small amounts of oxidizing sites, possibly Co^{3+} and/or cobalt oxide particles also exist. This is shown by the oxidation of part of CO to CO_2 and of NO to NO^+ at very low temperature as well as by the formation of Co^{3+} mononitrosyls upon adsorption of NO. These sites, although difficult to be evidenced by direct spectroscopic measurements, are likley the active sites for CH_4-SCR, where NO is activated as an adsorbed N_xO_y species able to react selectively with methane.

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Keywords: Selective catalytic reduction of NO_x; Active sites in Co-zeolites; IR study of SCR of NO Co-zeolites; *Ortho*-toluonitrile probe; External surface of Co-zeolite; Internal surface of Co-zeolite

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1. Introduction

Co containing zeolites, such as Co-FER, Co-MFI and Co-MOR, are the object of investigation because they are reported to be the most promising catalysts for reducing NO with methane in oxidizing atmosphere [1–4]. The elegant study of Satsuma et al. [5] showed that the diffusion of the hydrocarbons in the zeolite cavities is rate determining and this demonstrates that the reaction occurs in the zeolite channels. Co^{2+} ions exchanging the protons of the protonic zeolites are considered to be the active sites [6]. In a series of recent papers the UV–vis spectra of Co-FER, Co-MFI and Co-MOR have been studied in detail and assigned to Co^{2+} ions in different locations in the zeolite cavities [7–10]. On the other hand, Montanari et al. [11] demonstrated that even in very active catalysts a significant part of cobalt may be out of the zeolite channels and that even for formally overexchanged catalysts the real exchange of the protonic position may be only partial. In fact, the possible cooperation of protonic and Co cationic sites in partially exchanged Co-zeolites for the CH_4-SCR reaction has also been discussed [12]. On the other hand, Co^{2+} sites whose spectroscopic properties are very similar to those of Co-zeolites also occur at the external surface of Co-silica–alumina [11], but this catalyst is only active in the oxidation of NO to NO_2, without catalysing the SCR reaction with CH_4 [13]. While TPD data show that Co^{2+} ions in extraframework channel positions are apparently hardly reducible, more easily reducible Co species exist in catalytically active Co-zeolites [4,13]. These evidences allow us to suppose that Co ionic species other than Co^{2+} in ‘‘exchanging’’ positions may occur in the internal cavities and act in the catalytic reaction. These species may be isolated or clustered.

Co species on microporous and mesoporous surfaces are also active as catalysts for other reactions such as for the NH_3-SCR of NO_x [14] and for oxidation [15] and ammoxidation [16], while they are also of interest as precursors of catalysts for hydrogenation [17] and for the Fischer Tropsch reaction [18,19]. A detailed characterization of Co-oxide based materials may be helpful for developing new systems for the different catalytic applications.

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2. Experimental

2.1. Catalysts preparation

NH_4-FER (SiO_2/Al_2O_3 = 55, S_{BET} = 480 $m^2 g^{-1}$), NH_4-MFI (SiO_2/Al_2O_3 = 50, S_{BET} = 425 $m^2 g^{-1}$) and NH_4-MOR (SiO_2/Al_2O_3 = 20, S_{BET} = 480 m^2/g) supplied by Zeolyst were used as starting materials. NH_4-zeolites powders were contacted with a 0.02 M $(CH_3COO)_2Co{\cdot}4H_2O$ aqueous solution (10 g powder for 1 L solution) under stirring at a constant temperature of 353 K for 24 h. The resulting slurry was filtered and the solid washed three times with double distilled water. After centrifugation, powders were dried at 353 K for 10 h and calcined at 823 K for 4 h.

A similar procedure has been applied to the production of Co-silica–alumina starting from silica–alumina (13% Al_2O_3) from STREM Chemicals (300 $m^2 g^{-1}$). The resulting Co loadings are around 10% (w/w) for Co-silica–alumina and are 2.2% (w/w), 1.7% (w/w) and 4.9% (w/w) for Co-FER, Co-MFI and Co-MOR, respectively.

2.2. Surface characterisation

The IR spectra were recorded on a Nicolet Protégé 460 and on a Nicolet Magna 750 Fourier Transform instruments. The surface characterization has been performed using pressed disks of pure powders (15 mg for 2 cm diameter), activated by outgassing at 773 K into the IR cell. A conventional manipulation/outgassing ramp connected to the IR cell was used. The ammonia adsorption procedure involves contact of the activated samples disk with ammonia vapors at RT at a pressure of 15 Torr and outgassing in steps at RT and increasing temperatures. The adsorption of CO and of NO has been investigated in a home-made liquid-nitrogen cooled cell. The real adsorption and desorption temperature is 130 K or above.

3. Results

The IR spectra of pressed disks of the pure Co zeolite powders show the presence of residual hydroxy groups, as evidenced by the persistence of IR bands in the 3800–3500 cm^{-1} region. In Fig. 1, the spectra of H-MOR and Co-MOR samples are reported. The spectrum of H-MOR (Fig. 1a) has been studied in detail previously. The study of the adsorption of differently hindered nitriles [20,21] allowed us to assign the band at 3747 cm^{-1} to the OH stretching mode of terminal Si–OH bonds located at the external surface of the zeolite. The strongest band centered near 3605 cm^{-1} has been found to be actually composed of at least three components, one at 3609 cm^{-1}, one corresponding to the main maximum near 3605 cm^{-1} and one shoulder at 3588 cm^{-1}. The last one is for long known to be due to bridging Si–OH–Al groups located in the side pockets whereas for the two first ones different assignations are reported [20–23]. The shoulder at 3660 cm^{-1} is assigned to small amounts of extraframework material.

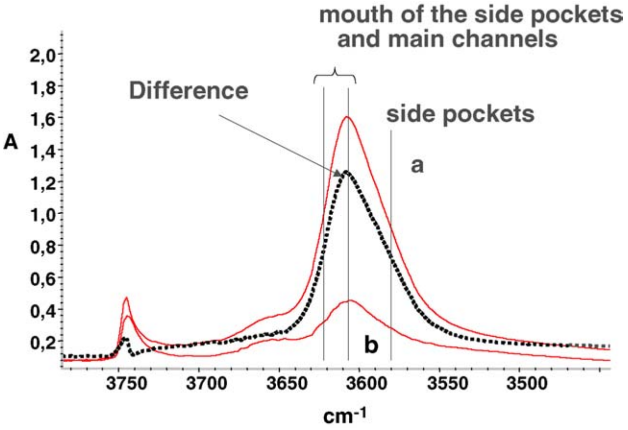

Fig. 1. FT-IR spectra of (a) H-MOR and (b) Co-H-MOR after outgassing at 773 K. Dashed line: the subtraction.

The spectrum of Co-MOR (Fig. 1b) presents also the bands discussed above. The band at 3747 cm^{-1} has in the spectrum of Co-MOR about 89% of the intensity observed for the original H-MOR, while the overall band centered at 3605 cm^{-1} retains in Co-MOR 33% of its intensity. This provides evidence for a only partial exchange (67%) of the exchangeable protons by Co. Also the spectrum of Co-MFI shows well evidently the residual bands of terminal silanols at 3747 cm^{-1} and the bridging OH's at 3610 cm^{-1}. As already discussed [11], for Co-MFI and Co-FER the exchange of bridging OH's is even smaller than for Co-MOR: 50% and 12%, respectively. For this reason hereinafter the samples will be denoted as Co-H-zeolites.

The comparison of the spectra of H-MOR and of Co-H-MOR (Fig. 1) as well as of their difference seems to indicate that the exchange has been a little more efficient for the species responsible for the main central maximum at 3605 cm^{-1} than for the others because on the spectrum b the two side components seem to be more resolved. Nevertheless, we must remind that the extinction coefficient corresponding to the various bridging OHs is not constant so that a more detailed study is required to better conclude. To have a characterization of the acidity of Co-zeolite catalysts we investigated the adsorption of ammonia. The IR spectra observed for Co-H-MFI (Fig. 2) show the appearance of very strong bands at 3358,

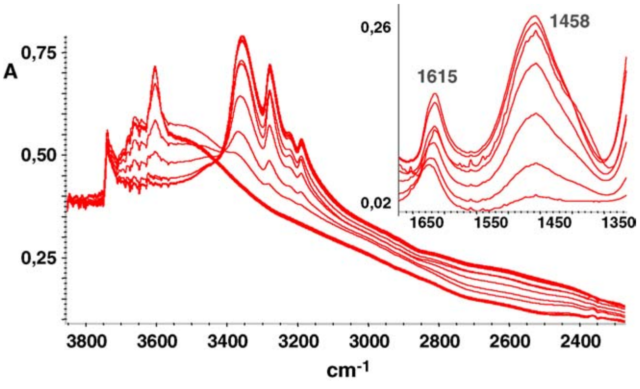

Fig. 2. FT-IR spectra of Co-H-MFI in contact with ammonia vapor at increasing coverages.

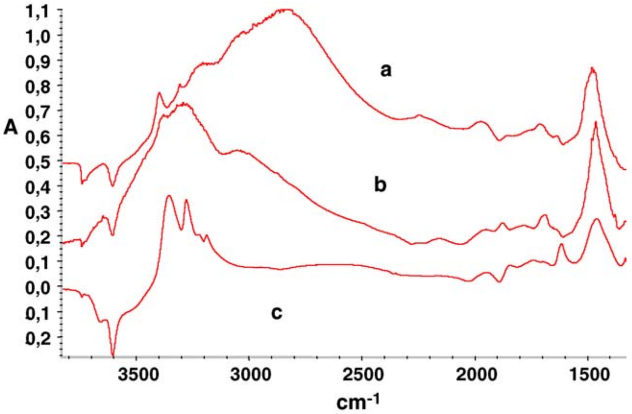

Fig. 3. FT-IR subtraction spectra: (a) H-MFI saturated with ammonia, (b) H-MFI saturated with ammonia and outgassed at 373 K, (c) Co-H-MFI saturated with ammonia.

3279, 3225 and 3189 cm^{-1}. These bands are due to the three NH stretchings and to the first overtone of the asymmetric deformation of coordinated ammonia over Co ions. This is confirmed by the detection of the asymmetric NH_3 deformation band at 1615 cm^{-1}. On the other hand, the complete disappearance of the band of bridging OHs at 3610 cm^{-1}, also corresponds to the formation of a strong band at 1458 cm^{-1}, typically due to the asymmetric deformation of ammonium ions. The N–H stretchings of ammonium ions (formed by ammonia protonation by the bridging OHs) give rise to a broad feature detectable in the region around 2600 cm^{-1}. In Fig. 3, the subtraction spectra observed after saturation with ammonia and after successive outgassing of H-MFI, as well as after saturation of Co-H-MFI with ammonia are compared. As discussed elsewhere [24], after saturation with ammonia the spectrum of H-MFI is dominated by the features of the dimeric cation $N_2H_7^+$, while after outgassing at 373 K the most intense bands are due to the monomeric ammonium cation NH_4^+. In the case of Co-H-MFI the predominance of coordinated ammonia is evident as an effect of the presence of Lewis acidic Co ions. This agrees with the very high amount of ammonia desorbed by Co-H-MFI, which is higher than on H-MFI, as well as for Co-H-FER higher than for H-FER [4]. These data provide evidence for the existence of well defined Lewis acidic Co ions and for the accessibility of the residual OHs (which are fully involved in the protonation of ammonia) to adsorbates. This also means that ion exchange with Co acetate did not cause pore obstruction.

In Fig. 4 the spectra of Co-H-FER as such and after adsorption of CO at 100 K are reported. The strong ν(CO) bands at 2137 and 2173 cm^{-1} are due to liquid-like CO and to CO H-bonded on the residual acidic bridging hydroxyls, respectively. In parallel with the formation of the band at 2173 cm^{-1}, in fact, the OH stretching band at 3603 cm^{-1} in the clean Co-H-FER sample shifts to 3303 cm^{-1}, while two additional components at 3470 and 3425 cm^{-1} are also observed and are assigned to the perturbation of the OH's of extraframework alumina particles (3664 cm^{-1} on the clean surface). The ν(CO) band at 2193–2204 cm^{-1}, not observed on H-FER, is due to CO adsorbed on Co^{n+} cations.

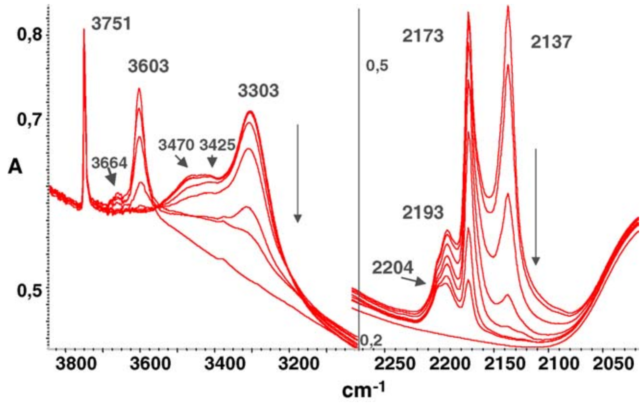

Fig. 4. FT-IR spectra of Co-H-FER after saturation with CO at 130 K and outgassing at increasing temperatures 130–180 K.

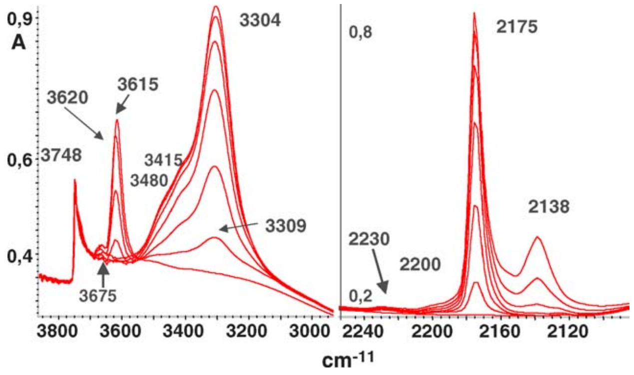

Fig. 5. FT-IR spectra of H-MFI after saturation with CO at 130 K and outgassing at increasing temperatures 130–180 K.

In Figs. 5 and 6 the spectra relative to the low temperature CO adsorption on H-MFI and Co-H-MFI are reported. In the case of H-MFI the more evident interaction is associated to the shift of the OH stretching band of the bridging OHs from 3615 to 3304 cm^{-1}, and to the CO stretching band at 2175 cm^{-1}. Additional OH stretching shoulders near 3480 and 3415 cm^{-1} are likely due to perturbation by adsorbed CO of the weak bands near 3675 cm^{-1} due to OHs on extraframework material. The further band at 2138 cm^{-1} is usually assigned to liquid-like CO. Very weak features at 2230 and 2200 cm^{-1} are due to CO

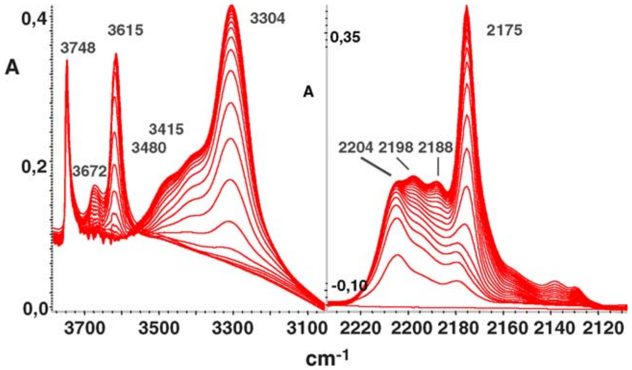

Fig. 6. FT-IR spectra of Co-H-MFI after saturation with CO at 130 K and outgassing at increasing temperatures 130–180 K.

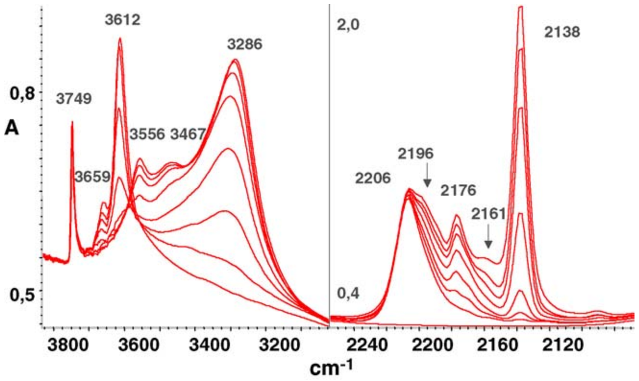

Fig. 7. FT-IR spectra of Co-H-MOR after saturation with CO at 130 K and outgassing at increasing temperatures 130–180 K.

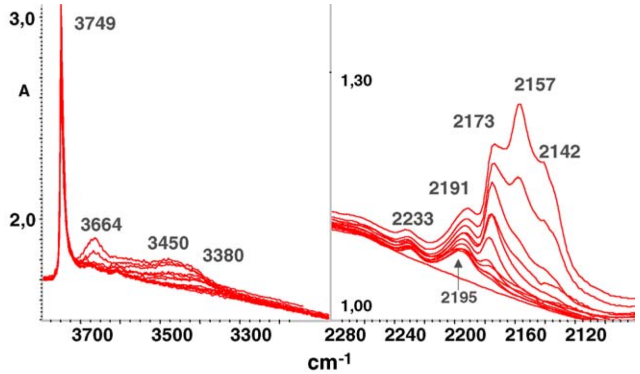

Fig. 9. FT-IR spectra of Co-SA after saturation with CO at 130 K and outgassing at increasing temperatures 130–180 K.

adsorbed on Al^{3+} Lewis sites. In the case of Co-H-MFI all this complex of bands is observed as well; additionally, strong components are detected too at 2204, 2198 and 2188 cm^{-1}, that must be assigned to carbonyls over Co^{n+} cations, as observed also by Campa et al. [6].

The spectra of CO adsorbed on Co-H-MOR, reported in Fig. 7, show again the features of CO adsorbed on the Brønsted acidic bridging OH [ν (OH) 3286 cm^{-1}, ν(CO) 2176 cm^{-1}] and liquid-like CO (2138 cm^{-1}) together with a strong band centered at 2206 cm^{-1} presenting a shoulder at 2196 cm^{-1}, certainly due to carbonyls on Co^{n+} centers. The data agree with those previously reported by Campa et al. [25].

The comparison of the spectra of CO adsorbed at low temperature on Co-H-FER, Co-H-MFI and Co-H-MOR (Figs. 4, 6 and 7) allow us to correlate the relative intensities of the complex band at 2210–2190 cm^{-1} (mostly due to CO adsorbed on cobalt ions) and the bands near 2173 cm^{-1} (assigned to CO interacting with the bridging OHs) to the relative exchange of the protons by Co ions, which in fact follows the trend MOR > MFI > FER.

To have further indications, we also reinvestigated the adsorption of CO on silica–alumina (SA) and Co-SA. Over SA (Fig. 8) the spectra of adsorbed CO show a band at very high frequencies (2231 cm^{-1}) and a broad component near 2200 cm^{-1}, which can be attributed to CO on Lewis acidic Al^{3+} ions. The bands at 2173 and 2156 cm^{-1} may be attributed to CO interacting with two different kinds of acidic hydroxy groups. In fact, although the spectrum of the clean silica–alumina only presents a single OH band at 3748 cm^{-1}, after adsorption of CO at least three weak components are observed in the OH stretching region, at 3667, 3580 and 3415 cm^{-1}, due to three different H-bonded complexes with CO. This agrees with previous studies that showed that the stretching modes of different OH groups with different acidic strength are superimposed into the band at 3748 cm^{-1} of SA [26]. On Co-SA (Fig. 9) the perturbed OH component at 3667 cm^{-1} presents a lower intensity than in the Co-free SA sample. Conjointly, when cobalt is present, the relative intensity of the 2157 cm^{-1} ν(CO) component is lower. Both previous results show a lower proportion of weak acid sites on the Co containing sample. This indicates that Co ions affect more the less acidic OHs, possibly because they give rise to more basic ligands for the cation. Moreover, a new strong band is observed at 2195 cm^{-1} certainly due to carbonyls on Co^{n+} centers.

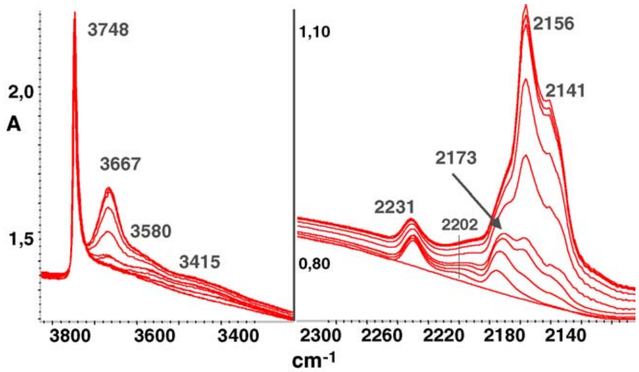

Fig. 8. FT-IR spectra of silica–alumina after saturation with CO at 130 K and outgassing at increasing temperatures 130–180 K.

In Fig. 10 the spectra of cobalt carbonyls over Co-zeolites and over Co-SA are compared with those found over Co-mesoporous silica–zirconia and silica [27]. A possible interpretation of this behavior is that the position of the band

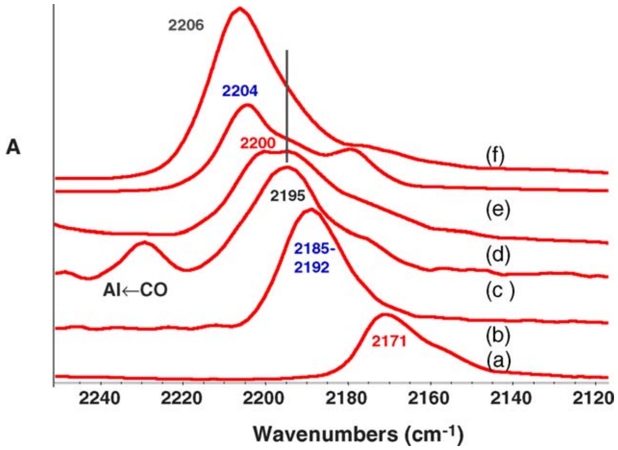

Fig. 10. FT-IR spectra of carbon monoxide adsorbed on Co-MCM41 (a), Co-MCM41-Si, Zr (b), Co-SA (c), Co-H-FER (d), Co-H-MFI (e), Co-H-MOR (f) after saturation with CO at 130 K and outgassing at ~180 K.

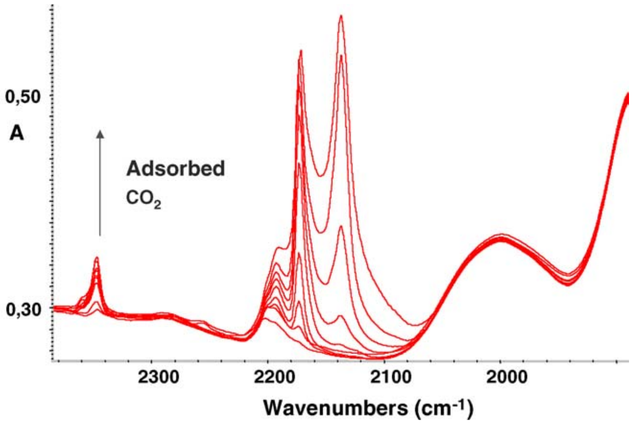

Fig. 11. FT-IR spectra of Co-H-FER after saturation with CO at 130 K and outgassing at increasing temperatures 130–180 K.

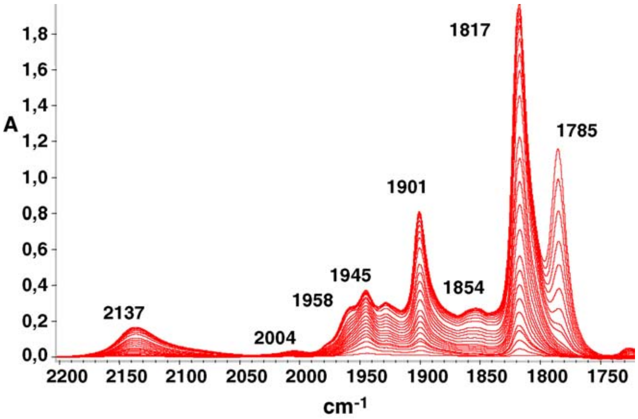

Fig. 13. FT-IR spectra of Co-H-MFI after contact with NO at 130 K at increasing coverages.

of Cobalt carbonyls depends on the ionicity of the framework. In practice, the higher the amount of Al^{3+} (or Zr^{4+}) ions actually dissolved in the silica-based framework, the higher the frequency.

A careful analysis of the spectra shows that on all Co-containing materials studied here, upon outgassing at temperatures near 100 K or more (see Fig. 11 for Co-H-FER), weak bands at 2350 cm^{-1} grow, providing evidence for the oxidation of CO to CO_2 by cobalt species. As a confirmation of the role of cobalt in oxidizing CO, no CO_2 is observed on Co-free samples.

To reveal the existence and the activity of Co ions at the external surface, we investigated the low temperature adsorption of CO over a sample previously saturated with *ortho*-toluonitrile (*o*TN). In fact, we previously found that *o*TN does not enter the cavities of Co-H-MFI, but produces well defined complexes with Co ions at the outer surface [11]. In fact, upon adsorption of *o*TN the band due to the bridging OHs, which are exclusively located in the internal channel surface, are not perturbed, while a complex with Co ions is evidenced by the formation of a C–N stretching band at 2248 cm^{-1}. After saturating the external surface of Co-H-MFI with *o*TN, we adsorbed CO at low temperature. The results are shown in Fig. 12. The adsorption of CO on *o*TN covered Co-H-MFI gives rise to the same features as on *o*TN-free zeolite, excepted for the band at 2204 cm^{-1}, which is strongly lowered in intensity and the band at 2188 cm^{-1} which is no more detectable. This last component should thus be reattributed to CO interaction with Co_xO_y mainly present on the outer surface. The spectra also show that *o*TN does not hinder the access of CO to the channels: in fact the residual hydroxyls are fully involved in H-bonding with CO. The spectra reported in Fig. 12 provide evidence that part of the Co ions (on which adsorbed CO forms carbonyls characterized by the νCO band at 2204 cm^{-1}) are located at the external surface and are ‘‘poisoned’’ by *o*TN adsorption.

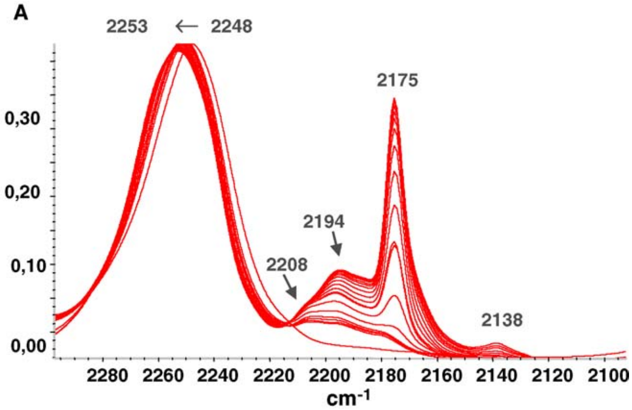

Fig. 12. FT-IR spectra of Co-H-MFI pretreated with *ortho*-toluonitrile vapor at room temperature and after saturation.

To have even more clear indications, we also investigated the low temperature adsorption of NO on Co-H-zeolites. The spectra relative to Co-H-MFI are reported in Fig. 13. As a further confirmation of the predominance of Co^{2+} ions, the spectra show as the most intense bands the couple at 1901, 1817 cm^{-1}, assigned to Co^{2+} dinitrosyls [28,29]. Moreover, bands at 2137 and 1945 cm^{-1} are usually assigned to NO^+ [30] species and to Co^{3+} mononitrosyls, respectively. The strong band at 1785 cm^{-1} is likely due, together with the weaker one at 1854 cm^{-1}, to *cis*-N_2O_2. Other weaker features are observed confirming the heterogeneity of the adsorbing sites.

4. Discussion

Several techniques may be applied to determine the state of the cations in metal zeolites. UV–vis studies have been applied widely for Co-zeolites and evidence for the presence, in all cases, of low coordination Co^{2+} ions in outgassed samples [7–11]. The nature and location of these sites has been investigated by other techniques such as EXAFS [10,31,32], theoretical calculations [33,34] and the Rietveld analysis of synchrotron XRPD [32]. A satisfactory agreement between these data seems to exist, e.g. for siting of Co^{2+} ions in the ferrierite. On the other hand, it seems interesting that in their EXAFS and XRD study Cruciani et al. only locate nearly 85% of the Co ions present in their sample in the interior of the FER structure [32], supporting our data that a non-negligible amount of Co sites may be located out of the channels or in alternative positions.

Here, both ammonia, CO and NO adsorption studies may be taken as confirmation of the predominance of Co^{2+} ions in the samples. TPR results revealed that 75–90% of Co species are actually very hardly reducible, but that the other Co species are quite easily reducible [4,13]. On the other hand, the oxidation of CO to CO_2 occurring (only in the presence of Co ions) already near 130 K provides evidence for the presence of strongly oxiding sites. These sites might be constituted by Co oxide particles. In fact, previous low temperature CO adsorption studies on Co_3O_4 showed a strong band at 2195 cm^{-1} [35], similar to that found here on szeolites, that may contain Co^{3+}–CO species. CO adsorbed at low temperature on $CoAl_2O_4$ [36,37] gave rise to band at slightly lower frequency (2170 cm^{-1}). On both Co_3O_4 and $CoAl_2O_4$ CO reduces the surface at room temperature giving rise to bands at lower frequencies assigned to lower-oxidation state Co-carbonyls. So, it seems possible that Co^{3+} species or cobalt oxide particles are also present and give rise to carbonyl species not easily distinguishable that those of Co^{2+} carbonyls. The *o*TN preadsorption confirms that part of Co^{n+} is actually located at the external surface, giving rise on Co-H-MFI to the higher frequency Co-carbonyls. On the other hand, NO adsorption studies seem to confirm the presence on outgassed vsamples of Co^{3+} ions and of the existence of oxidizing sites producing NO^+.

5. Conclusions

The data presented here unequivocally show that Co^{2+} in low coordination, well evident from UV spectra, is present in the internal cavities of Co-H-MOR, Co-H-MFI and Co-H-FER, but is also located in part at their external surface as well as at the external surface of Co-silica–alumina. In any case, such low-coordination Co^{2+} ions are actually not the most active species in these systems, while a fraction (25–10%) of cobalt sites (Co^{3+} or Co oxide particles) also exist and may have a predominant role in catalysis. It seems likely that oxidizing Co species are too few to be distinguished by UV–vis, but are revealed by the oxidation of CO to CO_2 and by the adsorption of NO. As shown by Satsuma et al. [5] the active sites for CH_4-SCR over Co-zeolites are certainly located at the internal channels. Most authors agree that the reaction involves a strongly adsorbed oxidized "N_xO_y" intermediate. Our data suggest that this intermediate is formed on oxidizing Co sites different from the most abundant Co^{2+} ions in substitutional positions but located in the channels of the zeolite.

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