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Infrared Spectroscopic Investigations of Carbon Monoxide physically adsorbed on Decationated Y-type Zeolite

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The physical adsorption of CO at low temperature on HY zeolite leads to the formation of three types of physisorbed CO, depending on the CO pressure. At low CO pressure, CO primarily interacts with HF hydroxyls through hydrogen bonding and gives rise to ν_{CO} at 2176 cm^{-1} (species A). Simultaneously, the ν_{OH} vibration of the perturbed hydroxyls is shifted by 298 cm^{-1} toward lower wavenumbers, which provides a measurement of the acid strength of the protons. The saturation of hydroxyl sites is followed by the formation of more weakly physisorbed CO (species C) exhibiting ν_{CO} at 2160 cm^{-1} , tentatively ascribed to CO adsorbed on framework oxygens acting as basic sites. At higher CO pressures, a liquid-like CO phase (species B, $\nu_{\text{CO}} = 2140\text{ cm}^{-1}$) forms extensively, exhibiting hindered rotational behaviour. The progressive formation of OH–CO complexes is accompanied by frequency shifts of all ν_{OH} and ν_{CO} vibrations, whether the corresponding species are directly involved or not in the CO adsorption. In particular, LF hydroxyls, although not interacting with physisorbed CO, experience coverage-dependent downward shifts. These phenomena are demonstrated to correlate better with CO-induced effects than with intrinsic acid strength heterogeneity.

In recent work,¹ IR spectroscopic investigation of the adsorption of CO at low temperature on various protonated zeolites and molecular sieves has been used to characterize the acid strength of the hydroxyl groups. The method was primarily based upon the wide shift of the stretching vibration of the surface hydroxyls hydrogen-bonded with physically adsorbed CO molecules at low temperature. The extent of this perturbation was related to the hydroxyl acid strength for zeolites of various structures and chemical composition. Some additional effects were observed as a function of coverage, which were ascribed to the acid strength heterogeneity of hydroxyls on the basis of theoretical calculations. However, a thorough IR investigation of the physical adsorption of CO onto a silica surface containing isolated OH groups has clearly demonstrated that purely physical effects, such as long-range electrostatic effects and solvent effects, were responsible for significant downward shifts of the OH and CO stretching modes at increasing CO coverages.² Since the pioneering work of Angell and Schaffer,³ studying by IR spectroscopy the adsorption of CO on X- and Y-type zeolites containing various cations, only very few papers were devoted to the investigation of the adsorption of CO on zeolites.^{4–7}

In the present work, we perform a detailed IR investigation of the physical adsorption of CO at low temperature on a protonated Y zeolite (HY) in order to characterize the basic modes of interaction of CO with the zeolite surface. We show that CO primarily interacts with hydroxyl groups located in the large cavities of the zeolite *via* hydrogen bonding, while protons located in the small cavities appear to be inaccessible to CO. An additional type of adsorbed CO was observed, ascribed to CO weakly interacting with the oxygen atoms of the Si–O–Si groups of the structure. At higher CO pressures, a liquid-like CO phase develops, exhibiting hindered rotational behaviour, as observed on silica surfaces. ν_{OH} shifts observed upon CO interaction with hydroxyls can be used to estimate their acidic character. The coverage dependence of the OH and CO stretching frequencies was related to CO-induced effects rather than to an intrinsic acid strength distribution of hydroxyl groups.

Experimental

IR Cell Description

An all-glass IR cell, as shown in Fig. 1, was used. The main advantage of the cell is to allow all kinds of treatments from

100 K up to 900 K: high temperatures are convenient for both catalyst activation and *in situ* IR studies of catalysts under reaction conditions, while low temperatures allow IR physisorption studies. An interesting feature of the cell lies in the design of the all-quartz sample holder. The sample was deposited directly on the CaF_2 plate by spraying of a suspension of the powder sample in ethanol.² Heat conduction was ensured by a CaF_2 window of the same diameter introduced into the sample holder together with the pellet. The temperature of the sample was measured with a chromel–alumel thermocouple inserted between the CaF_2 support and the quartz tube without any cement. The cell was connected to a conventional glass vacuum system allowing a base pressure as low as 10^{-6} Torr,[†] and equipped with a high-precision capacitance gauge measuring up to 10 Torr.

Sample Composition

The H form of Y zeolite was obtained by conventional exchange of NaY (supplied by Union Carbide) in an aqueous solution of ammonium chloride at 353 K, followed by the subsequent decomposition of ammonium ions under vacuum at 623 K. The chemical composition of the resulting solid determined by chemical analysis was found to be: $\text{Na}_{5.7}\text{H}_{49.7}\text{Al}_{55.4}\text{Si}_{136.6}\text{O}_{384}$.

Sample Preparation

The method of sample preparation has been described previously.² Typically, the zeolite was ultrasonically dispersed in ethanol (0.3 g zeolite per 30 cm^3 ethanol). The resulting suspension was then sprayed onto a 18 mm diameter CaF_2 plate maintained at 373 K, until 5–8 mg of sample were deposited onto the plate. The heat conduction through the sample, ensured by the CaF_2 plate, was previously demonstrated to generate temperature gradients across the sample of less than 4 K at liquid-nitrogen temperature.² All the zeolite samples were activated *in situ* up to 623 K under vacuum, following a standard heating procedure consisting of raising the temperature at a rate of 2 K min^{-1} from room temperature up to 623 K. This activation treatment allows the slow decomposition of ammonium ions to form protons without affecting the structure of the zeolite framework. Helium (0.5 Torr) was admitted onto the sample and the U-tube filled with liquid

[†] 1 Torr = (101 325/760) Pa.

Fig. 1 Schematic representation of the IR cell

nitrogen so as to decrease the sample temperature to 120 K. The sample was then evacuated before admitting small CO doses into the cell and the temperature raised by 50 K. Small CO doses were then successively admitted into the cell and the thermocouple temperature was simultaneously observed to decrease progressively from 140 K (for the first CO doses) down to 113 K for CO pressures higher than 1 Torr.

IR Measurements

All IR data were recorded using a Fourier-transform Bruker IFS48 at a resolution of 2 cm^{-1} . All spectra in the ν_{CO} region have been compensated for the CO gas phase by subtracting the CO gas-phase absorbance measured through a zeolite-free plate under the same conditions (CO pressure, temperature), as well as the zeolite background under He at 120 K, from the sample spectrum.

Results

IR Measurements of CO Physisorption on HY: Influence of CO Coverage

Fig. 2 shows the spectral development in the CO stretching region for CO physically adsorbed on the HY sample at 113 K as a function of increasing CO pressure. The CO pressure was varied from 0.01 to 10 Torr, which corresponded to relative CO pressures, P/P_0 in the range 10^{-5} – 10^{-2} .

At low coverage, the spectrum is characterized by a single ν_{CO} band developing at 2175 cm^{-1} . This band, referred to as species A, shifts slightly towards lower wavenumbers with increasing coverage. At higher CO coverages, a new ν_{CO} band develops at 2140 cm^{-1} , while the growth of a shoulder at *ca.* 2160 cm^{-1} can also be observed. The bands at 2140 and 2160 cm^{-1} will be shown to correspond to two additional adsorbed CO species different from species A and denoted as species B and C, respectively. Increasing the CO pressure

causes the development of wings above and below the ν_{CO} bands of species A, B and C. Decreasing the CO pressure shows the reversibility of the CO adsorption process, causing progressively the reversal of the effects observed upon adsorption and leading finally to the complete removal of physisorbed CO species.

The integrated intensities of species A, B and C obtained for increasing CO pressure have been measured to characterize the nature of these species further. The method used for this purpose is schematically represented in Fig. 3. We constructed a symmetric peak for species B by reflecting the low-wavenumber half of the peak through the band centre at 2140 cm^{-1} . The resulting synthetic peak for species B was then subtracted from the total CO adsorption band envelope, which led to the band envelope corresponding to A and C. This relies upon the plausible assumption that wings are related to species B exclusively, which will be discussed further. A similar construction was then operated for the species A band. Subtracting the synthetic peak of species A from the envelope of the A and B bands finally resulted in the species C ν_{CO} feature.

The resulting integrated intensities of the ν_{CO} bands corresponding to species A, B and C have been plotted as a function of CO pressure in Fig. 4. In the first stages of CO adsorption, both A and C form, but the A band develops rapidly while the species C integrated intensity does not vary significantly. At higher CO pressures, the species A band saturates while B and C develop simultaneously. Then, the C band intensity comes to a plateau while B keeps growing with increasing CO pressure.

IR Measurements of the Interaction of Physisorbed CO with Zeolitic Hydroxyls

Simultaneously, the spectral modifications in the ν_{OH} region were recorded and reported in Fig. 5. The initial spectrum corresponding to the HY zeolite activated under vacuum at

Fig. 2 Low-temperature IR spectra of CO physisorbed on HY zeolite for increasing CO pressures. A, Low-pressure range: (a) 0.04, (b) 0.045, (c) 0.051, (d) 0.079, (e) 0.198, (f) 0.506 Torr. B, High-pressure range: (g) 1.033, (h) 2.033, (i) 5.10, (j) 10.00 Torr

673 K exhibits two intense features at 3640 and 3550 cm^{-1} . These bands are ascribed to hydroxyl groups bridging two adjacent SiO_4 and AlO_4 tetrahedra of the zeolite structure, formed upon the decomposition of ammonium ions. The existence of two distinct ν_{OH} vibrations originates from the two different locations for the bridging hydroxyl groups.⁸ The so-called HF species vibrating at 3640 cm^{-1} are known to be located in the supercages, while the species vibrating at 3550 cm^{-1} , the so-called LF hydroxyls, are thought to sit in small cavities. As a consequence, LF hydroxyls are inaccessible to most reactants because of the restricted dimensions of the six-ring windows. Terminal SiOH analogous to isolated silanol groups observed on SiO_2 surfaces can also be observed, corresponding to hydroxyl groups on the outer surface of the zeolite crystals. These silanol groups, vibrating at the same position as SiO_2 isolated silanol groups, i.e. 3740 cm^{-1} , are very few compared with the bridging hydroxyl species and therefore exhibit a negligible ν_{OH} band.

It can be observed from Fig. 5 that, as more CO is admitted onto the sample, the ν_{OH} vibration at 3640 cm^{-1} is continuously depleted, while a broad intense feature forms at 3355 cm^{-1} . The band at 3550 cm^{-1} is simultaneously observed to remain fairly constant in intensity, while its position shifts to lower frequencies. The simultaneous and

Fig. 3 Scheme of the procedure used to fit ν_{CO} bands of CO species A, B and C

opposite variations of the bands at 3640 and 3355 cm^{-1} indicates that the broad intense feature at 3355 cm^{-1} must be ascribed to HF OH groups interacting with physisorbed CO. Hydroxyl groups located in the small cavities cannot be reached by CO. Increasing CO coverage is observed to cause upward shifts of these two bands. High CO pressures ($P_{\text{CO}} > 0.2$ Torr) cause ultimately the complete disappearance of the 3640 cm^{-1} band. The later stages of the CO adsorption cause

Fig. 4 Plot of the ν_{CO} species A (∇), B (+) and C ($\diamond$) peak intensities vs. CO pressure

Fig. 5 Low-temperature IR spectra of the ν_{OH} region for CO physisorption on HY zeolite at increasing CO pressures. A, Low-pressure range: (a) initial spectrum under 0.5 Torr He, then after introducing CO at: (b) 0.04, (c) 0.045, (d) 0.051, (e) 0.059, (f) 0.079, (g) 0.105, (h) 0.198 Torr. B, High-pressure range: (i) 0.303, (j) 0.717, (k) 1.033, (l) 5.10, (m) 10.00 Torr

a significant downward shift and a decrease of the intensity of the remaining ν_{OH} vibrations at 3550 and 3355 cm^{-1} .

The variation of the intensities (in absorbance units) of ν_{OH} bands as a function of CO pressure is shown in Fig. 6. Clearly, the disappearance of the HF band at 3640 cm^{-1} is observed to follow strictly the formation of the broad intense feature at lower frequencies. At high CO coverages, when all HF hydroxyls interact with physisorbed CO, the absorbance of the associated-OH band is observed to decrease slightly together with the intensity of the 3550 cm^{-1} feature.

IR Investigation of CO Physisorption on HY at Varying Temperatures

IR spectra of CO physisorption at increasing temperatures in the ν_{CO} and ν_{OH} spectral regions have been recorded at a constant CO pressure of 5 Torr. It resulted in a continuous desorption of physically adsorbed CO with increasing temperature. At 216 K, the CO desorption is complete and the intensity of the HF hydroxyls is restored.

The basic assumptions on which the Langmuir model is based are fulfilled when considering the localized character of

Fig. 6 Plot of the peak intensities of the ν_{OH} bands vs. CO pressure: (Δ) 3650 cm^{-1} , ($\square$) 3550 cm^{-1} , ($\circ$) 3350 cm^{-1}

the physical adsorption of CO on hydroxyls: (i) well defined localized sites; (ii) one CO molecule per site; (iii) all sites energetically equivalent; (iv) no interaction between molecules on adjacent sites. By assuming coverage independence of the molar absorption coefficient of CO species A, we can estimate the enthalpy of adsorption of this species from the Arrhenius plot of the equilibrium constant shown in Fig. 7 and calculated as follows. The equilibrium constant may be written:

$$K_{\text{eq}} = \Theta_{\text{CO}}/P_{\text{CO}}(1 - \Theta_{\text{CO}})$$

and, considering that the fractional coverage, Θ_{CO} , is equal to the absorbance ratio $A_{\text{CO}}/A_{\text{CO}}^{\text{max}}$ measured for species A:

$$K_{\text{eq}} = (A_{\text{CO}}/A_{\text{CO}}^{\text{max}})/P_{\text{CO}}[1 - (A_{\text{CO}}/A_{\text{CO}}^{\text{max}})]$$

The enthalpy of adsorption for species A, deduced from a least-squares data fit of the Arrhenius plot, is found to be $-11.3 \text{ kJ mol}^{-1}$. This value is comparable to that calculated for CO interacting with silica surface isolated hydroxyls ($-10.9 \text{ kJ mol}^{-1}$).

Discussion

Hydrogen Bonding of CO with Hydroxyl Groups

As demonstrated by the depletion of the 3640 cm^{-1} band simultaneously with the formation of a strong broad feature at lower wavenumbers, the physical adsorption of CO on HY zeolites primarily occurs on the more easily accessible OH groups, *i.e.* HF groups vibrating at 3640 cm^{-1} , via hydrogen bonding. This result is analogous to that observed for CO physisorbed on isolated SiOH groups of SiO_2 surfaces, where it has been suggested that SiOH groups interact specifically

Fig. 7 Arrhenius plot for physisorbed CO species A on HY

with CO to form a surface complex

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.²

The acidic character of the HF OH groups of HY zeolites compared with isolated OH groups of SiO_2 leads to a stronger perturbation of CO interacting specifically with them, and consequently to a stronger upward of ν_{CO} relative to the CO gas-phase absorption. The observed 36 cm^{-1} ν_{CO} shift of CO hydrogen-bonded with HF hydroxyls in HY compared with 15 cm^{-1} in the case of SiO_2 supports this statement. Similarly, the ν_{OH} vibration of HY HF hydroxyls interacting with CO is expected to be more strongly affected than for SiO_2 . In this case, 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 ν_{CO} shifts. In HY, ν_{OH} at 3640 cm^{-1} is observed to shift by 298 cm^{-1} instead of 92 cm^{-1} for SiO_2 at low CO coverage.

In zeolites, the formation of SiOH-CO complexes is also a direct probe for the accessibility of the hydroxyl groups to CO. The slight perturbing effect of CO on LF species is therefore an indication of either their low acidic character or their inaccessibility to CO. The localization of the LF species in small cavities⁸ supports the accessibility point of view. However, it must be mentioned that high CO coverages affect the 3550 cm^{-1} band, even if the perturbation appears to be much weaker than for the 3640 cm^{-1} band. The decrease of the 3550 cm^{-1} absorbance, observed at high CO coverages, could be due to specific interaction of LF hydroxyls with CO generating hydrogen bonding and/or a broadening effect. The former interpretation would imply the formation of an additional broad band in the region of ν_{OH} corresponding to associated hydroxyls, which is not observed but cannot be totally ruled out because of the broad ν_{OH} envelope. Alternatively, CO-induced perturbations of the LF feature at high CO coverage could be ascribed to purely physical effects, denoted as solvent effects, responsible for downward frequency shifts and intensity decreases, which will be discussed further.

High CO coverage is clearly shown to induce the development of the 2140 cm^{-1} feature. This feature, denoted as species B, also observed in the case of CO physisorption on SiO_2 surfaces, forms with pronounced rotational wings, similar to those observed for liquid CO. It is ascribed to the multilayer formation, in which CO exhibits hindered rotational behaviour.²

Long-range Electrostatic Effects

The data in Fig. 2 and 5 clearly show coverage-dependent frequency shifts for ν_{OH} and ν_{CO} vibrations. The frequencies of the stretching vibrations of the associated OH and the corresponding CO species A have been plotted as a function of CO pressure in Fig. 8. Two distinct regions, A and B may be distinguished, which coincide, respectively, with the successive formation of OH—CO species for $P_{\text{CO}} > 1$ Torr and the liquid-like CO phase at high CO pressures. When almost no liquid-like CO phase is observed (region A), OH and CO species A involved in the OH—CO entities experience, with increasing coverage, opposite and reduced frequency shifts

Fig. 8 Frequency variations of the stretching vibrations of CO species and associated HF hydroxyls as a function of CO pressure: (∇) CO species A, ($\circ$) associated OH

relative to HF free OH and gas-phase CO, respectively. Similar observations have been made by Kubelkova *et al.* on various zeolites and ascribed to an intrinsic acid strength heterogeneity of the hydroxyl groups in zeolite supercages rather than to a coverage induced effect.¹ The higher the acid strength of the hydroxyls, the stronger the perturbation of both OH and CO stretching vibrations. Therefore, stronger acid sites are expected to adsorb CO first and generate stronger vibrational shifts. As more CO is admitted, weaker sites can interact with CO and cause smaller vibrational shifts, which is observed experimentally. Their conclusions were supported by quantum-chemical calculations based upon small molecular cluster models. These models have been shown to be sufficient to describe the intrinsic properties of the hydroxyls but neglect all effects due to long-range interactions such as cage dimensions.⁹ Recent calculations have demonstrated the necessity of considering long-range electrostatic effects to describe the zeolite properties better.¹⁰ The alternative interpretation is related to a coverage-induced effect. In the study of CO physisorption on SiO_2 surfaces by Beebe *et al.*,² the observed coverage-dependent frequency shifts of CO and OH vibrations have been explained on the basis of purely electrostatic arguments. The formation of hydrogen bonding was supposed to decrease the average electrostatic field induced by free hydroxyls, because of local shielding effects. As a result, the frequencies and the intensities of the vibrations of CO and associated OH were expected to decrease, which agreed well with the experimental observations. In the case of HY zeolite, the observed coverage effects are different: ν_{OH} of the associated HF hydroxyls and ν_{CO} vary oppositely with coverage, as far as HF hydroxyls are not saturated with CO. We must therefore take into account an additional contribution involving long-range electrostatic effects, which may dominate the effects observed on SiO_2 .

Recently, a detailed analysis of XPS core-level and valence-band results for various zeolites has been carried out by Barr.¹¹ The key aspect of this excellent work was to demonstrate that the oxygen atoms of the zeolite framework are subject to extensive polarization. For instance, decreasing the Al content in the zeolitic framework enhances the overall covalency of the oxide because of the increasing number of covalent Si—O bonds, while, on the other hand, the fewer Al—O (and O—H) bonds are forced to be more ionic, that is more acidic. Let us apply these simple ideas to CO physisorption on bridging hydroxyls in HY. Interacting a CO molecule with a hydroxyl would result in a higher

ionicity/polarization of the O—H bond (as demonstrated by large downward ν_{OH} shifts) and finally in a higher ionicity of the involved O—Al bond. The compensating effect is the depolarization of the surrounding oxygens, decreasing the ionicity of corresponding hydroxyls, which would result in a progressive decrease of the acid strength with increasing coverage.

Electrostatics might well account for the coverage effects. A general decrease of the electrostatic field in the supercage, due to shielding of free hydroxyls upon hydrogen bonding, is expected to affect not only the OH and CO oscillators involved in the SiOH—CO complexes, when physisorbing CO in HY zeolite, but also the ionicity of the oxygens, located in the supercages, not directly perturbed by CO. Therefore, decreasing the average electrostatic field in the supercage would result in decreasing the mean ionicity of the hydroxyl oxygens of the supercage. This can be related to the average decrease of the corresponding Brønsted acidity and, consequently, to a weaker interaction of CO with HF hydroxyls. This is in qualitative agreement with our experimental findings.

On the other hand, a decrease of the average charge on the oxygens in the large cavities should be accompanied by an increase of the charge on the oxygens in small cavities, as required by charge-balance considerations. This is expected to perturb the LF hydroxyl frequency. In Fig. 9, we have plotted the wavenumbers of the OH stretching vibrations corresponding to free HF species (not covered with adsorbed CO) and LF species as a function of CO pressure. It is clearly observed that the LF band shifts towards lower wavenumbers with increasing coverage while free HF species experience high-frequency shifts. It must be kept in mind that, in the considered domain of CO pressures, the LF species band intensity is observed to remain strictly constant. This indicates that no CO interacts with LF hydroxyls. This excludes ascribing LF band shifts to direct interaction with CO. This strongly supports the electrostatic argument, according to which the charge on the oxygens in the small cavities would increase. The very low frequency of the LF band compared with that of the HF band is generally explained by electrostatic interactions with the surrounding oxygens. An increase of the charge of these oxygens should lead to an increase of the electrostatic interactions and cause a downward shift to be observed. These results strongly suggest that changes in the local charge distribution in the zeolite framework could be responsible for the significant shifts of the vibration bands of the hydroxyls not directly perturbed by CO. This interpre-

Fig. 9 Frequency behaviour of free HF hydroxyls (Δ) and LF hydroxyls ($\square$) at increasing CO pressures

tation is also consistent with the general shift observed for all the vibration bands associated with OH—CO entities. A mean decrease of the local negative charge distribution on the oxygens located in the supercages is expected to decrease the net charge on the HF protons, reducing the mean Brønsted acidity of these hydroxyls and thus the mean ν_{OH} and ν_{CO} band shifts.

The frequency shift of ν_{OH} of the associated hydroxyls relative to the free HF hydroxyl ν_{OH} has been plotted as a function of CO pressure in Fig. 10. The observed variation is quite consistent with a coverage-dependent decrease of the mean acid strength of HF hydroxyls. The value extrapolated at zero coverage may be considered to be a measurement of the intrinsic acid strength of hydroxyls in zeolites of varying structure and varying chemical composition. This value is found to be 298 cm^{-1} for HY zeolite.

At high CO coverages, when the multilayer forms extensively, the vibrations ν_{OH} and ν_{CO} associated with OH—CO entities experience downward shifts, suggesting the same physical effect for both species. Similar shifts have been reported for CO physisorption on SiO_2 surfaces with the for-

Fig. 10 Plot of frequency shifts of ν_{OH} of associated hydroxyls relative to ν_{OH} of free hydroxyls vs. CO pressure: (a) free HF hydroxyls, (b) associated HF hydroxyls, (c) $\nu(\text{free OH}) - \nu(\text{associated OH})$

mation of the liquid-like CO phase on the surface and ascribed to solvent effects.²

Interpretation of the 2160 cm⁻¹ Feature

From Fig. 4, it appears that CO species C characterized by the 2160 cm⁻¹ band do form after CO species A and tend to saturate while CO species B increase with increasing CO pressure. This indicates that CO species C correspond to CO interacting with specific sites of the zeolite, weaker than the HF hydroxyls, which is also consistent with a weaker ν_{CO} shift relative to the CO gas-phase absorbance than is found for the species A ν_{CO} . The assignment of these sites to LF hydroxyls can be ruled out on the basis of the non-perturbation of the LF band at this stage of the CO physisorption.

The formation of extraframework Al species originating from a partial dealumination of the HY framework, although most unlikely under the activation conditions carried out in our experiments, cannot be totally excluded. Residual Na cations are still present in the sample, even after thorough exchange with ammonium, as indicated by chemical analysis results. Both sites, non-framework Al species and, to a lesser extent, Na cations, can act as electron-accepting (Lewis acid) sites and interact with CO. However, CO adsorbed on the former has been shown to give rise to ν_{CO} bands in the region 2230–2190 cm⁻¹,¹² while CO interacting with sodium cations exhibits an intense band at 2170 cm⁻¹.³ The spectral region involved for CO adsorbed on both sites clearly rules out the assignment of the band at 2160 cm⁻¹ to the physisorption of CO on these sites. Moreover, the fact that no band could be observed above 2170 cm⁻¹ rules out the presence, in the HY sample, of Lewis acid type sites in the form of extraframework Al species.

The frequency observed for species C is quite consistent with CO hydrogen-bonded with isolated surface hydroxyl groups analogous to those encountered on SiO₂ surfaces ($\nu_{\text{CO}} = 2158 \text{ cm}^{-1}$).² However, these sites are very few in HY zeolite compared with bridging hydroxyl groups, such that the corresponding ν_{CO} band intensity is expected to be very small. This interpretation is contradictory to the high intensity of the species C absorption.

For these reasons, we ascribe CO species C to CO interacting with framework oxygens, that is framework Si—O—Si entities. This would imply the interaction of CO through the O end of the molecule, according to the C^{δ-}—O^{δ+} polarity of the molecule. This assignment is also consistent with the fact that the multilayer does form extensively after the saturation of all the surface sites of the zeolitic pores, i.e. hydroxyls and Si—O—Si oxygen atoms. Negatively charged oxygens in zeolite frameworks have already been shown, by IR¹³ and neutron powder diffraction studies,¹⁴ to act as basic sites and interact with benzene molecules.

Conclusions

This study of the physical adsorption of CO at low temperature on a protonated Y zeolite has led to the following conclusions: CO primarily interacts specifically with bridging hydroxyl groups located in the large cavities of the zeolite pores via hydrogen bonding. This leads to the formation of CO species A characterized by a ν_{CO} band arising at 2176

cm⁻¹. The ν_{OH} vibration of the hydroxyls involved in the hydrogen bonding is strongly shifted by 298 cm⁻¹ towards lower wavenumbers. CO species A interacts with hydroxyls by means of 5 σ donation from the carbon end of CO to the proton of the hydroxyl, leading to a slight strengthening of the C—O bond and therefore to an increase by 36 cm⁻¹ of ν_{CO} relative to the gas-phase value.

In contrast, there is no interaction of CO with the hydroxyl groups located in the small cavities of the zeolitic pores, revealing their low acidic character compared with those located in the large cavities and/or their inaccessibility to the CO molecule.

A second form of physisorbed CO species, called CO species C with $\nu_{\text{CO}} = 2160 \text{ cm}^{-1}$, is formed at higher CO pressures, when all CO species A have been formed. It has been tentatively ascribed to CO specifically interacting with the oxygen atoms of framework Si—O—Si groups through the oxygen end of the CO molecule.

At higher CO coverages, a third form of physisorbed CO forms extensively, called CO species B with $\nu_{\text{CO}} = 2140 \text{ cm}^{-1}$. This species is analogous to the one observed at high CO coverages on SiO₂ surfaces and corresponds to multilayer formation. It exhibits hindered rotational behaviour, as shown by the appearance of wings above and below the band at 2140 cm⁻¹.

In the CO pressure range of the specific formation of OH—CO complexes, free hydroxyl groups located in large and small cavities experience strong and opposite coverage-dependent frequency shifts. This phenomenon is ascribed to changes in the charge distribution in the zeolite framework induced upon CO physisorption. The coverage-dependent frequency shifts observed for all bands are therefore thought to be correlated to a CO-induced effect rather than to an intrinsic acid strength distribution.

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