J|A|C|S
ARTICLES

Investigation of Acid Sites in a Zeotypic Giant Pores Chromium(III) Carboxylate

Alexandre Vimont,[†] Jean-Michel Goupil,[†] Jean-Claude Lavalley,[†] Marco Daturi,[*,†]
Suzy Surblé,[‡] Christian Serre,[‡] Franck Millange,[‡] Gerard Férey,[‡] and
Nathalie Audebrand[§]

Contribution from the Laboratoire Catalyse et Spectrochimie, UMR 6506, CNRS, ENSICAEN and Université de Caen, 6, Boulevard Maréchal Juin, 14050 Caen Cedex, France, Institut Lavoisier, UMR CNRS 8637, Université de Versailles Saint-Quentin-en-Yvelines, 45 avenue des Etats-Unis, 78035 Versailles Cedex, France, and Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR CNRS 6511, Université Rennes I, Avenue du général Leclerc, 35042 Rennes Cedex, France

Received October 18, 2005; E-mail: marco.daturi@ensicaen.fr

Abstract: A study of the zeotypic giant pores chromium(III) tricarboxylate $Cr^{III}_3OF_x(OH)_{1-x}(H_2O)_2\cdot\{C_6H_3-(CO_2)_3\}_2\cdot nH_2O$ (MIL-100) has been performed. First, its thermal behavior, studied by X-ray thermodiffractometry and infrared spectroscopy, indicates that the departure of water occurs without any pore contraction and no loss in crystallinity, which confirms the robustness of the framework. In a second step, IR spectroscopy has shown the presence of three distinct types of hydroxy groups depending on the outgassing conditions; first, at high temperatures (573 K), only Cr−OH groups with a medium Brønsted acidity are present; at lower temperatures, two types of $Cr-H_2O$ terminal groups are observed; and at room temperature, their relatively high Brønsted acidity allows them to combine with H-bonded water molecules. Finally, a CO sorption study has revealed that at least three Lewis acid sites are present in MIL-100 and that fluorine atoms are located on a terminal position on the trimers of octahedra. A first result of grafting of methanol molecules acting as basic organic molecules on the chromium sites has also been shown, opening the way for a postsynthesis functionalization of MIL-100.

Introduction

The synthesis of hybrid inorganic−organic nanoporous solids is still very active, and the number of new hybrid solids is steadily increasing in the past few years. This approach gives a new dimension to the domain of porous compounds.[1] The large number of existing organic linkers and the unique physical properties of inorganic materials lead to a modulation of both the shape and the size of the pores and the properties of the final porous materials.[2−5] In these structures, organic moieties, such as diphosphonates or dicarboxylates, act as pillars or linkers relating inorganic layers, chains, or clusters of transition or rare-earth metals. In the field of metal carboxylates, some of us initiated a global study of the trivalent metal dicarboxylate systems in water, which recently led to the characterization of the two chromium(III) dicarboxylates with giant pores labeled MIL-100 and MIL-101 (MIL for Materials of Institut Lavoisier).[6−8] These solids are unique in terms of pore size with cages of free diameter between 25 and 34 Å and huge Langmuir surface areas (3100 and 5900 $m^2\ g^{-1}$, respectively). Consequently, such solids are good candidates for many applications, such as the insertion of large molecules, notably the trapping of wasted organic molecules, a challenge in the field of green chemistry.[9] The peculiar surface and the specific design of the cages are also of a great interest in catalysis, at least as high as that manifested for zeolites and MCM-like materials. Moreover, the gigantism of the pore size in these crystallized materials (a variance to MCM-type mesoporous solids) allows conceiving catalytic reactions with organic molecules larger than those currently used in zeolitic materials. However, prior to any application, the precise characterization of these porous solids is vital. It is well established that catalytic and adsorption properties strongly depend on the nature of the surface sites (i.e., Brønsted and Lewis acid or basic sites) and on the oxidation degree of the exposed cation.[10] Therefore, the characterizations of the acidic and redox properties of the material are crucial to

---

[†] Université de Caen.

[‡] Université de Versailles.

[§] Université Rennes I.

(1) Schüth, F.; Sing, K. S. W.; Weitkamp, J. *Handbook of Porous Solids*; Wiley-VCH: Weinheim, Germany, 2002; Vol. 3.

(2) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982.

(3) Férey, G.; Latroche, M.; Serre, C.; Loiseau, T.; Millange, F.; Percheron-Guegan, A. *Chem. Commun.* **2003**, 2276.

(4) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127.

(5) Chae, H. K.; Siberio-Perez, D. Y.; Kim, J.; Go, Y.; Eddaoudi, M.; Matzger, A. J.; O'Keeffe, M.; Yaghi, O. M. *Nature* **2004**, *427*, 523.

(6) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F.; Dutour, J.; Surblé, S.; Margiolaki, I. *Science* **2005**, *309*, 2040.

(7) Férey, G.; Serre, C.; Mellot-Draznieks, C.; Millange, F.; Surblé, S.; Dutour, J.; Margiolaki, I. *Angew. Chem., Int. Ed.* **2004**, *43*, 6296.

(8) Férey, G.; Mellot-Draznieks, C.; Serre, C.; Millange, F. *Acc. Chem. Res.* **2005**, *38*, 217.

(9) Anastas, P. T.; Kirchhoff, M. M. *Acc. Chem. Res.* **2002**, *35*, 686.

10.1021/ja056906s CCC: $33.50

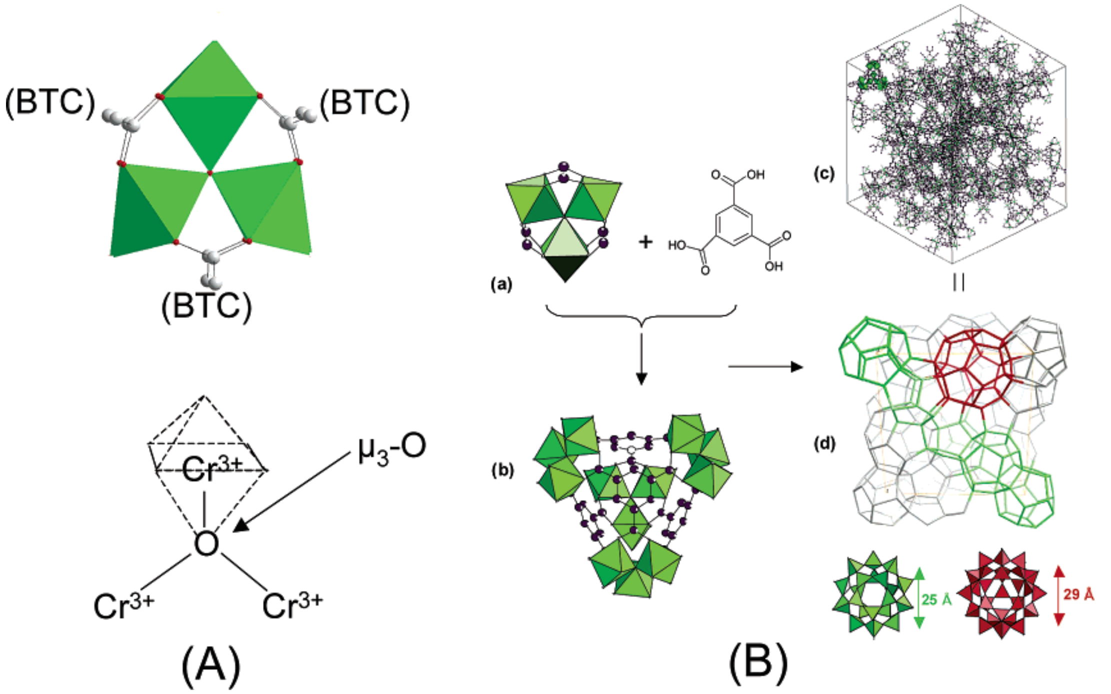


Figure 1. Structure of MIL-100; (A) trimers of chromium octahedra sharing a common vertex μ_3-O. (B): (a) The primary building unit (trimer of chromium octahedra) and the organic ligand; (b) the hybrid supertetrahedron; (c) a unit cell of MIL-100 with a supertetrahedron drawn in a polyhedral mode; (d) schematic view of the MTN topology of MIL-100 with the two types of cages present (free apertures given in angstroms).

evaluate the catalytic and the adsorptive properties of a solid in heterogeneous catalysis. Infrared spectroscopy is the most powerful technique to identify the active sites in this type of zeolitic system.[11] In the present paper, using IR spectroscopy of adsorbed probe molecules, we report the first characterization of the surface and of the nature of the adsorbed species present into the pores of MIL-100 at various stages of hydration. Our goal was to identify and quantify the Brønsted and Lewis acid sites by adsorption of basic probe molecules and to evidence the unusual interaction of the adsorbed water species with the surface. In addition, MIL-100, which is a chromium trimesate with the following chemical composition $(Cr^{III}_3OF_x(OH)_{1-x}(H_2O)_y)\{C_6H_3-(CO_2)_3\}_2\cdot zH_2O$ ($y + z \approx 28$), exhibits a cationic framework with a negative default charge per trimer of chromium octahedra, which is compensated by one fluorine atom per three chromia. The second aim of this study was the localization of these fluorine atoms and their effects on the acid properties of the solid.

Results and Discussion

Thermal Behavior. MIL-100 is a chromium carboxylate built up from trimers of chromium octahedra sharing a common vertex μ_3-O (Figure 1A). The trimers are then linked by the benzene-1,3,5-tricarboxylate (BTC) moieties in such a way that this leads to the formation of hybrid supertetrahedra which further assemble into a zeolitic architecture of the MTN-type (Figure 1B). Its thermal behavior was investigated previously,[7] and TGA indicated a huge departure of free water (~30% in weight) below 373 K followed by a slow release of bound water between 373 and 523 K and finally the destruction of the framework at about 600 K. At this stage, the questions were the following: where are the water molecules localized, and what are the consequences of the water departure? We first analyzed the dehydration process using infrared spectroscopy (Figure 2). The spectrum of MIL-100 (Figure 2) reveals two massifs in the middle infrared range: one in the low wavenumber region (1700−1300 cm^{-1}), which characterizes the carboxylate groups of the framework (intense bands at 1640 and 1390 cm^{-1}); another in the 3800−3000 cm^{-1} region, due to the stretching modes of OH groups, on which the present study will be focused. Additional bands due to the water molecules are also present at higher wavenumbers ($\nu + \delta(H_2O)$

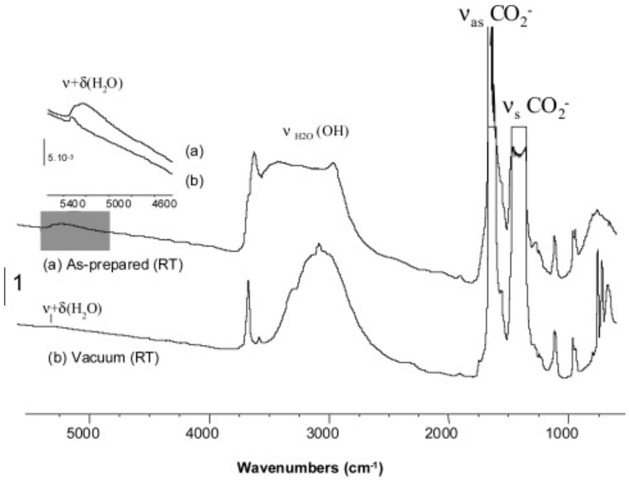


Figure 2. Infrared spectra of MIL-100; (top) as-prepared; (bottom) after outgassing at room temperature. The inset corresponds to a magnification of the rectangular gray zone of the RT spectrum.

---

(10) Boehm, H. P.; Knozinger, H. Nature and Estimation of Functional Groups on Solid Surfaces. In *Catalysis Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: Berlin, 1984; Vol. 4, pp 40−189.

(11) (a) Payen, E.; Grimblot, J.; Lavalley, J. C.; Daturi, M.; Maugé, F. In *Handbook of Vibrational Spectroscopy*; Chalmers, J. M., Griffiths, R., Eds.; John Wiley & Sons Ltd.: Chichester, UK, 2002; Vol. 4, pp 3005−3041. (b) Zecchina, A.; Spoto, G.; Bordiga, S. In *Handbook of Vibrational Spectroscopy*; Chalmers, J. M., Griffiths, R., Eds.; John Wiley & Sons Ltd.: Chichester, UK, 2002; Vol. 4, pp 3042−3071.

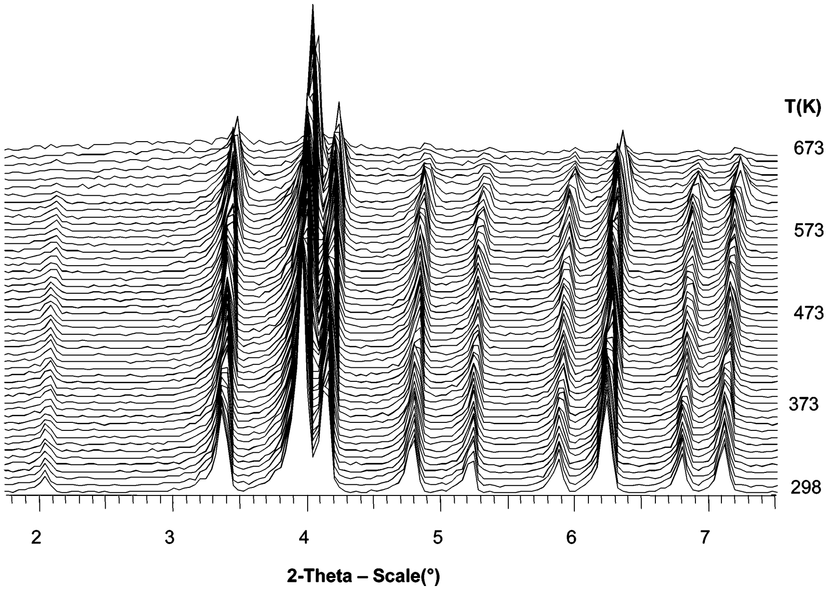


Figure 3. Temperature X-ray diffraction pattern of MIL-100 (under primary vacuum).

~ 5300 cm^{-1}). On the spectrum of the as prepared sample (Figure 2a), the frequency of this combination band is relatively low (5200 cm^{-1}), showing the presence of H-bonded H_2O species. This combination band disappears by evacuation at room temperature (RT) which removes water condensed in cages. A sharp band near 5300 cm^{-1} (Figure 2b) remains in the spectrum of the evacuated sample, revealing that some water molecules persist on the sample. Considering the composition of MIL-100, $Cr_3FO(H_2O)_x\{C_6H_3-(CO_2)_3\}_2 \cdot yH_2O$ ($x + y \sim 28$), it appears that the free water (denoted yH_2O) can be evacuated quite easily at room temperature under vacuum. As we will see later, the total removal of the remaining water molecules (denoted xH_2O) requires both vacuum and heating (<473 K). X-ray diffraction under primary vacuum (Figure 3) indicates that no significant change occurs both in terms of crystallinity and cell volume (cell contraction of 2−3% only) between room temperature and 573 K; above 623 K, the structure collapses.

Finally, this preliminary study indicates that the complete desorption of free and bound water molecules from MIL-100 occurs at low temperature while keeping the integrity of its porous framework. The next part of this study concerns the analysis of the different acid sites of MIL-100 upon the different stages of hydration in order to specify the water adsorption sites.

Analysis of the Hydroxy Groups. The complexity of the IR profile depends on the hydroxylation degree of the surface. A series of spectra have been recorded after outgassing the sample from room temperature to high temperature (573 K). Nevertheless, the spectra are discussed from the less to the more complicated (from the higher outgassing temperature to room temperature). First, two main ν(OH) peaks, characteristic of the hydration or hydroxylation status of MIL-100, are observed within the 3580−3600 and 3680−3700 cm^{-1} ranges, respectively (Figure 4). On the basis of the position of these bands, observed at various outgassing temperatures, we will describe in this section subsequently the different Cr−OH, Cr−H_2O, and Cr−H_2O/H_2O species present in MIL-100 at the different stages of the dehydration process (see Table 1).

First, the presence of Cr−OH groups at high temperatures (573 K) is discussed (Figure 4a). Only one OH band is present at 3585 cm^{-1}. Its intensity is greater when the sample was outgassed at lower temperature (473 K) (Figure 4b), and it is stronger at 373 K (Figure 4d). This vibration cannot be ascribed to a water molecule since no corresponding band characteristic of the $\nu + \delta(H_2O)$ combination mode is observed in the 5000−5400 cm^{-1} range (see Figure 4a and 4b). In addition, one observes a combination band at 4295 cm^{-1} (Figure 4, inset A) whose intensity varies in parallel to the intensity of the previous band (3585 cm^{-1}) as a function of the outgassing temperature applied. This combination band is sensitive to the H/D exchange by D_2O treatment (see Figure 4, inset B), confirming its assignment to a $\nu + \delta$(OH) mode. This demonstrates that OH groups bound to chromium atoms are present in the structure, as it will be further discussed in this paper.

Second, at lower temperatures, water molecules bound to the chromium sites are present (423 K, Figure 4c) since one observes ν(OH) bands at 3700 and 3608 cm^{-1}, as well as a sharp band at 5274 cm^{-1}, characteristic of molecular water adsorption. H_2O is an amphoteric molecule, which can interact both with acidic surface sites (lone pair of the electron-donor oxygen atom) and with basic sites (hydrogen bonding). This leads either to a blue shift of the $\delta(H_2O)$ mode and a red shift of the ν(OH) bands when an hydrogen bond is created, or to a less extended lowering of the ν(OH) mode and a rather low wavenumber position of the $\delta(H_2O)$ mode in the other case.[12,13] Table 1, first line, summarizes the characteristic vibrations [$\nu_3(\nu_a)$, $\nu_1(\nu_s)$, $\nu_2(\delta(H_2O))$] of the free water molecule in an inert solvent.[14] When several types of adsorbed water species are present, the study of the $\nu + \delta(H_2O)$ combination bands in the 5000−5300 cm^{-1} range allows one to assign ν(OH) and $\delta(H_2O)$ bands to each type of water adsorbed configuration.[12] Moreover, this allows one to calculate the bending mode frequency, not directly accessible due to the presence of intense bands of the carboxylates. From a $\nu_2 + \nu_3$ frequency at 5274 cm^{-1} (Figure 4c), and a ν_3 at 3700 cm^{-1}, taking into account an anharmonicity coefficient of 22 cm^{-1},[14] we deduce a $\delta(H_2O)$ mode at 1596

---

(12) Burneau, A. *J. Mol. Liq.* **1990**, *46*, 99.
(13) Falk, M. *Spectrochim. Acta* **1984**, *40A*, 43.
(14) Burneau, A.; Corset, J. *J. Chim. Phys.* **1972**, *69*, 171.

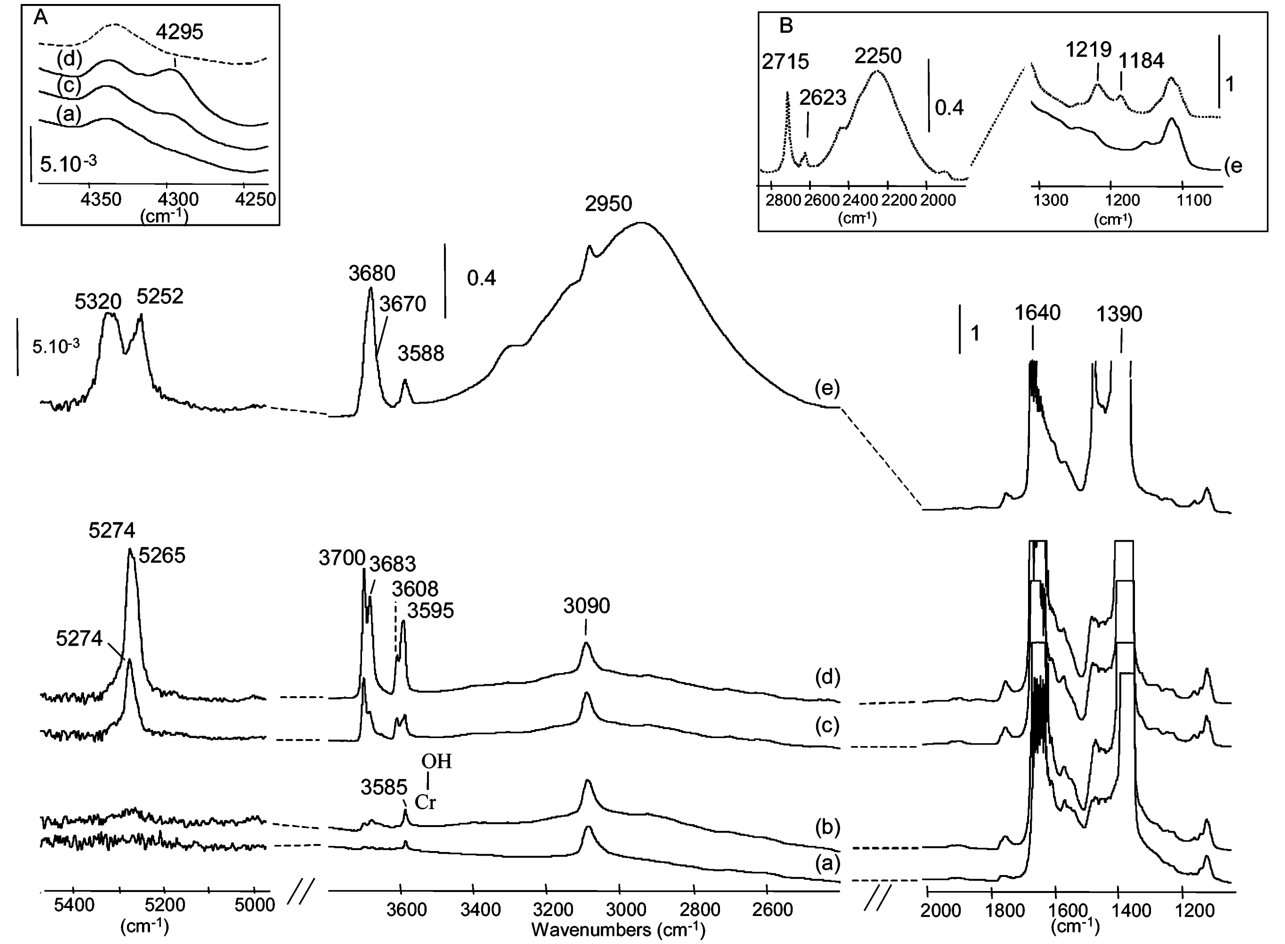


Figure 4. Absorbance spectra of MIL-100 recorded at 100 K after outgassing during 2 h at 573 K (a), 473 K (b), 423 K (c), 373 K (d), RT (e). Inset A: Spectra of MIL-100 in the 4200−4400 cm^{-1} range (dotted line, spectrum of MIL-100 previously outgassed at 473 K, after introduction of D_2O vapor into the cell ($P(D_2O) = 1333$ Pa), and evacuation at 373 K). Inset B: Spectra of MIL-100, previously outgassed at 473 K, after introduction of D_2O vapor into the cell ($P(D_2O) = 1333$ Pa), and evacuation at room temperature (dotted line).

Table 1. Wavenumbers of the Characteristic Infrared Bands of Water in MIL-100[a]

water species	ν_3 (ν_a) (cm^{-1})	ν_1 (ν_s) (cm^{-1})	$\nu_2 + \nu_3$ (cm^{-1})	ν_2 (δH_2O) (cm^{-1})
H_2O in inert solvent[12]	3710	3619	5284	1598
$\underline{H_2O} \rightarrow Cr^{3+}$ (species 1)	3700	3608	5274	1596^b
$\underline{H_2O} \rightarrow Cr^{3+}$ (species 1′)	3683	3595	5265	1604^b
$\underline{H_2O}\cdots H_2O \rightarrow Cr$	3680 (2715)	3588 (2623)	5252 (∼3915 weak)	1603^c (1184)
$\underline{H_2O}\cdots\underline{H_2O} \rightarrow Cr$	3670 (2715)	2950 (2250)	5320 (∼3915)	1650^c (1219)

[a] Values in parentheses are those observed after dehydration at 473 K, treatment under $Pe(D_2O) = 1333$ Pa, and evacuation at room temperature. [b] Values calculated from the $\nu_2 + \nu_3$ and ν_3 bands, using a coefficient of anharmonicity equal to 22 cm^{-1}. [c] Values calculated from $\delta(D_2O)$ frequency.

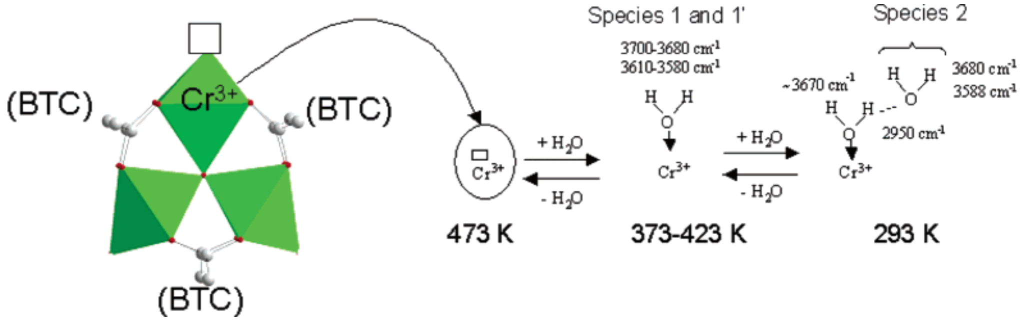
cm^{-1}. The remaining band at 3608 cm^{-1} is assigned to the ν_1 mode of a first type of water molecule, denoted species **1**. Looking at spectrum 4d (evacuation at 373 K), we observe also additional peaks at 5265, 3683, and 3595 cm^{-1}, which imply the existence of a second type of adsorbed water molecules, denoted species **1′**, exhibiting a $\delta(H_2O)$ mode at 1604 cm^{-1} (see Table 1). The position of both bending modes is characteristic of water molecules coordinated on a surface. In particular, Zecchina et al. attributed such positions to water molecules bound to coordinatively unsaturated sites (cus) of Cr^{3+} on the surface of Cr_2O_3.[15] Accordingly, species **1** and **1′** water molecules (acting as electron donors) are coordinated to two different unsaturated Cr sites, showing their heterogeneity. Such interactions explain the rather high thermal stability of the corresponding species since they are coordinated to Lewis acid sites.

At lower temperature (RT, Figure 4e), at least two types of adsorbed water molecules are present which do not correspond to the previous species **1** and **1′** since the spectrum is quite different, with two strong $\nu + \delta(H_2O)$ bands at 5320 and 5252 cm^{-1}. The ν_3 mode gives rise to a band at 3680 cm^{-1}, relatively broad with a shoulder at 3670 cm^{-1}. This would lead to $\delta(H_2O)$ bands at about 1662 and 1594 cm^{-1} masked by the carboxylate bands. To directly observe such bending modes, hydration experiments with D_2O have been performed (see caption for Figure 4 for experimental details), the $\delta(D_2O)$ band being expected in the 1100−1250 cm^{-1} range, a transparent IR region for this material (Figure 4, inset B). First, the spectrum presents $\nu(OD)$ bands at 2715, 2623, and about 2250 cm^{-1} which are in

---

(15) Zecchina, A.; Coluccia, S.; Guglielminotti, E.; Ghiotti, G. *J. Phys. Chem.* **1971**, *75*, 2774.

Scheme 1. Location and Interaction of Water Molecules with cus Cr^{3+}



agreement (ν(OH)/ν(OD) ratio ~1.36 [13]) with the ν(OH) bands observed previously with H_2O (Figure 4e) at 3680, 3588, and 2950 cm^{-1}, respectively. At lower wavenumbers, new bands are observed at 1219 and 1184 cm^{-1} due to $\delta(D_2O)$ modes. The presence of two bands confirms the occurrence of two types of water species. Taking into account a $\delta(H_2O)/\delta(D_2O)$ ratio equal to 1.354,[16] the frequency of the corresponding $\delta(H_2O)$ modes can be estimated at 1650 and 1603 cm^{-1}. These values are close to those expected from the analysis of the ν(OH) and $\nu + \delta(H_2O)$ band positions and satisfy the Teller−Redlich product rule. This confirms that the two types of water species adsorbed on the surface after outgassing at room temperature are quite different from the aforementioned species **1** and **1′**. The band at 1650 cm^{-1} is unusually high for the bending vibration mode of water. Such a blue shift, 52 cm^{-1}, is only observed when the water molecule is a strong hydrogen donor.[12,14] This is also evidenced by a broad band at a very low wavenumber, 2950 cm^{-1} (Figure 4e), assigned to the ν_1(OH) mode of water, strongly downward shifted by the formation of hydrogen bonding.[12] The corresponding decoupled ν_3 mode would give rise to the shoulder present at 3670 cm^{-1}. The low values of the bending modes of the second species, $\delta(H_2O)$ and $\nu + \delta(H_2O)$ bands at 1603 and 5252 cm^{-1}, respectively, are related to the electron-donor character of H_2O, typical for water molecules interacting via the oxygen atom.[17] Moreover, the observation of both hydrogen-donor and electron-donor water molecules after outgassing MIL-100 at room temperature indicates the presence of additional water molecules, denoted species **2**, not bound to chromium atoms but in strong interaction with the terminal water molecules **1** and **1′**. Hydrogen-bonded molecules alone would present, in fact, the ν_3 and ν_1 modes at about 3680 and 3588 cm^{-1}, respectively (see Table 1). This does not exclude the presence of extra water molecules forming $H_2O\cdots(H_2O)_n$ multimers due to the donor−acceptor properties of water. The different types of water species formed from H_2O addition to cus Cr^{3+} and their corresponding thermal stability are presented in Scheme 1. The coordinatively unsaturated site is localized on the top of the chromium octahedron.

In addition, the 3585 cm^{-1} sharp band previously assigned to Cr−OH groups and well apparent in the spectrum Figure 4b is lacking in spectrum 4e, suggesting that the corresponding hydroxy groups are perturbed when a large amount of water remains; this could occur if extra water molecules are hydrogen-bonded to these OH groups, which would imply that they present some Brønsted acidity. Experiments involving CO adsorption reported below will confirm such an hypothesis.

Measurement of the Brønsted Acidity. CO can probe both Lewis and Brønsted acid sites.[18] When probing Brønsted sites, it gives rise to H-bonded CO molecules, and both ν(OH) and ν(CO) shifts depend on the strength of the acid sites: the greater their acidity, the lower the ν(OH) frequency, the higher the ν(CO) perturbed frequency. Interestingly, CO is a suitable probe molecule to characterize the cationic sites because the ν(CO) frequency is very sensitive to the local cationic environment. To perform such analysis, we have used a method consisting on the introduction of calibrated small quantities of CO (typically 100 μmol per gram of sample) followed by IR spectroscopy; details are given in the Experimental Section. In this section, the CO adsorption will be applied on MIL-100 outgassed at various temperatures in order to evaluate the Brønsted acidity of the various OH groups present into the pores of MIL-100. This concerns the Cr−OH groups, the coordinated water molecules **1** and **1′**, and finally the species **2**, that is, water molecules in strong hydrogen-bonded interactions with species **1** and **1′**. The evolution of the ν(OH) and ν(CO) bands as a function of the amount of adsorbed CO will be detailed first, then the appearance of new bands will be explained.

At a first step, we present the different types of bands observed during the adsorption of CO at 100 K on MIL-100 outgassed at increasing temperatures (Figure 5a−g). Three main ν(CO) bands are observed: (i) the band centered at 2160 cm^{-1} corresponds to CO interacting with Brønsted acid sites; (ii) a massif at higher frequency (2215−2180 cm^{-1}) is assigned to CO coordinated on Lewis acid sites, that is, coordinatively unsaturated Cr sites (cus Cr); (iii) a third band at 2138 cm^{-1}, which corresponds to physisorbed species, will not be considered in the present study.

Scrutinizing first the spectrum of MIL-100 outgassed at 473 K, we mainly observe Cr−OH groups, as demonstrated by the ν(OH) band at 3585 cm^{-1} reported in Figure 6a, where the spectrum originally presented in Figure 5d has been retreated and zoomed for the sake of clarity. The introduction of a large amount of CO (Figure 6b) shows that only part of these hydroxy groups is perturbed. By contrast, the ν(OH) band of residual adsorbed water at about 3700−3650 cm^{-1} (Figure 6b) is totally affected. To differentiate the acidity of both species, evacuation at 100 K has been performed (Figure 6c). The subtracted spectrum before and after CO evacuation (Figure 6b−c) shows that only Cr−OH groups interacting with CO species are affected by the evacuation. It allows us to deduce that CO adsorption shifts the 3585 cm^{-1} band to 3495 cm^{-1} ($\Delta\nu$(OH) = 90 cm^{-1}). This indicates that the Cr−OH groups are slightly acidic with an acidity close to that of silanol groups in silicalite

---

(16) Downey, J. R.; Choppin, G. R. *Spectrochim. Acta* **1974**, *30A*, 37.
(17) Falk, M.; Ayers, G. P.; Pullin, A. D. E. *Spectrochim. Acta* **1976**, *32A*, 1641.
(18) Hadjiivanov, K. I.; Vayssilov, G. N. *Adv. Catal.* **2002**, *47*, 307.

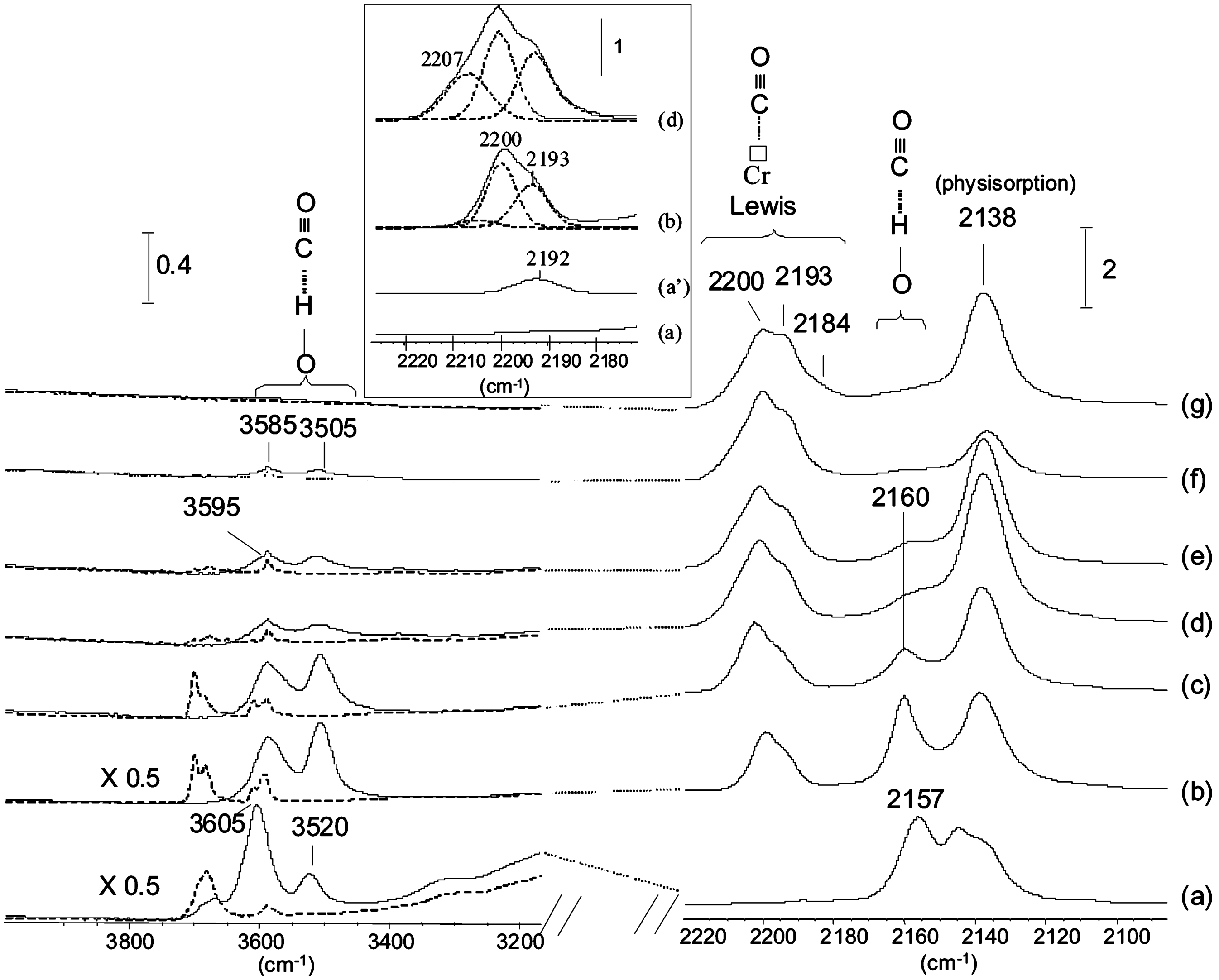


Figure 5. Spectra of MIL-100 recorded at 100 K after outgassing during 2 h at RT (a) during 12 h (spectrum a′ inset), 373 K (b), 423 K (c), 473 K (d), 523 K (e), 573 K (f), 623 K (g). (Dotted line, before CO adsorption; solid line, after introduction into the IR cell of an equilibrium pressure of CO equal to 266 Pa).

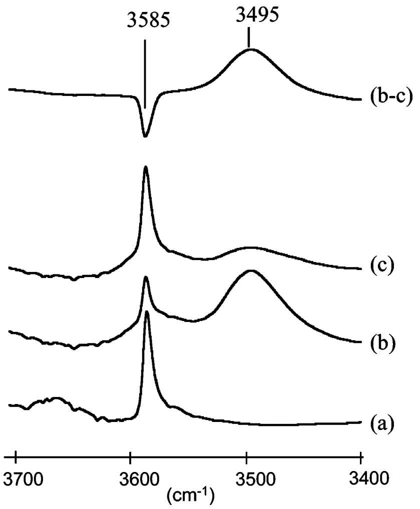


Figure 6. Spectra of MIL-100 outgassed at 473 K recorded at 100 K (a), after introduction of 266 Pa of CO at equilibrium pressure (b), then outgassed at 100 K during 30 s (c).

($\Delta\nu$(OH) = 100 cm^{-1}),[19] meanwhile explaining their sensitivity to water molecules adsorbed on the inactivated sample, as described above. On Cr_2O_3, it has been reported previously that single-bonded OH groups (type I) give rise to high frequency ν(OH) (3638 and 3618 cm^{-1}) with no acidity detectable by the CO probe, while bridged OH groups (type II and III) exhibit lower ν(OH) frequencies and higher acidity (type III, $\Delta\nu$(OH) = 73 cm^{-1}; type II, $\Delta\nu$(OH) = 63 cm^{-1}).[20] Consequently, this high acidity and the low ν(OH) wavenumber of Cr hydroxy groups are in favor of a bridged conformation. The presence of fluorine could also explain their low ν(OH) wavenumber and their stronger acidity as compared to that of α-Cr_2O_3 since it has been reported on fluorinated alumina that hydroxy groups exhibit a higher Brønsted acidity and then lower wavenumber ν(OH) bands than those detected on pure alumina.[21]

CO adsorption experiments were performed on MIL-100 evacuated at 373 K to evaluate the acidity of the terminal water molecules **1** and **1′**. Introduction of a small amount of CO (0.77 mmol·g^{-1}) gives rise to perturbed ν(OH) and ν(CO) bands at 3505 and 2163 cm^{-1}, respectively, as reported in Figure 7. The

---

(19) Zecchina, A.; Bordiga, S.; Spoto, G.; Marchese, L.; Petrini, G.; Leofanti, G.; Padovan, M. *J. Phys. Chem.* **1992**, *96*, 4991.
(20) Zaki, M. I.; Knözinger, H. *Mater. Chem. Phys.* **1987**, *17*, 201.
(21) Ghost, A. K.; Kydd, R. A. *Catal. Rev.-Sci. Eng.* **1985**, *27*, 539.

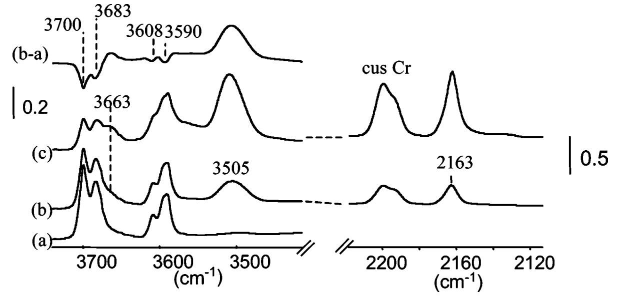
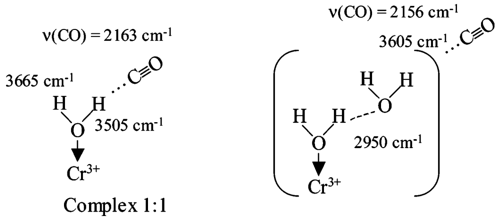


Figure 7. Infrared spectra recorded at 100 K of MIL-100 outgassed at 373 K (a), after introduction of increasing doses of CO at 100 K: (b) 0.77 and (c) 1.76 mmol·g^{-1}.

Scheme 2. Interaction of CO Molecules with Adsorbed Water Molecules



subtracted spectrum shows the decrease of the ν_3 (3700 and 3683 cm^{-1}) and ν_1 bands (3608 and 3590 cm^{-1}) of species **1** and **1′**, whereas a new ν(OH) band develops at 3663 cm^{-1}.

In fact, CO adsorption on coordinated water molecules gives rise to a complex denoted 1:1 (see Scheme 2), inducing a decoupling of the two water stretching OH modes, one strongly perturbed at 3505 cm^{-1} (hydrogen-bonding interaction), and one "free" near 3665 cm^{-1} (i.e., at 20−40 cm^{-1} lower than the coupled ν_3 mode of the free molecule).

The 1:1 complex is characterized by a $\Delta\nu$(OH) shift of 160 cm^{-1} (uncoupled ν(OH), 3665 cm^{-1}; perturbed band, 3505 cm^{-1}). This indicates an acidity clearly higher than that of Cr−OH groups, but close to that of alkali-exchanged faujasite zeolites ($\Delta\nu$(OH) = 160 cm^{-1}),[22] or P−OH groups of phosphated silica ($\Delta\nu$(OH) = 180 cm^{-1}) for which H_0 (the Hammett constant) is equal to −6.[23] Nevertheless, such an acidity is lower than that of the HY zeolites, for instance ($H_0 = -9$).[23] By analogy with the results reported elsewhere in liquid phase,[24] all these features can be interpreted as a cooperative effect of the cation on the coordinated water molecule. Previous studies of complexes of water (HOD) in solution with electron acceptors of different strength, from $SbCl_3$ to $AlCl_3$, show that Brønsted acidity is created by water coordination. The higher the polarizing power of the cation, the stronger the created Brønsted acidity.[25] The cus Cr sites, as it has been well-established previously,[25] polarize the coordinated water molecule and increase its hydrogen-donor properties. This well explains the strong H-bonding formation occurring on MIL-100 outgassed at RT involving species **1** or **1′** and a second water molecule, termed species **2**, as it will be shown in the next section.

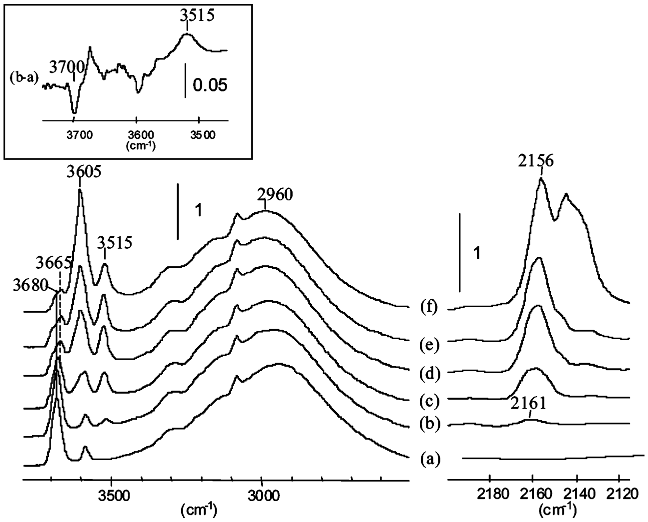


Figure 8. Infrared spectra recorded at 100 K of MIL-100 outgassed at room temperature (a), after introduction of increasing doses of CO at 100 K: 0.44 mmol g^{-1} (b), 1.15, 2.53, and 3.10 mmol g^{-1} (c−e, respectively), then introduction of an equilibrium pressure (P = 200 Pa) (f).

Finally, CO sorption is applied on MIL-100 outgassed at room temperature, which mainly presents additional water molecules, such as species **2**, which are hydrogen-bonded to the coordinated water molecules **1** and **1′** and well characterized by a broad ν(OH) band at 2960 cm^{-1} (Figure 8). CO addition does not displace the hydrogen-bonded water molecule since the intensity of the broad ν(OH) band near 2960 cm^{-1} is not affected. However, the first CO added molecules lead to infrared features, that is, perturbed ν(CO) and ν(OH) bands at 2161 and 3515 cm^{-1}, respectively (Figure 8b), close to those reported above when CO adsorbs on water-coordinated species. Besides, the subtracted spectrum (Figure 8b−a) indicates that the water-coordinated molecules **1** and **1′** are even present at room temperature since the high frequency ν(OH) shoulder at 3700 cm^{-1} has disappeared upon CO addition. Further CO addition mainly gives rise to a new intense ν(CO) band at 2156 cm^{-1}. This band is related, in the ν(OH) range, to the formation of a ν(OH) perturbed band at 3605 cm^{-1}. From the position of the ν(CO) band, a $\Delta\nu$(OH) shift lower than 90 cm^{-1} is expected. This well explains the corresponding decrease of the ν(OH) band intensity of species **2** at about 3680 cm^{-1} when CO is added. This ν(CO) band at 2156 cm^{-1} is characteristic of the acidity of the hydrated sample, and it is clearly higher than that reported for CO interacting with ice[26] and close to that of silanol groups,[19] indicating that the OH groups of species **2** present a lower Brønsted acidity than species **1** and **1′**. This is in agreement with what has been observed on hydrated β-zeolites for which the Brønsted acid strength of the water molecule in the (Zeo)−OH$\cdots$OH$_2$ complex (Zeo−OH: bridged acid hydroxy group) is much lower (ν(CO) = 2162 cm^{-1}) than that of the initial bridged hydroxy group (ν(CO) = 2175 cm^{-1}).[27]

Characterization of the Lewis Acid Sites. This section concerns the study by CO adsorption of the different Lewis acid sites present in MIL-100. First, spectra at 100 K of MIL-100 activated by evacuation at increasing temperatures, that is, from RT to 623 K, are reported in Figure 5. On the sample activated only 2 h at RT (Figure 5a, inset), no ν(CO) band clearly appears above 2180 cm^{-1}, showing that Lewis acid sites are fully covered by water. This situation changes when increasing the

---

(22) Lavalley, J. C.; Anquetil, R.; Czyzniewska, J.; Ziolek, M. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1263.
(23) Lavalley, J. C.; Jolly-Feaugas, S.; Janin, A.; Saussey, J. *Mikrochim. Acta* **1997**, *14*, 51.
(24) Kammer, T.; Lucks, W. A. P. *J. Chim. Phys.* **1993**, *90*, 1643.
(25) Busca, G. *Phys. Chem. Chem. Phys.* **1999**, *1*, 723.
(26) Palumbo, M. E. *J. Phys. Chem. A* **1997**, *101*, 4298.
(27) Paze, C.; Bordiga, S.; Lamberti, C.; Salvalaggio, M.; Zecchina, A.; Bellussi, G. *J. Phys. Chem. B* **1997**, *101*, 4740.

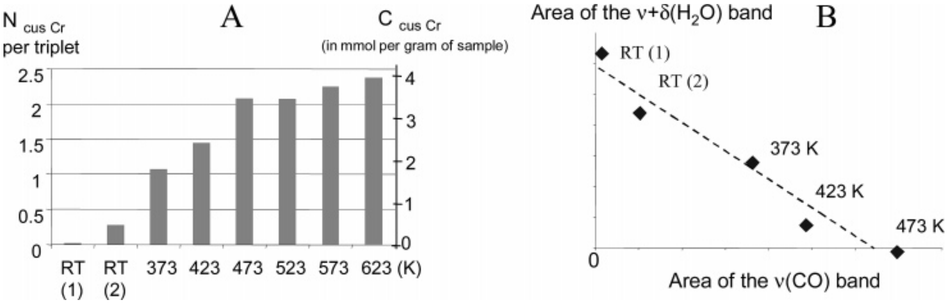


Figure 9. (A) Variation of the number of cus Cr^{3+} per triplet of octahedra detected by CO adsorption on MIL-100 versus the temperature of activation. RT (1) sample outgassed at room temperature for 2 h. RT (2) sample outgassed at room temperature for 12 h. (B) Variation of the $\nu + \delta(H_2O)$ band of adsorbed water on MIL-100 versus the area of the ν(CO) band of CO coordinated to cus Cr^{3+}.

outgassing time at room temperature with a CO adsorption characterized by a rather broad band (FWHM = 10 cm^{-1}) centered at 2192 cm^{-1} (Figure 5a′, inset). In the spectra of the sample activated at 373 K, this band still appears, but another component (shoulder) shows up at about 2200 cm^{-1} (Figure 5b). At higher activation temperatures, a high wavenumber component near 2207 cm^{-1} is clearly observed (Figure 5c−f). When the temperature reaches 623 K, a supplementary very weak band is noted at 2184 cm^{-1} (Figure 5g), which could be due to the beginning of the degradation of the material since it has been shown previously that this temperature is close to that of the degradation of the framework.[7] So, this band is not considered as characteristic of the structure of the MIL-100 and will not be discussed further.

The presence of three ν(CO) bands belongs either to the heterogeneity of the Lewis acid sites or to a band splitting, induced by coupling between CO adsorbed species on the same site. The latter phenomenon can eventually be particularly important at high CO coverage. To determine its contribution, the use of an isotopic mixture of ^{12}CO and ^{13}CO has been performed. Since no decoupling phenomena have been shown by isotopic ^{12}CO dilution (see details in Supporting Information), we can discard such possibility and conclude that the ν(CO) components do not result from a band splitting, as observed previously with dicarbonyl species on chromia,[28] but from the heterogeneity of the Lewis acid sites in MIL-100.

To determine the concentration of cus Cr sites, CO has been quantitatively adsorbed on the solid activated at various temperatures (see details in Supporting Information). The concentration of free Lewis acid sites versus the temperature of activation is shown in Figure 9A. As expected, the amount of free Lewis acid sites increases with the activation temperature up to 473 K. This is due to the progressive bound water desorption when the temperature of activation increases. Indeed, the relative amount of water mainly coordinated on the solid (deduced from the integrated area of the $\nu + \delta(H_2O)$ band) conversely varies with the amount of coordinated CO, as shown in Figure 9B. For an activation temperature of 473 K, the number of Lewis acid sites detected by CO corresponds to the quantity of cus Cr present in the totally dehydrated material. This concentration is about 3.5 μmol mg^{-1}, which corresponds to 2.1 sites per trimer of octahedra (this ratio is related to the presence of F in the coordination sphere of Cr^{3+}, as discussed below).

Table 2. Relation between the Fluorine Content in MIL-100 and the Fraction of Undetected Cr^{3+} by CO

treatment temperature	molar ratio[a] F/Cr	fraction of Cr^{3+} undetected by CO[b]
473 K	0.285	0.30
573 K	0.270	0.28

[a] Determined from elemental analysis. [b] Using ϵ(CO) equal to 2.1 cm μmol^{-1}.

Localization of the Fluorine Atoms. As previously said, MIL-100 is a fluorinated solid with approximately one fluorine atom per trimer of chromium octahedra composition. On the basis of X-ray diffraction data, it was not possible to determine the localization of these atoms, either on a terminal position bound to chromium atoms or as a free counteranion in some of the cages present in MIL-100. In this part, we will shed some light on the position of the fluorine atoms using a quantification of CO adsorption results.

The exact molar ratio F/Cr of the same solid used for the IR experiments was determined by elemental analysis (Table 2) and is equal to 0.285. The activation at 473 K does not modify this ratio, showing that fluorine ions are strongly bound to the wall. This ratio slightly decreases when the solid is activated at 573 K, in agreement with a destabilization of the structure. First, the nonactivated sample contains a large amount of water molecules, about 9 H_2O per Cr, as measured by TGA analysis. This study has shown that coordinated water molecules are still present in the sample outgassed at room temperature, but they completely disappear after outgassing at 473 K. Figure 9B shows that the sites liberated by water desorption are involved in CO adsorption. On the solid activated at 473 K, free of water molecules, quantification of coordinated CO molecules leads to a CO/Cr ratio equal to 0.7. Since each chromium octahedron possesses one terminal group, the maximum and theoretical value is equal to 1. The difference, that is, the fraction of Cr sites undetected by CO, is then equal to 0.3. This value is very close to the F/Cr ratio (0.285) reported in Table 2. This gives a fundamental result, that is, that fluorine atoms fill up the coordination of some Cr sites, preventing CO or H_2O coordination on the top of the Cr octahedra. The electroneutrality of the material implies an anion/Cr ratio equal to 0.333. Since the F/Cr ratio is lower (0.285), it indicates that other anionic species are present. Free hydroxy groups were characterized by a ν(OH) band at 3585 cm^{-1} and considered as bonded to chromium ions. Since it is not possible to directly quantify them, we consider that hydroxy groups compensate the missing negative charge, leading to a general formula $Cr_3OF_{0.85}(OH)_{0.15}(H_2O)_2\{C_6H_3-$

---

(28) Mihaylov, M.; Penkova, A.; Hadjiivanov, K.; Knozinger, H. *J. Phys. Chem. B* **2004**, *108*, 679.

$(CO_2)_3\}_2 \cdot 26H_2O$. The weak intensity of the corresponding ν(OH) band at 3585 cm^{-1} is in agreement with the low amount of expected OH^- groups. As for the amount of H_2O, outgassing experiments at room temperature for different lapses of time show that it is difficult to obtain only coordinated species **1** and **1′** at the surface, and therefore, the number of such species is difficult to calculate. Further heating at 573 K slightly decreases the amount of fluorine (Table 2) and strongly decreases that of Cr−OH groups (Figure 5). These results suggest the beginning of structure modifications. It could result from HF evolution formed by condensation of Cr−F and Cr−OH entities. HF departure has been shown on CrF_3 material by thermal treatment under vacuum or under flow at temperatures as low as 373 K.[29] This HF evolution would be one of the reasons for the framework decomposition of MIL-100 observed between 548 and 673 K.

The average number of fluorine per trimer of chromium octahedra is equal to 1, but the issue at this stage was to determine if a distribution of the terminal fluorine atoms on the trimers occurs in MIL-100, that is, if trimers with 0, 1, 2, or 3 fluorine atoms are present or not. Previous experiments have shown that the Lewis acid sites of MIL-100 are heterogeneous with CO detecting three types of Lewis acid sites (ν(CO) bands at 2207, 2200, and 2193 cm^{-1}) and H_2O adsorption giving rise to two distinct coordinated species (species **1** and **1′**). The difference in the number of different species detected by these two probe molecules is probably related to the greater sensitivity of the ν(CO) vibrator for the cationic sites. A first hypothesis for explaining the heterogeneity of the Lewis acid sites would be that several oxidation states (Cr(IV)[18] or Cr(II)[30]) are present for Cr in MIL-100, which is ruled out by UV−vis spectroscopy (not shown here), confirming the presence of chromium only in the 3+ oxidation state. Thus, our explanation for the presence of three ν(CO) bands concerns a heterogeneity in the fluorine distribution near the Cr^{3+} sites. It is well-known that the addition of fluorine noticeably increases the acid strength of the Lewis sites.[21] In our case, the higher the fluorine atom number on a triplet, the stronger the Lewis acidity of cus Cr and the higher the ν(CO) frequency. Thus, on the basis of a random distribution of fluorine atoms on Cr sites within each trimer, with 2, 1, or 0 fluorine atoms per trimer, a 18, 45, or 37% distribution, respectively, is awaited, as detailed in Table 3. Interestingly, the relative intensity of the three ν(CO) bands at 2207, 2200, and 2193 cm^{-1} is in agreement with this statistical repartition (Table 3). Experiments on a nonfluorinated MIL-100 sample would be extremely interesting to check such a hypothesis. However, all attempts to obtain such solid were not successful since only poorly crystallized samples were obtained to date.

Grafting of Organic Molecules. Results reported above indicate that MIL-100 possesses both Lewis and Brønsted acid sites; the latter comes from both Cr−OH groups and coordinated water. These important results suggest that it should be possible to substitute water by an organic molecule presenting OH groups, such as alcohols, either to modify the Brønsted acidity or to modify its sorption properties. We will report below some preliminary results relative to methanol grafting. For this study, CD_3OH has been used for spectroscopic reasons (the $\nu(CD_3)$ vibrations (2300−2050 cm^{-1}) being less affected by Fermi resonance than the corresponding $\nu(CH_3)$ modes of CH_3OH[31]).

Table 3. Repartition of the cus Cr^{3+} in MIL-100 Determined by CO Adsorption

configuration of fluorine atom into one triplet of octahedron			position of the ν(CO) band (cm^{-1})	measured relative intensity of the bands	awaited relative proportion of each observable site[a]
☐ Cr	☐ Cr	☐ Cr	2193	0.33	0.374
F Cr	☐ Cr	☐ Cr	2200	0.44	0.447
F Cr	F Cr	☐ Cr	2207	0.23	0.179

[a] Considering a random repartition of the fluorine atom on the material (with a molar ratio F/Cr equal to 0.85/3), the probability to obtain a triplet of octahedra with 0, 1, 2, and 3 F atoms is 0.366, 0.437, 0.174, and 0.023, respectively (sites with 3 F atoms are not observable, hence they are not considered in the relative proportions in the table).

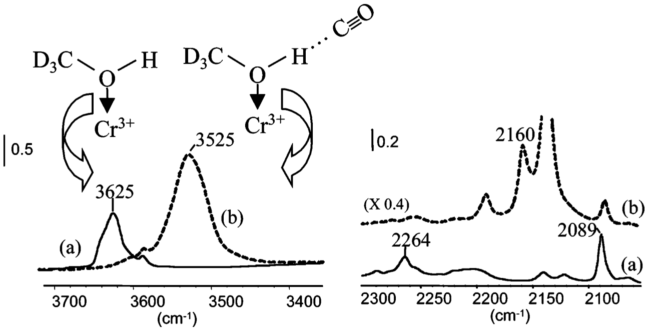


Figure 10. IR spectrum of MIL-100 previously dehydrated at 573 K after introduction of methanol-d_3 in excess at room temperature (532 Pa at equilibrium pressure) and then evacuated at 373 K overnight (a), following by introduction of CO (266 Pa at equilibrium pressure) (b).

On the MIL-100 sample previously dehydrated at 523 K, deuterated CD_3OH methanol in excess has been introduced at room temperature and then evacuated at 373 K overnight. The spectrum of the persisting methanol species (Figure 10a) presents the characteristic bands of coordinated methanol: a strong ν(OH) band at 3625 cm^{-1} and two $\nu(CD_3)$ bands at 2264 and 2089 cm^{-1}, upward shifted relative to the frequencies of liquid methanol.[31] It is worth noting that despite the long evacuation time, the strong intensity of methanol bands indicates the higher stability of the species formed with respect to what was observed for water. This can be ascribed to the higher basicity of the oxygen atom of the methanol molecule. CO introduction on such modified material (Figure 10b) gives rise to a ν(CO) band at 2160 cm^{-1} and to a red shift of the methanol ν(OH) band of about 100 cm^{-1}. These values are lower than those observed in the case of water and are explained by the lower Brønsted acidity of methanol.

This first result is of a great importance since the grafting of a wide range of basic organic molecules (alcohols, amines, etc.) can probably be forecasted with a reasonable stability on MIL-100, leading to a modulation of its catalytic, separation, or sorption properties.

Conclusion

This study has first evidenced a very unusual adsorption mode of water molecules in a porous chromium carboxylate: water

---

(29) Francke, L.; Durand, E.; Demourgues, A.; Vimont, A.; Daturi, M.; Tressaud, A. *J. Mater. Chem.* **2003**, *13*, 2330.

(30) Davydov, A. A. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 913.

(31) Busca, G.; Rossi, P. F.; Lorenzelli, V.; Benaissa, M.; Travert, J.; Lavalley, J. C. *J. Phys. Chem.* **1985**, *89*, 5333.

molecules coordinated on chromium atoms are free from any interaction by hydrogen bonding with the adjacent oxygen of the inorganic chromium trimer. This is very different from adsorbed water on metal oxides or cationized zeolites, which generally involves $M^{\delta+}-O^{\delta-}$ Lewis acid−base pair sites that might further dissociate leading to hydroxy groups. Such differences show that MIL-100 framework does not present any significant basicity. This peculiarity is an important feature of MIL-100; it can be ascribed to the relevant covalent character of the benzene−tricarboxylate entities building the framework, which therefore could give rise to adsorption or catalytic properties different from those of metal oxides.

Second, Brønsted acidity is present in MIL-100, resulting from both Cr−OH groups and coordinated water due to a cooperative effect of the cation on the coordinated water molecule. This outstanding result is due to the presence of the Brønsted acidity of the OH groups from the terminal water molecules, polarized by the chromium atoms. To further increase this acidity for catalytic applications, it could be pertinent to act on the following parameters: (i) the polarizing power of the cation; (ii) the initial Brønsted acidity of the coordinated molecules. Consequently, it will be interesting to extend this study to analogues of MIL-100 having a higher polarizing power than Cr^{3+}, such as Fe^{3+}, or replacing the terminal water molecules with molecules with a stronger acidity.

Finally, the preliminary results about substitution of the terminal water molecules by methanol show that the grafting of basic groups directly on the chromium atoms is possible in MIL-100. This opens the way for a modulation both of the strength of the Brønsted acid sites as well as the sorption or separation properties of MIL-100.

Experimental Section

Synthesis: Due to the difficulty of avoiding the presence of significant amount of metallic chromium during the synthesis conditions reported previously for MIL-100, another synthetic route involving chromium(VI) oxide as the source was developed. To 100 mg of chromium(VI) oxide CrO_3 were added 210 mg of trimesic acid, 0.2 mL of a 5 M hydrofluorohydric solution, and 4.8 mL of deionized water, and the mixture was stirred a few minutes at room temperature. The slurry was then introduced in a Teflon-lined Paar hydrothermal bomb and set 4 days at 493 K. The resulting green solid was washed with deionized water and acetone and dried at room temperature under air atmosphere.

X-ray Thermodiffractometry. X-ray thermodiffractometry, performed in the furnace of a Siemens D-5000 diffractometer in the $\theta-\theta$ mode ($\lambda_{Cu}K_{\alpha} = 1.5406$ Å) under primary vacuum, shows several steps in the decomposition of MIL-100. Each pattern was recorded within the 1.5−15° (2θ) with a 2 s/step scan which gave an approximate 1 h length for each pattern at the corresponding temperature. The heating rate between two temperatures was of 5 K/min.

FTIR Spectroscopy. Samples were pressed (10^9 Pa) into self-supported disks (2 cm^2 area, 7−10 mg cm^{-2}). They were placed in a quartz cell equipped with CaF_2 windows. A movable quartz sample holder permits adjustment of the pellet in the infrared beam for spectra acquisition and to displace it into a furnace at the top of the cell for thermal treatments. The cell was connected to a vacuum line for evacuation, calcination steps ($P_{residual} = 10^{-3}-10^{-4}$ Pa), and for the introduction of CO gas into the infrared cell. Spectra were recorded at room temperature. In the CO adsorption experiment, the temperature of the pellet was decreased to about 100 K by cooling the sample holder with liquid N_2 after quenching the sample from the thermal treatment temperature. The addition of accurately known increments of CO probe molecules in the cell (a typical increment corresponds to 100 μmol of CO per gram of material) was possible via a calibrated volume (1.75 cm^3) connected to a pressure gauge for the control of the probe pressure ($1-10^4$ Pa range). The CO pressure inside the IR cell was controlled by another pressure gauge ($1-10^3$ Pa range). Transmission IR spectra were recorded in the 500−5600 cm^{-1} range, at 4 cm^{-1} resolution, on a Nicolet Nexus spectrometer equipped with an extended KBr beam splitting device and a mercury cadmium telluride (MCT) cryodetector.

Supporting Information Available: The use of an isotopic mixture of ^{12}CO and ^{13}CO in order to determine the contribution of the coupling between the CO-adsorbed species on the same site to the ν(CO) band splitting, and the quantification of the concentration of cus Cr sites on MIL-100 by CO adsorption. This material is available free of charge via the Internet at http://pubs.acs.org.

JA056906S