Impact of Deactivation Conditions on the Acidity of Y Zeolites Used in the Formulation of FCC Catalysts, Studied by FTIR of Adsorbed CO

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Two Y zeolites (FAU) used in the formulation of commercial FCC catalysts were studied with progressive CO adsorption by FTIR at 77 K. We investigated changes in the type, concentration, and strength of the acid sites when the zeolites were deactivated under conditions that simulate the regenerator of a commercial FCC unit. Y zeolites treated with steam and subsequent removal of the extralattice aluminum species showed pores and defects in structure allowing diffusion of CO molecules toward low-frequency (LF)OH groups in the beta cavity, while in zeolites with plenty of extraframework aluminum, these sites were not accessible. Strong Brønsted acid sites were found with the position of a perturbed –OH band as low as 3180 cm^{-1}, a ν_{CO} at 2183 cm^{-1}, a ΔOH of 443 cm^{-1}, and a proton affinity (PA) of 1084 kJ mol^{-1}. Hydrothermal treatment at 1061 K in an air–steam mixture destroyed the zeolite acid sites, including the extraframework aluminum –OH groups. Knowledge about the changes in the acidity of the zeolite and the other FCC catalyst components under conditions that simulate deactivation in a FCC regenerator unit will improve the selection and evaluation of catalysts for commercial units. © 2002 Elsevier Science (USA)

1. INTRODUCTION

FCC has been the most important process in the oil refining industry for over 60 years because it produces the greatest volume of valuable products per barrel of crude. During the operation, the catalyst is subject to continuous cycles of reaction and regeneration. These cycles take a few seconds in the reactor and about 7 to 15 min in the regenerator. Here the catalyst encounters temperatures from 773 to 1063 K and high steam concentrations (∼20% steam, with an excess of oxygen). These conditions, making up a reducing environment in the reactor (presence of hydrogen) and a strongly oxidizing environment in the regenerator, reduce the activity and modify the selectivity and stability of the zeolite and of the catalyst. To correctly evaluate and select

catalysts for commercial units, it is necessary to simulate the ECAT (equilibrium catalyst) properties and characteristics in the laboratory. There are several deactivation methods (1–5) for this purpose. However, there is little information about the changes in catalyst acidity during these deactivations, and the catalyst deactivated by means of these methods does not reproduce the coke and hydrogen selectivity of the ECAT, which are essential parameters for defining catalyst behavior. To understand and to explain these differences, it is necessary to study the effect of deactivation conditions on acidity and on the acid sites of the zeolite, the catalyst's most important components.

FTIR of adsorbed CO is one of many analytic methods used to study acidity in dealuminated Y zeolites (6–11). The IR spectrum of HY zeolite and its dehydrated form shows three main bands in the –OH region: 3720–3750, 3600–3650, and 3530–3580 cm^{-1}. The band with the highest frequency is due to the ≡Si–OH groups in the terminal or internal positions of the zeolite's outer surface. Bands at 3738 and 3743 cm^{-1} are assigned to –OH groups in framework and nonframework silicon species (11). The middle high-frequency (HF)OH band, with ν_{OH} at 3600–3650 cm^{-1}, has been assigned to bridging ≡Si(OH)Al≡ groups (the Brønsted sites), which are the strongest acid sites located in the supercage of the zeolite. Those of lower (LF)OH frequency, at 3530–3580 cm^{-1}, were assigned to groups located in the zeolite beta cage (7–9).

CO adsorption at low temperatures results in the formation of the –OH––CO complex, with bands in two important regions of spectrum; 1, the perturbed –OH groups generate broad bands from 3660 to 3210 cm^{-1}, whose position depends on proton strength and, 2, the frequency of the characteristic CO stretching bands between 2143 and 2181 cm^{-1}, also depends on the strength of the acid site (8). CO adsorbed on strong Lewis sites produces bands between 2240 and 2200 cm^{-1}, due to CO stretching coordinated with the aluminum cation Al^{3+} in the structure and in nonframework position (12).

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This appears to be the first investigation of the acidity of two types of commercial Y zeolites as a function of deactivation conditions normally found in the FCC regenerator. Two types of Y zeolites were used in this study, whose acids sites were studied by FTIR CO adsorption at 77 K.

2. EXPERIMENTAL

2.1. Materials

This study was carried out with two commercial USY zeolites provided by W. R. Grace (see Table 1). The USY 1 zeolite is characterized by a unit cell size (UCS) of 24.52 Å and a high concentration of extraframework aluminum species because it was treated with steam at 823 K. The USY 2 zeolite is obtained from the USY 1 using an additional treatment with steam at the same temperature and subsequent removal of the extraframework aluminum with NH_4SO_4/H_2SO_4 at a pH of 2.9 (19). This zeolite has a UCS of 24.32 Å. The high-purity CO used (99.999%) was obtained from Mathesson & Co. Any trace of water in the CO was removed using a liquid nitrogen trap in the injection system of the FTIR cell.

2.2. Methods

The stainless-steel Dewar cell used in the present work to study the IR spectra of adsorbed CO at liquid nitrogen temperature was described elsewhere (13). The cell is connected to a quartz reactor and a high-vacuum system reaching pressures from 10^{-6} to 10^{-7} Torr (1 Torr = 133.3 N m^{-2}). The cell allows the degasification of the sample and different treatments with temperatures of up to 923 K. To simulate the deactivation conditions of the commercial process in the laboratory, the zeolites were deactivated in a fixed-bed reactor in an dry air and in an atmosphere of 40% air–steam, at 1061 K for 5 h.

Zeolite samples were pressed into 10 mg · cm^{-2} self-supporting pellets. To remove water and to eliminate any organic impurities the pellets were heated in a vacuum (10^{-6} Torr) at 623 K for several hours. The "fresh" zeolite was subject only to these conditions. The sample was cooled to the temperature of liquid nitrogen and the spectrum was measured before CO adsorption. CO was dosed at pressures from 0.05 to 9.5 Torr. To reduce the temperature gradient across the sample and improve its thermal contact at 77 K, about 0.8 Torr of He gas was admitted into the sample compartment of the cell before recording spectra at 77 K. To obtain a new spectrum at higher CO pressures, the zeolite was thoroughly cleaned and the new CO concentration was admitted. The amount of the adsorbed molecules was calculated from the gas pressure drop in the known volume of the gas-handling manifold. The spectra were obtained with a Nicolet FTIR 510 Instrument at 4-cm^{-1} spectral resolution by coadding 128–1024 scans, depending on the spectral range studied. The spectra were handled using the Grams 32 software. The absorbance of samples increased from ca. 1 at 1500 cm^{-1} to 2 at 4000 cm^{-1}, due to the scattering. To eliminate this background absorption in the spectrum of adsorbed CO, the spectrum of the sample before adsorption was subtracted in the entire –OH region. Baseline correction proceeded. The deconvolution of each spectrum was made using the second-derivative approach.

3. RESULTS AND DISCUSSION

3.1. The USY 1 Zeolite

This zeolite was analyzed as follows: **1**, "fresh"; **2**, deactivated at 1061 K in a fixed-bed reactor for 5 h in a dry air atmosphere; and **3**, deactivated at 1061 K with an air–steam mixture for 5 h (Fig. 1). The IR spectrum of this type of zeolite is quite complex. The deconvolution of the spectrum (Fig. 2) shows a series of superposed bands that correspond to the following –OH groups: **1**, ≡Si–OH groups located between 3746 and 3730 cm^{-1}; **2**, –OH groups in extraframework aluminum species at 3700 and 3675 cm^{-1} (14); **3**, (HF)OH groups at 3639 and 3600 cm^{-1} located in the supercage (6); and **4**, a very broad band at 3555 cm^{-1} assigned to the (LF)OH groups located in small cavity (6). It can be observed that the greatest concentration of these zeolite –OH groups is located on the extraframework aluminum species between 3700 and 3675 cm^{-1}.

Cairon *et al.* (8) studied a Y zeolite treated with steam at 860 K whose extraframework aluminum was partially removed with aqueous HCl. There is no band in the spectrum at 3700 cm^{-1} and a small band is found at 3675 cm^{-1}. CO adsorption produces two bands of perturbed –OH groups, at 3210 and 3290 cm^{-1}, associated with the bands at 3602 and 3633 cm^{-1} (HF). Simultaneously, bands were
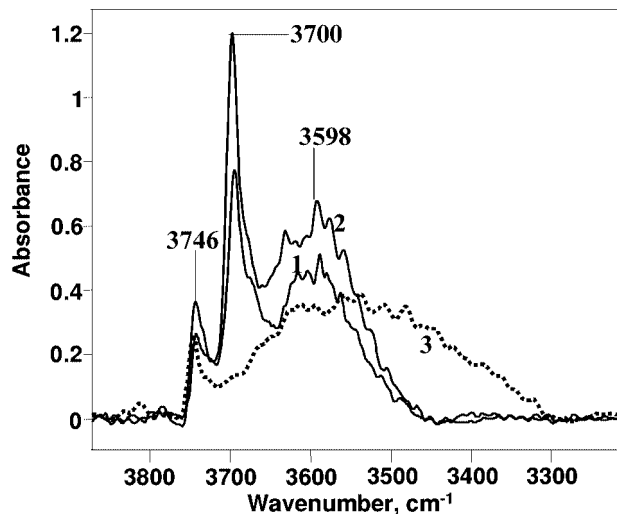

FIG. 1. IR spectra of USY 1 zeolite evacuated at 623 K. **1**, "Fresh"; **2**, deactivated at 1061 K, 5 h, in dry air; **3**, deactivated at 1061 K, 5 h, in air containing ~40% steam.
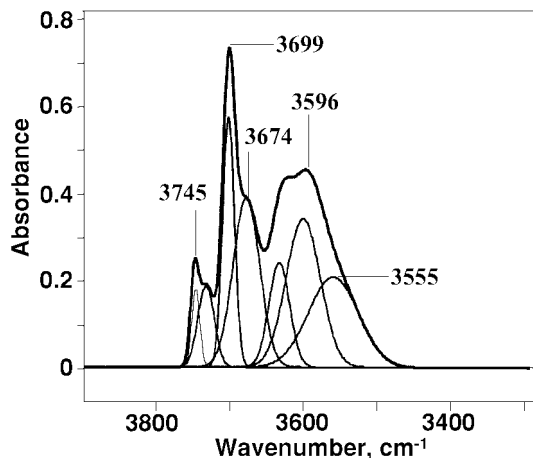
FIG. 2. IR spectrum of fresh USY 1 zeolite; deconvolution of the –OH bands.

FIG. 4. Changes in the IR spectrum of USY 1 zeolite after adsorption of 0.67 (**1**), 2.4 (**2**), 3.5 (**3**), and 6.1 (**4**) μmol $\cdot$ mg^{-1} of CO at 77 K. Absorption of the sample before CO addition is subtracted.

found at 3425 and 3475 cm^{-1}, the latter being associated with the band at 3675 cm^{-1}. These bands were associated with ν_{CO} vibrations at 2179, 2171, and 2164 cm^{-1}, respectively.

The –OH region of our USY 1 zeolite spectrum is much more complex than that obtained by Cairon *et al.* due to the relatively high concentration of extraframework aluminum species, the –OH groups vibrating in these positions, and the presence of Na$^+$ ions. CO adsorption (Fig. 3) shows ν_{CO} at 2178 cm^{-1}, asymmetric to lower frequency with a shoulder a 2173 cm^{-1}. These two bands are associated with those at 3368 and 3470 cm^{-1} for the –OH–CO complex (Fig. 4). The CO band moves toward lower frequencies by increasing CO concentration. Echoufi and Gélin (6) assigned the band at 3355 cm^{-1} with the perturbed (HF)OH groups at
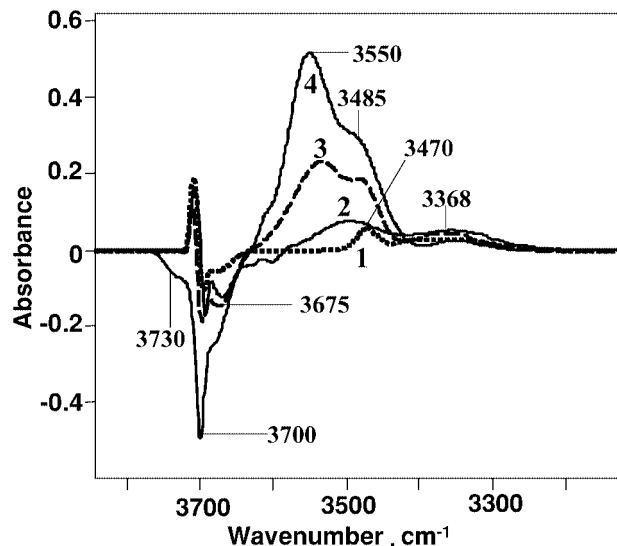
3640 cm^{-1}. The presence of the band at 3368 cm^{-1} may be assigned to the same perturbed –OH groups. Nevertheless, their concentration is relatively low, or they are blocked by the presence of –OH groups in extraframework aluminum species. Since this zeolite has a certain concentration of Na$^+$ ions, the band at 2173 cm^{-1} may be influenced by the presence of this cation (7, 10, 15).

After subtracting the spectrum before CO adsorption is subtracted (Fig. 4), bands are found at 3550 and 3485 cm^{-1} (spectrum **4**), associated with those of unperturbed hydroxyls at 3700 and 3675 cm^{-1} and with ν_{CO} at 2168 and 2162 cm^{-1}, respectively. These series of bands are very similar to those observed in the study carried out on alumina (16) obtained by others with an alumina–silica sample (8) and should be due to the fact that the ν_{OH} group at 3675 cm^{-1} is slightly more acid than the ν_{OH} group at 3700 cm^{-1}. There is no band at 3660 cm^{-1} of the $\equiv$Si–OH––CO complex, nor a ν_{CO} at 2158 cm^{-1}, which raises the question of whether these sites are accessible, whether they are blocked by the high concentration of –OH groups on extraframework aluminum species, and whether it is necessary to work at higher CO pressure. This is why the negative shoulder at 3730 cm^{-1} cannot be associated with these groups, but rather must be associated with alumina–silica complexes. The USY 1 zeolite deactivated at 1061 K in a dry air atmosphere has the same type of bands as the fresh zeolite.

The ν_{CO} between 2200 and 2150 cm^{-1} shows only a broad band. On the other hand, the perturbed (HF)OH groups for the stronger acid sites produces ν_{OH-CO} of over 3300 cm^{-1}, indicating that its acidic strength is not very high. The Si/Al ratio and the ^{29}Si MAS NMR spectra (not shown) mainly
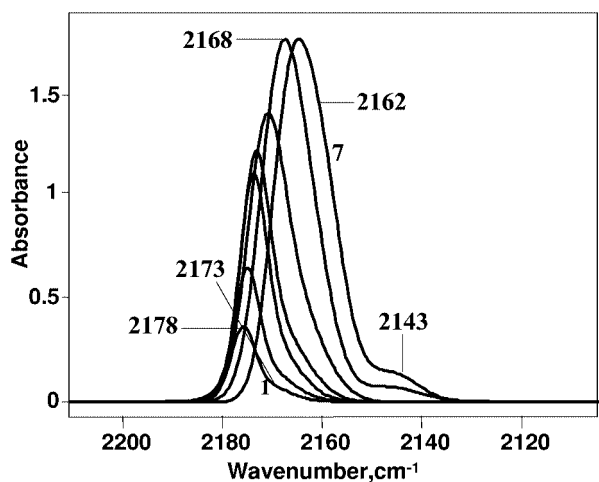

FIG. 3. IR spectrum of fresh USY 1 zeolite after adsorption of CO at 77 K and concentrations between 0.32 (**1**) and 6.03 (**7**) μmol $\cdot$ mg^{-1}. The spectrum of the sample before adsorption is subtracted.

show $\equiv$Si(1Al), $\equiv$Si(2Al), and $\equiv$Si(3Al) and a low concentration of $\equiv$Si(4Al) and $\equiv$Si(0Al). The strong (HF)OH acid sites normally are observed between 2184 and 2179 cm^{-1} (8, 16). The blocking of these strong acid sites by extraframework aluminum species and/or that of the adsorption sites would explain the behavior of this zeolite. On the other hand, the nonperturbed (LF)OH groups may be explained by the nonaccessibility of the CO, due to the presence of extraframework aluminum species at the entrance of the micropores and/or the blocking of these sites.

Finally, we would like describe the effect of high-temperature steam on this zeolite (Fig. 5). A slight decrease in silanol groups is observed. The band at 3700–3675 cm^{-1} disappears completely and a very broad band is formed between 3700 and 3300 cm^{-1}. This spectrum is similar to that of an alumina calcined at high temperature (16–18). CO adsorption generates bands at 2167 and 2141 cm^{-1}. However, the deconvolution (box in Fig. 6) shows four very distinct bands at, 2167, 2160, 2141, and 2134 cm^{-1}, assigned, respectively, as follows: **1**, amorphous alumina–silica similar to that of an alumina calcined at high temperature (16); **2**, silanol groups ($\equiv$Si–OH); **3**, physically adsorbed CO; and **4**, CO adsorbed by the oxygen end on –OH groups (27). Lewis sites are not observed. This may be because the degasification conditions used (3 h at 623 K and 10^{-6} torr) are not sufficient to free the –OH groups adsorbed by hydrating the sample. CO adsorption in the –OH region is very complex and the bands are not very distinct, but the intensity of the main broad band increases, with $\nu_{OH\equiv CO}$ around 3580 cm^{-1}. The silanol groups' perturbed band is observed at 3747 cm^{-1}.

From these results we conclude that steam treatment (similar to what takes place in the commercial FCC regenerator) destroys the strong acid sites of the zeolite. It
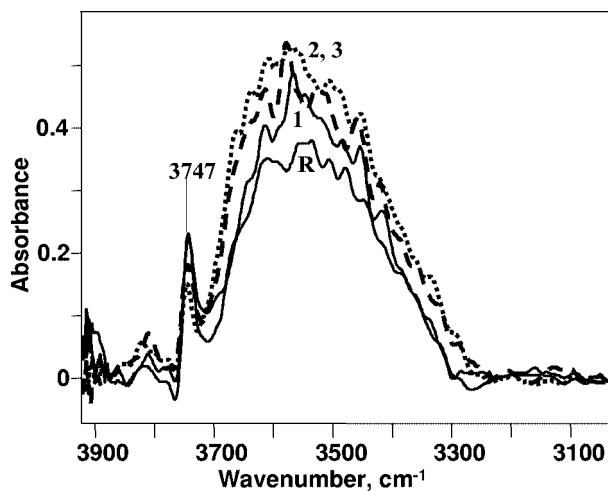

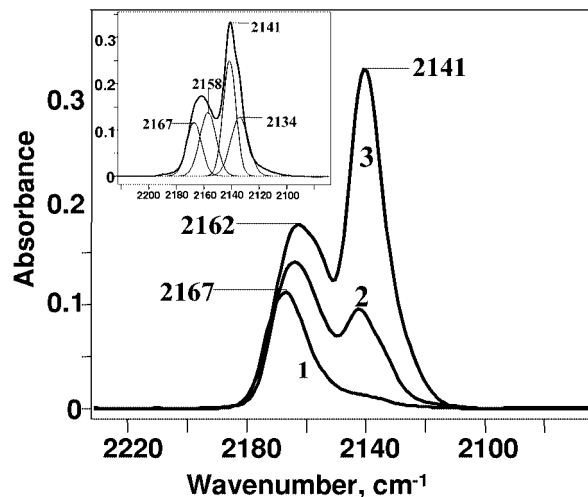**FIG. 6.** IR spectrum of USY 1 zeolite deactivated at 1061 K, 5 h, in ~40% air–steam mixture. CO concentration: **1**, 0.22; **2**, 0.45; and **3**, 1.35 μmol · mg^{-1}. Absorption of the sample before CO addition is subtracted.

generates a series of amorphous nonstructural species similar to those of an alumina–silica calcined at high temperatures. It is also possible that the remaining strong acid sites are blocked by the amorphous species generated during steam treatment. Peters and co-workers (19) state that during the use of an FCC catalyst, hydrothermal dealumination results in removal of as much as 90% or more of the tetrahedrally coordinated aluminum atoms from the zeolite framework. The decrease in the cell unit dimension from 24.52 to 24.34 Å would explain the destruction of strong acid sites and the zeolite dealumination.

3.2. The USY 2 Zeolite

This zeolite was analyzed as follows: **1**,"fresh", and **2**, deactivated at 1061 K in a fixed-bed reactor for 5 h in a dry air atmosphere (Fig. 7). These spectra are quite simple and are typical of a zeolite with few extraframework aluminum species, in which $\equiv$Si–OH bands appears at 3740 cm^{-1}, (HF)OH at 3628 cm^{-1}, and (LF)OH at 3550 cm^{-1}. Using the integral area of each of these bands (normalized at 10 mg · cm^{-2}) as a measurement of the –OH group population, we found that thermal treatment at 1061 K removes 39% of the $\equiv$Si–OH groups (band from 3750 to 3700 cm^{-1}), 55% of the (HF)OH groups (band from 3660 to 3585 cm^{-1}), and 84% of the (LF)OH groups (band from 3585 to 3450 cm^{-1}). Considering that the amount of zeolite in the pellet for the thermally deactivated sample was 14 wt% higher, it is clear in the spectrum that the thermal treatment produces a loss of the different –OH groups and generates new –OH species. Comparing the spectral differences (Fig. 7) and the data in Table 1, it can be concluded that thermal treatment at 1061 K considerably decreases the zeolite –OH groups without notably modifying other

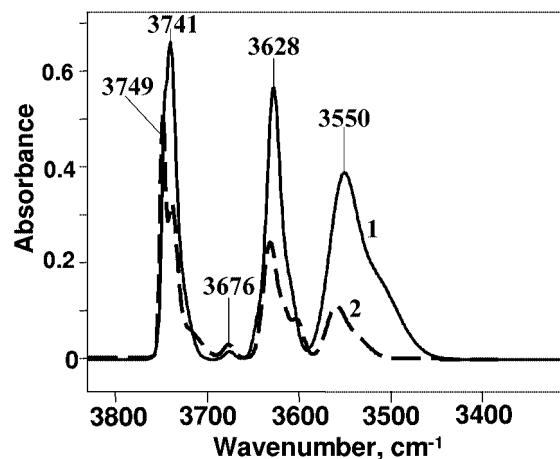**FIG. 5.** IR spectrum of USY 1 zeolite, deactivated at 1061 K, 5 h, in ~40% air–steam mixture (ν_{-OH} bands). **R**, Sample before CO adsorption. **1**, 0.22; **2**, 0.45; and **3**, 1.35 μmol · mg^{-1} of CO.

FIG. 7. IR spectra at 77 K of USY 2 zeolite. **1**, "Fresh" zeolite; **2**, calcined with dry air in a fixed-bed at 1061 K, 5 h.

FIG. 8. IR spectrum of the "fresh" USY 2 zeolite; deconvolution of the –OH bands.

properties, such as UCS, number of Al atoms/cell, and micropore and external area, whose differences are within the standard errors of the analytical methods.

The three bands of fresh USY 2 zeolite are asymmetric. Deconvolution of the first (Fig. 8) suggests three components for the $\equiv$Si–OH band: 3748, 3742, and 3731 cm^{-1}. The (HF)OH band also presents three components, 3646, 3628, and 3611 cm^{-1}, and the (LF)OH band has two components, 3553 and 3522 cm^{-1} (a small band can be observed at 3676 cm^{-1}). The spectrum of the zeolite calcined in dry air at 1061 K shows the same bands with slight displacements (not shown). In agreement with these spectra, thermal dehydroxylation at 1061 K in dry air substantially increases $\equiv$Si–OH concentration at 3749 cm^{-1} (isolated silanols) at the expense of the $\equiv$Si–OH groups at 3742 and 3731 cm^{-1} and slightly increases the –OH groups in the nonframework aluminum.

The –OH groups in the zeolite supercage forming a bridge between two adjacent SiO$_4$ and AlO$_4$ are identified

TABLE 1

Zeolite Properties

	Zeolite USY 1			Zeolite USY 2	
Properties	Fresh	Calcined^a	Steamed^b	Fresh	Calcined^a
UCS (Å$\pm$ 0.002)	24.518	24.514	24.345	24.326	24.301
Al/UCS, *DRX	37	37	18	16	13
Si/Al, DRX	4.2	4.2	11.7	11	13.7
Micropore area (m^2/g)	656	621	606	619	570
Micropore volume (cm^3/g)	0.278	0.263	0.234	0.258	0.235
Mesopore area (m^2/g)	100	91	107	144	132

^{a} At 1061 K, 5 h, dry air.
^{b} At 1061 K, 5 h, 40% steam–air.

by the band at 3628 cm^{-1} (7–9). The band at 3550 cm^{-1} from the (LF)OH groups in small cavities are considered inaccessible for most molecules (6–8, 20). In dealuminated Y zeolites, Zecchina and Otero (12) assigned the band from 3750 to 3745 cm^{-1} to isolated $\equiv$Si–OH groups on the outer surface and the band from 3720 to 3700 cm^{-1} to silanols on inner sites. Janin *et al.* (11), with HY zeolite and dealuminated H–beta zeolite (*BEA), assigned the band 3749–3747 cm^{-1} to the $\equiv$Si–OH groups attached to amorphous silica–alumina debris. These groups are affected by the pyridine at 423 K. The band at 3746–3744 cm^{-1} was assigned to extraframework $\equiv$Si–OH groups attached to silicon-rich amorphous debris (which incidentally does not interact with pyridine at 423 K). Finally, the third component, at 3738–3736 cm^{-1} corresponds to terminal $\equiv$Si–OH groups attached to the framework and that do not interact with pyridine at 423 K either (11).

The fresh USY 2 zeolite (Fig. 9) shows that the first CO molecules (0.065 μmol · mg^{-1}) interact with the (HF)OH groups, producing two bands: ν_{OH} at 3182 and 3242 cm^{-1}. When CO concentration is increased (0.255 μmol · mg^{-1}) most of the (HF)OH groups are perturbed and a new band at 3347 cm^{-1} appears. The 3242 cm^{-1} band is slightly displaced toward 3270–3265 cm^{-1}. When CO is increased (0.520 μmol · mg^{-1}), the middle band at 3265 cm^{-1} continues increasing in intensity and begins saturating $\equiv$Si–OH groups and an asymmetric band appears at 3660 cm^{-1}. There is also a decrease in the intensity of the band at 3550 cm^{-1}, without new bands for the –OH–CO complex.

In the CO stretching region (Fig. 10), Lewis acid sites between 2240 and 2200 cm^{-1} are not observed. The first CO molecules interact with the strongest acid site (HF)OH groups, ν_{CO} at 2183 cm^{-1}, asymmetric to lower frequency and whose deconvolution presents a peak at 2179 cm^{-1}. These two ν_{CO} bands, at 2183 and 2179 cm^{-1}, correspond to
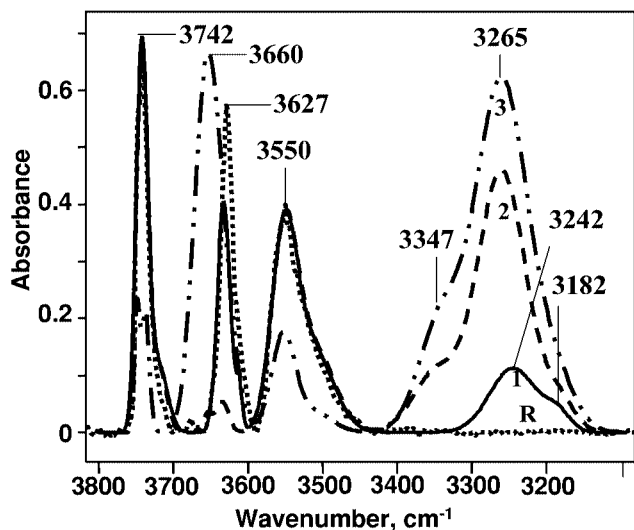
FIG. 9. IR spectrum of "fresh" USY 2 zeolite; CO adsorption at 77 K ($\nu_{-OH=CO}$ bands). **R**, Sample before CO adsorption. CO concentration: **1**, 0.065; **2**, 0.255; **3**, 0.52 μmol · mg^{-1}.

FIG. 11. Changes in the IR spectrum of "fresh" USY 2 zeolite after adsorption of 0.06 (**1**), 0.25 (**2**), and 1.67 (**3**) μmol · mg^{-1} of CO at 77 K. Absorption of the sample before CO addition is subtracted.

ν_{OH--CO} at 3182 and 3242 cm^{-1}, respectively. As CO concentration is increased, the band at 2183 cm^{-1} is slightly displaced, to 2180 cm^{-1}, and the band at 2179 cm^{-1} is displaced to 2172 cm^{-1}. A shoulder appears at 2163 cm^{-1}, associated with the –OH groups at 3347 cm^{-1}. With increasing coverage of the surface this band shifts slightly, to 2159 cm^{-1}, coinciding with the band at 3660 cm^{-1} for the $\equiv$SiOH--CO complex.

To explain the ν_{OH--CO} and ν_{CO} displacement and the decrease in the (LF)OH band intensity, spectrum subtraction was carried out before CO adsorption (Fig. 11). The nega-
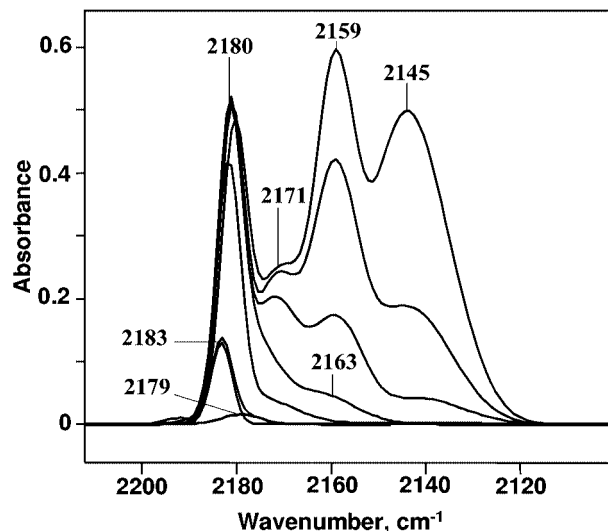
tive band at 3628 cm^{-1} (spectrum **2**) shows the perturbation of the strongest (HF)OH acid sites. The negative band at 3550 cm^{-1} (spectrum **3**) arises from the perturbed (LF)OH band and it is related to the increased intensity of the 3268-cm^{-1} band. The band at 3656 cm^{-1} shows the $\equiv$Si–OH$\equiv$CO complex, related to the negative band at 3741 cm^{-1} and the shoulder at 3725 cm^{-1}. In the CO region, the band at 2183 cm^{-1}, which is displaced to 2180 cm^{-1}, and the initial band at 2179 cm^{-1} are associated with the three (HF) bands (Fig. 12). The shift of the band from 2179 to 2170 cm^{-1} is related to the perturbed LF(OH) groups and the shift of the 2163 band to 2159 cm^{-1} is related to the $\equiv$Si–OH groups. The subtraction of the spectra after

FIG. 10. IR spectrum of "fresh" USY 2 zeolite. CO adsorption at 77 K (ν_{CO} bands); CO concentration between 0.05 and 2.5 μmol · mg^{-1}. Absorption of the sample before CO addition is subtracted.
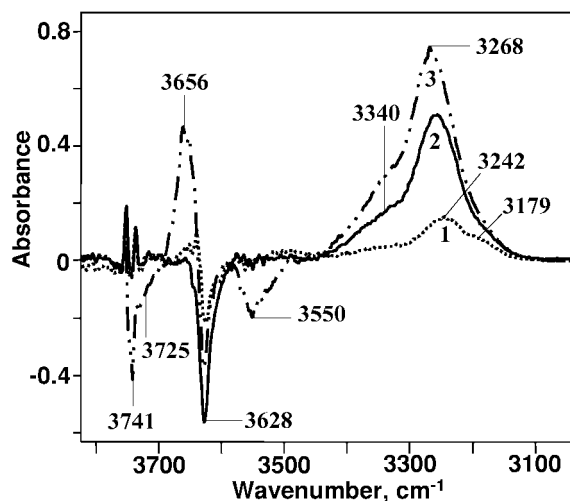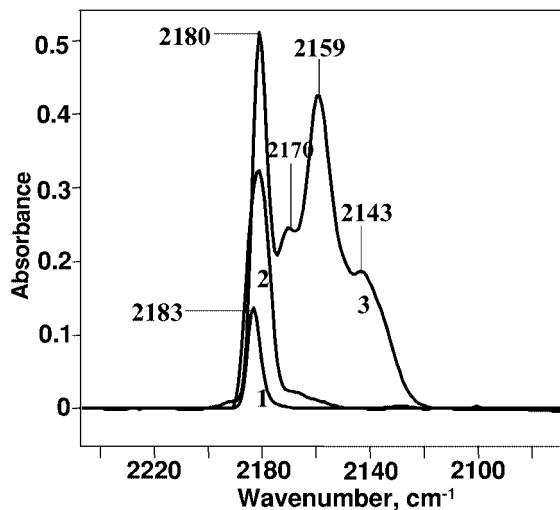

FIG. 12. IR spectrum of "fresh" USY 2 zeolite after adsorption of 0.06 (**1**), 0.25 (**2**), and 1.67 (**3**) μmol · mg^{-1} of CO at 77 K (ν_{CO} bands). Spectrum of the sample before CO adsorption is subtracted.
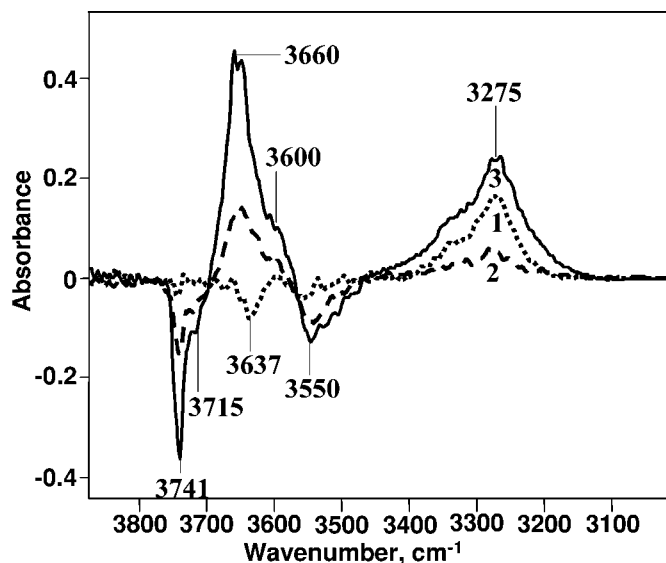
FIG. 13. Changes in the IR spectrum of "fresh" USY 2 zeolite after adsorption of 0.52 (**1**), 1.03 (**2**), and 1.67 (**3**) μmol $\cdot$ mg^{-1} of CO at 77 K. Spectrum after saturating the (HF)OH groups is subtracted at CO concentration of 0.25 (**1**, **3**) and 0.52 (**2**).

saturation of most of the (HF)OH groups helps to identify some important differences (Fig. 13). The small negative band at 3637 cm^{-1} (spectrum **1**) indicates the presence of remaining (HF)OH sites. The perturbation of this group increases the intensity of the bands at 3275 cm^{-1} and ν_{CO} at 2179 cm^{-1} (Fig. 14). The small band at 3550 cm^{-1} suggests that this CO concentration (1.03 μmol $\cdot$ mg^{-1}) perturbs the (LF)OH groups. Although no additional bands
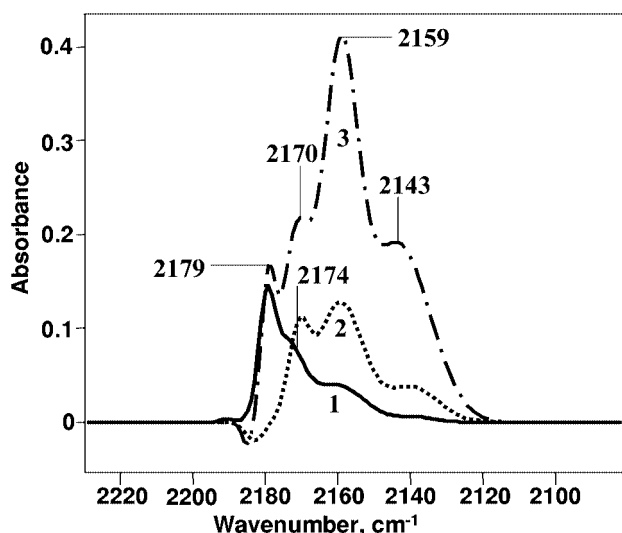

FIG. 14. IR spectrum of "fresh" USY 2 zeolite after adsorption of 0.52 (**1**), 1.03 (**2**), and 1.67 (**3**) μmol $\cdot$ mg^{-1} of CO. Spectrum after saturating the (HF)OH is subtracted at CO concentration of 0.25 (**1**, **3**) and 0.52 (**2**) (ν_{CO} bands).

are observed for the –OH––CO complex, there is a ν_{CO} shoulder at 2174 cm^{-1}. The (LF)OH groups and $\equiv$Si–OH groups change simultaneously. With these results, it can be concluded that the (LF)OH groups in this zeolite are accessible, shifting the $\nu_{OH––CO}$ from 3268 to 3275 cm^{-1} and ν_{CO} from 2174 to 2170 cm^{-1}. The disappearance of the 2179 cm^{-1} peak confirms that the strong (HF)OH acid sites were completely perturbed.

The perturbation of (LF)OH groups has been reported by other authors (6, 8, 21). Maache *et al.* (21), in a study on H–mordenite dealuminated with steam and treated with HNO$_3$, reported the perturbation of the (LF)OH groups, whose CO adsorption produces $\nu_{OH––CO}$ at 3325 cm^{-1} and ν_{CO} at 2169 cm^{-1}. The fresh USY 2 zeolite allows CO adsorption in some (LF)OH groups. Subtracting this spectrum leads to the conclusion that after saturating the (HF)OH groups are saturated, the perturbation of the (LF)OH groups begins, generating a negative band at 3550 cm^{-1}.

This is an important result because the commercial production of the USY zeolite has a relatively high-temperature steam treatment, which produces extraframework aluminum. Peters and co-workers (19) state that during this dealumination process, bonds to aluminum are replaced by silicon associated with hydroxyl groups and these silanol groups are related to the formation of a secondary mesopore surface and other defective structures resulting from the loss of aluminum from the framework (19). The formation of this secondary porosity allows a small molecule such as CO to access the –OH groups in the small cavities. Diffusion of the reactants and accessibility to the acid sites can be improved by removing this extraframework aluminum, because this type of aluminum may block the entrance to these pores and/or somehow block the adsorption site. CO adsorption on these sites generates bands for the –OH––CO complex at the same frequencies as those of the (HF)OH groups. However, these sites are less acidic and, thus, displace the ν_{OH} and ν_{CO} bands toward higher and lower frequencies, respectively. As mentioned above, this displacement would be related to the heterogeneity of the acid sites on the surface. The physical CO adsorption produces the band at 2143 cm^{-1}.

The USY 2 zeolite deactivated in dry air at 1061 K (Fig. 15) shows the same fresh zeolite bands for ν_{OH} and ν_{CO}, along with a new band at 3465 cm^{-1}, which will be analyzed subsequently. Unlike the fresh zeolite (spectra **3** and **4**), where all of the (HF)OH groups have been neutralized and the perturbation of the $\equiv$Si–OH groups has begun ($\nu_{OH––CO}$ at 3658 cm^{-1}), the bands between 3400 and 3100 cm^{-1} show the same intensity, indicating that the few (LF)OH groups left after treatment with dry air at 1061 K are not accessible or are blocked by the species generated during deactivation. The main difference is the presence of Lewis acid sites for low CO concentrations, ν_{CO} at 2220, 2215, and 2206 cm^{-1} (box in Fig. 16). Their
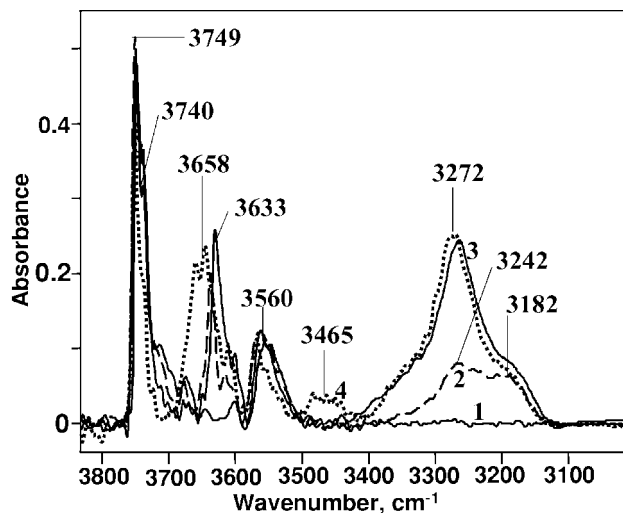
FIG. 15. IR spectrum of USY 2 zeolite deactivated in a fixed bed with dry air at 1061 K, 5 h. CO adsorption at 77 K ($\nu_{OH=CO}$ bands). Spectrum before CO adsorption (**1**) and after addition of 0.100 (**2**), 0.242 (**3**), and 1.59 (**4**) μmol·mg^{-1} of CO.

FIG. 17. IR spectrum of USY 2 zeolite deactivated in dry air at 1061 K, 5 h, after adsorption of 0.10 (**1**) and 0.24 (**2**) μmol·mg^{-1} of CO, subtracting the sample before CO addition. Spectrum subtracted after saturating HF(OH) groups. CO concentration: 0.49–0.10 (**3**) and 1.19–0.24 (**4**) μmol·mg^{-1} ($\nu_{OH=CO}$ bands).

concentration is low and they are the ones that adsorb the first CO molecules.

The subtraction spectra allows a more precise assignment of the bands (Figs. 17 and 18). The same ν_{OH} and ν_{CO} bands of the fresh zeolite are observed at low concentrations (spectra **1** and **2**). By subtraction of the spectrum after saturation of the (HF)OH groups (spectra **3** and **4**), the band at 3185 cm^{-1} disappears and the one at 3272 cm^{-1} decreases considerably. This indicates that the first CO molecules

completely perturb the strongest acid sites. There is no negative band at 3550 cm^{-1}, corroborating the fact that the remaining (LF)OH groups are not accessible and/or they are blocked by the species generated during treatment. The negative band at 3675 cm^{-1} shows the –OH groups on extraframework aluminum species producing ν_{OH} at
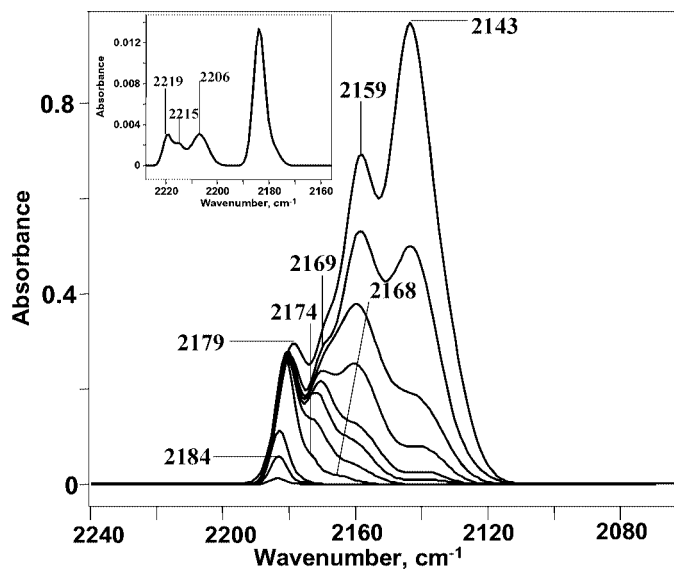

FIG. 16. IR spectrum of USY 2 zeolite deactivated in a fixed bed with dry air at 1061 K, 5 h. CO adsorption at 77 K (ν_{CO} bands). CO concentration between 0.02 and 3.5 μmol·mg^{-1}.
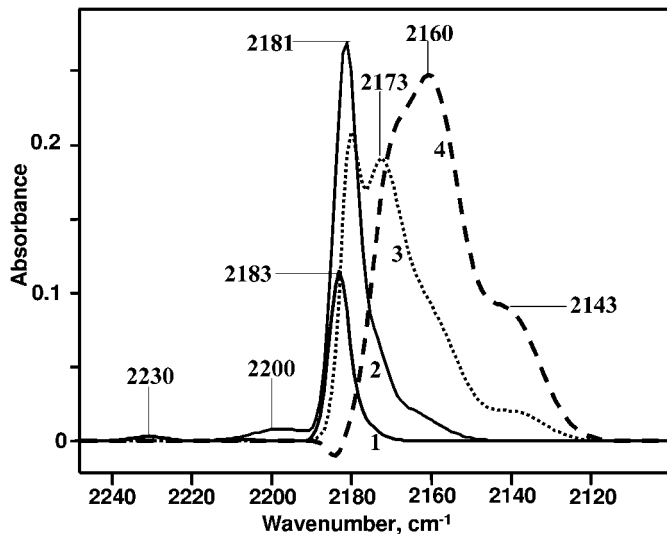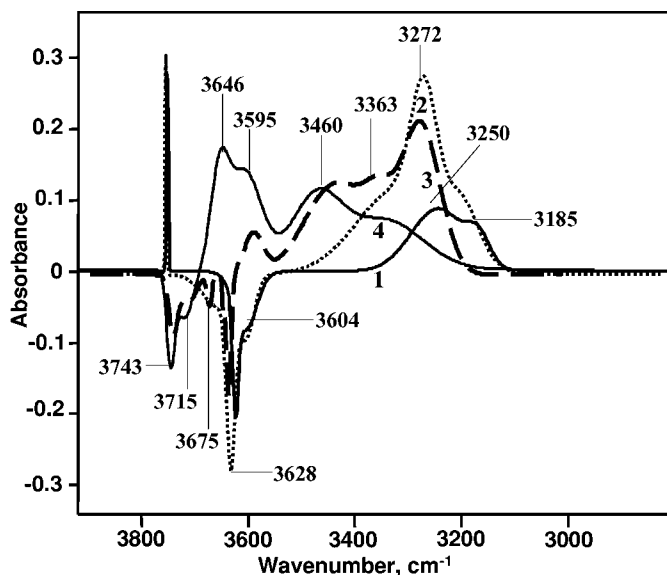

FIG. 18. IR spectrum of USY 2 zeolite deactivated in dry air at 1061 K, 5 h, after adsorption of 0.10 (**1**) and 0.24 (**2**) μmol·mg^{-1} of CO, subtracting the sample before CO addition. Spectrum subtracted after saturating the (HF)OH groups. CO concentration 0.49–0.10 (**3**) and 1.19–0.24 (**4**) μmol·mg^{-1} (ν_{CO} bands).

3465 cm^{-1} and ν_{CO} at 2173 cm^{-1}. Cairon *et al.* (8) reported ν_{OH--CO} bands at 3410 and 3465 cm^{-1} in steam-treated Y zeolites associated with a ν_{CO} band at 2172 cm^{-1} and assigned to –OH groups in extraframework positions. The negative bands at 3743 and 3715 cm^{-1} correspond to the ≡Si–OH groups, producing ν_{OH} at 3646 and 3595 cm^{-1}. The presence of these two silanol groups explains the movement of the ν_{CO} band from 2163 to 2159 cm^{-1}.

In CO adsorption studies in dealuminated Y zeolites, the literature reports the presence of acid sites (6, 8, 9, 12, 15, 22, 23). It is generally accepted that the observed upward shift of the ν_{CO} band relative to the gas-phase CO absorption can be ascribed to a strengthening of the C≡O bond resulting from the removal of electron density from the slightly antibonding CO 5σ orbital by the electropositive hydrogen of the hydroxyl group (6, 26). The acidic character of the (HF)OH groups of the Y zeolites compared with silica ≡SiOH groups supports this statement. The CO hydrogen bonded with the USY 2 (HF)OH produces an upward shift of 40 cm^{-1}, while with the silica ≡SiOH the shift is 15 cm^{-1} (band at 2158 cm^{-1}) (16). Similarly, the ν_{OH} vibration of the USY 2 (HF)OH groups interacting with CO is more strongly affected than for that with the silica. According to Echoufi and Gélin (6), the downward shift of ν_{OH} should be a more sensitive probe of the acidic character of the hydroxyls because of the large observed shifts compared with the ν_{CO} shifts. In this study, the USY 2 ν_{OH} at 3628 cm^{-1} is observed to shift to 3182 cm^{-1} (446 cm^{-1}), while the silica ≡SiOH groups (not shown) (16) shift from 3747 to 3660 cm^{-1} (~90 cm^{-1}).

The strongest acid site reported by the literature is ν_{OH--CO} at 3210 cm^{-1}, with a proton affinity of 1107 kJ mol^{-1} and a ν_{CO} at 2181 cm^{-1} (22). Our work has found a stronger site with a $\nu_{OH≡CO}$ at 3182–3177 cm^{-1}, a proton affinity of 1085 kJ mol^{-1}, and a ν_{CO} at 2183 cm^{-1}. The proton affinity of different bridging hydroxyls groups in several zeolites between 1204 and 1139 kJ mol^{-1} was reported by Kubelková *et al.* (22), who consider that as proton affinity decreases, the acid site is stronger. Based on these interpretations, it can be concluded that this site is quite strong and that it has –OH groups attached to tetracoordinated silicon and aluminum. Peters and co-workers (19), in a ^{1}H/^{29}Si CP/MAS study of a Y zeolite dealuminated with steam and washed with a (NH$_4$)$_2$SO$_4$/H$_2$SO$_4$ solution, reported the presence of four bands assigned to the following groups: Si(OSi)$_4$, Si(OSi)$_3$(OAl), Si(OSi)(OAl)$_2$OH, and Si(OSi)$_2$(OAl)OH. Considering that the USY 2 zeolite, unlike one used by Peters and co-workers, had an additional steam treatment, it could be predicted that this zeolite contains most –OH groups at 0-NNN and 1-NNN sites. The latter are less acidic and this would explain the displacement of the bands mentioned above (23, 24).

When CO concentration is increased, the frequencies of the stronger –OH groups are displaced toward higher fre-

quencies as their coverage is increased, reaching a maximum of about 3200 and 3272 cm^{-1}. Also, ν_{CO} at 2184 and 2179 cm^{-1} are shifted to lower frequencies, with a minimum of 2180 and 2170 cm^{-1}. This band displacement can be explained as the result of the interaction of CO molecules adsorbed on acid sites with different strengths. That is, it can be attributed to the heterogeneity of the zeolite's acid site strength. The –OH band shift measured for very low coverage characterizes the acid strength of the most acidic bridging hydroxyls, whereas the value obtained for complete coverage can be considered to correspond to mean acidity of bridging hydroxyls in the framework (22).

4. ACID SITES CONCENTRATION

The surface concentration can be measured, assuming that the Beer–Lambert law is applicable to the bonds of adsorbed CO molecule and the different acid site (25); i.e.,

$$A = A_o \cdot C_s \cdot \rho,$$

where A is the observed integral absorption for the analytical band in cm^{-1}, A_o is the integral intensity of the band for a concentration of 10^{-6} mol liter^{-1}, C_s is the concentration of surface centers in micromoles per milligram of sample, and ρ is the amount of sample in milligrams exposed to 1 cm^2 of a cross section of the light beam. The $C_s\rho$ product corresponds to micro-moles of adsorbate in 1 cm^2 of a cross section of the light beam. The slope of the A vs $C_s\rho$ plot (Fig. 19) corresponds to the value of A_o, that is, the molar absorption coefficient (ε). With the volumetric method (25), a plot was obtained for the different bands of both zeolites and for a silica sample. Table 2 shows the different values found for each of the bands studied.

Unfortunately the A_o coefficient has been obtained only in a few cases. Gruver *et al.* (9) report a value of 0.95 ± 0.11 μmol^{-1} · cm for the ν_{CO} between 2177 and 2173 cm^{-1} assigned to –OH groups attached with silicon and aluminum tetrahedrons in the USY zeolite. Here the USY 1
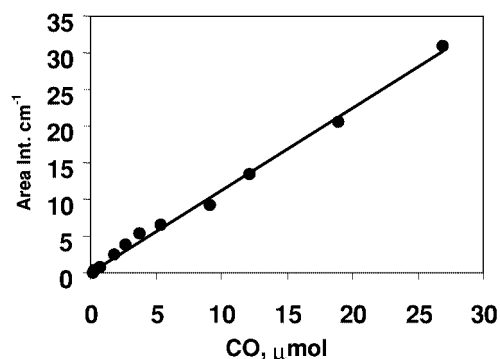

FIG. 19. Molar integrated absorption coefficient. Peak integrated area vs CO concentration (micromoles) for a USY 2 deactivated at 1061 K, 5 h, in dry air, ν_{CO} bands between 2184 and 2135 cm^{-1}.

TABLE 2

Molar Integrated Absorption Coefficient for Silica and Zeolite Samples

Material	ε (μmol$^{-1}\cdot$cm)							Perturbed band (cm^{-1})	
	νCO bands (cm^{-1})			ν(OH–CO) bands (cm^{-1})				HF(OH)	LF(OH)
	2183–2162	2178–2154	2158–2136	3333–3178	3360–3550	3660–3600	3700–3674	3649–3600^a	3550–3500^b
Silica			1.4			7.0			
USY 1		1.0			1.4		0.4		
USY 2	1.4			14.0				5.2	1.7

^{a} HF(OH).
^{b} LF(OH).

zeolite with ν_{CO} between 2178 and 2154 cm^{-1} obtained a value of 1.0 μmol$^{-1}\cdot$cm. The USY 2 zeolite between 2184 and 2162 cm^{-1} had a value of 1.4 μmol$^{-1}\cdot$cm, and between 2162 and 2145 cm^{-1}, the coefficient changed slightly, to 1.1 μmol$^{-1}\cdot$cm. The change in slope is possibly due to the perturbed weaker acid sites. These values coincide with those reported, although the calculation methods used were different. Cairon *et al.* (8) used an average value of 3.0 μmol$^{-1}\cdot$cm for $\varepsilon_{(SiOH)}$ to calculate $\varepsilon_{(CO)}$ for the band at 2157 cm^{-1}, obtaining a value of 2.7 μmol$^{-1}\cdot$cm in an alumina–silica sample. In this study, with a silica sample the same band yielded a value of 1.4 μmol$^{-1}\cdot$cm. For the negative band between 3750 and 3700 cm^{-1}, a value of 2.3 μmol$^{-1}\cdot$cm was obtained. Cairon *et al.* (8) reported $\varepsilon_{(HF)OH}$ of 7.5 and 4.7 μmol$^{-1}\cdot$cm for the $\varepsilon_{(3602)OH}$. We obtained a value of 5.2 μmol$^{-1}\cdot$cm for the (HF)OH between 3649 and 3600 cm^{-1}.

Using the coefficients reported in Table 2 and the areas of each of the bands, we calculated the concentrations of the different acids groups in the zeolites with an estimated error of 15%. The fresh USY 2 zeolite showed a concentration of 0.58 μmol$\cdot$mg^{-1} for the $\equiv$Si–OH groups and with ε_{SiOH} it was 2.3 μmol$^{-1}\cdot$cm. The same groups calculated with the $\equiv$SiOH=CO band between 3660 and 3600 cm^{-1} have a concentration of 0.41 and 0.48 μmol$\cdot$mg^{-1} with a negative band from 3747 to 3727 cm^{-1}. Considering an average of 0.44 μmol$\cdot$mg^{-1} and a concentration of 0.58 μmol$\cdot$mg^{-1} for the $\equiv$Si–OH groups, the CO in testing conditions has perturbed an average of 77% of these groups. However, a result of 0.37 μmol$\cdot$mg^{-1} is obtained by using the area of the band at 2157 cm^{-1}, equivalent to 64% of the existing $\equiv$Si–OH groups. This result leads to the recommendation of using the $\equiv$SiOH=CO band at 3660 cm^{-1} to calculate the concentration of $\equiv$Si–OH groups. The USY 2 zeolite showed a content of 0.26 μmol$\cdot$mg^{-1} for (HF)OH groups. This was calculated for the band from 3647 to 3600 cm^{-1} and with $\varepsilon_{HF(OH)}$ of 5.2 μmol$^{-1}\cdot$cm. These acid sites are distributed by 9, 54, and 37% for bands at 3645, 3627, and 3610 cm^{-1}, respectively (Fig. 8). The same calculation, but using a ν_{OH--CO} between 3180 and 3347 cm^{-1} and ε of 14.0 μmol$^{-1}\cdot$cm, and assuming that at a CO con-

centration of 0.255 μmol$\cdot$mg^{-1} all of the HF(OH) are disturbed, yields 0.35 μmol$\cdot$mg^{-1}. This value is very close to the previous one. The difference may be due to the contribution of LF(OH) groups and/or to the different adsorption coefficient used. Nevertheless, when considering a ν_{CO} between 2182 and 2170 cm^{-1} and ε of 1.4 μmol$^{-1}\cdot$cm, a concentration of 0.27 μmol$\cdot$mg^{-1} is obtained. When considering the 3180- to 3400-cm^{-1} band, a concentration of 0.54 μmol$\cdot$mg^{-1} is obtained. The difference is attributed to the perturbed LF(OH) groups. The total number of LF(OH) groups is 1.28 μmol$\cdot$mg^{-1}, calculated with $\varepsilon_{LF(OH)}$ of 1.7 μmol$^{-1}\cdot$cm. The concentration of the (LF)OH groups that interact with the CO, calculated with a negative band at 3550 cm^{-1}, is 0.74 μmol$\cdot$mg^{-1}, equivalent to 58% of these groups, whose differences can explain that not all of these groups are accessible to CO molecule or that it is necessary to use a higher CO pressure.

The following concentrations are obtained for the USY 2 zeolite, calcined at 1061 K in dry air for the different –OH groups: $\equiv$Si–OH group, 0.38 μmol$\cdot$mg^{-1}; (HF)OH, 0.13 μmol$\cdot$mg^{-1}; and (LF)OH groups, 0.22 μmol$\cdot$mg^{-1}. The same HF(OH) groups, calculated with the bands between 3336–3199 and 2180–2168 cm^{-1}, report a value of 0.18 μmol$\cdot$mg^{-1}. These results permit the calculation of the dehydroxylation produced by the thermal treatment. The HF(OH) groups are reduced by 52%, the LF(OH) groups by 82%, and the silanol groups by 34%. A concentration of 0.34 μmol$\cdot$mg^{-1} was obtained with the fresh USY 1 zeolite for $\equiv$Si–OH groups, 5.3 μmol$\cdot$mg^{-1} for extraframework aluminum species (bands at 3700 and 3675 cm^{-1}), and 0.42 μmol$\cdot$mg^{-1} for (HF)OH groups (bands at 3639 and 3604 cm^{-1}), calculations that were based on the same $\varepsilon_{(HF)OH}$ as for the USY 2 zeolite. Calculating these results for the maximum CO concentration (6.13 μmol$\cdot$mg^{-1}) and using the bands between 3550 and 3350 cm^{-1} (spectrum **4**, Fig. 4) we obtain a total concentration of 4.3 μmol$\cdot$mg^{-1}. This is equivalent to 81% of the total number of OH groups in extraframework aluminum. Using the negative band between 3700 and 3675 cm^{-1}, we obtain a concentration of 4.1 and 3.7 μmol$\cdot$mg^{-1} for the ν_{CO} between 2170 and 2162 cm^{-1} (spectrum **7**, Fig. 3). Considering these results

and the detailed analysis of the two zeolite spectra, we conclude that CO adsorption on the USY 1 zeolite, characterized by a relatively high concentration of extraframework aluminum, takes place preferentially on the –OH groups attached to these species, which may be blocking the accessibility of the stronger HF(OH) acid sites. The total number of –OH groups with a band from 2170 to 2162 cm^{-1} for the USY 1 zeolite treated at 1061 K 5 h in dry air was 4.9 and 5.3 μmol · mg^{-1} for bands from 3550 to 3350 cm^{-1}, results very similar to those obtained for the fresh zeolite, indicating that the USY 1 zeolite is more resistant to thermal treatment at high temperature than the USY 2 zeolite with nonframework aluminum and that the mobility of the USY 2 proton is higher.

5. CONCLUSIONS

FTIR and CO adsorption at low temperatures is an excellent technique for studing the nature and concentration of the different –OH groups in acid solids. It is necessary to study three important zones of the spectrum: –OH stretching bands between 3800 and 3500 cm^{-1}, the bands of the perturbed –OH, $\nu_{OH\equiv CO}$ complex between 3700 and 3100 cm^{-1}, and the ν_{CO} bond stretching between 2240 and 2130 cm^{-1}. Y zeolites with high extraframework aluminum concentrations have very complex and very difficult to analyze FTIR spectra, while Y zeolites without this type of –OH groups have quite simple spectra, with three typical and very distinct bands: $\equiv$Si–OH groups at 3747 cm^{-1}, (HF)OH at 3628 cm^{-1}, and (LF)OH at 3550 cm^{-1}. Steam-treated Y zeolites with extraframework aluminum removed by any known method give more access to the CO molecule, which makes possible the coordination to (LF)OH groups. Thermal treatment in dry air and temperatures of 1061 K decreases the concentration of –OH groups in zeolites previously treoted with steam. In this case, the (LF)OH groups are mostly affected. After this treatment, the remaining (LF)OH groups are not accessible or they are partially blocked by the species generated. The USY 2 zeolite with a UCS of 24.32 Å and very little extraframework aluminum has a quite strong acid site, ν_{OH} at 3180 cm^{-1}, ν_{CO} at 2183 cm^{-1}, a ΔOH of 443 cm^{-1}, and a proton affinity (PA) of 1084 kJ mol^{-1}, unlike the minimum reported in the literature of 1107 kJ mol^{-1} (22).

The USY 1 zeolite with a UCS of 24.52 Å and a relatively high extralattice aluminum content has ν_{OH-CO} of 3390 cm^{-1}, identifying the most acidic site, ν_{CO} at 2178 cm^{-1}, and a PA of 1200 kJ mol^{-1}, which raises the question of whether or not the strongest sites are blocked. Steam treatment at 1061 K of this zeolite destroys the –OH groups with the highest acidity, including the –OH groups attached with the extralattice aluminum species, leaving –OH groups of low acidity with ν_{CO} stretching at 2171 and 2167 cm^{-1}. The

band of the OH$\equiv$CO bond is difficult to identify on the spectrum; however, by subtracting a spectrum a bands show up at 3585 and 3467 cm^{-1}.

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