

An FTIR Study of Zeolite Theta-1

F. Geobaldo,[†] S. Fiorilli,[†] B. Onida,[†] G. Giordano,[‡] A. Katovic,[‡] and E. Garrone^{*,†}

Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, Corso Duca degli Abruzzi 24, I-10129 Torino, Italy, and Dipartimento di Ingegneria Chimica e dei Materiali, Università della Calabria, via P. Bucci, I-87030 Rende (CS), Italy

Received: June 21, 2002; In Final Form: November 29, 2002

The acidic properties of two samples of zeolite Theta-1 (Si/Al = 25 and 50) have been studied as the propensity to form hydrogen bond with several probes. The adsorption of small molecules (N₂ and CO) at a nominal temperature of 77 K leads to bathochromic shifts in the OH stretching vibration of the Si(OH)Al groups close to those observed with ZSM-5 and H-MOR, so suggesting comparable acidity. The corresponding values measured with propene, a bulkier molecule, are instead somewhat smaller than those observed with the same reference zeolites. This is ascribed to the proximity of the walls surrounding the Si(OH)Al site, with which secondary (van der Waals) interactions may occur, hampering the purely hydrogen-bonding phenomenon. This same geometric constraint may be the reason for the unexpected absence of proton transfer to propene and for the exceptionally low OH stretching frequency (3598 cm⁻¹) of free Si(OH)Al species. No Lewis acidity was found. With the sample richer in Al some dealumination took place; because of their mono-dimensional nature, a remarkable fraction of channels are blocked by a relatively small amount of debris, with the exclusion of a sizable fraction of Si(OH)Al sites.

1. Introduction

Synthetic high-silica zeolites are catalysts extensively used in the oil industry. Channels and cavities of their aluminosilicate framework provide both high surface area and shape-selectivity, while hydroxyl groups linking aluminum and silicon atoms in the framework are responsible for Brønsted acidity. This, together with Lewis acidity arising from exposed Al species, has been investigated by various techniques,^{1,2} such as calorimetry,³ temperature-programmed desorption,⁴ and IR.⁵ IR allows the direct observation of the behavior of the OH groups either interacting or not with adsorbed species, and also provides information on Lewis sites.

The present work deals with Theta-1, a highly siliceous zeolite with TON structure, belonging to the group of medium-pore zeolites including ZSM-5, ZSM-11, and ZSM-35. The TON structure consists of a linear mono-dimensional 10-membered rings channels with openings of only 4.5 × 5.5 Å (smaller than those of the other zeolites in the group),^{6,7} all running along the [001] direction without any intersection.⁸ This feature imparts zeolite Theta-1 a remarkable selectivity in catalytic applications,^{9–11} like dewaxing,¹² xylene isomerization,¹³ alkylation of aromatic hydrocarbons,¹⁴ and the isomerization of *n*-butene to isobutene.¹⁵ Conversion of light alkanes into aromatic hydrocarbons, an important reaction from the industrial point of view, can be successfully carried out over Ga- or Zn-modified Theta-1 zeolite,^{16–18} while the isomorphous substitution with Fe makes this material active in the decomposition of N₂O.¹⁹

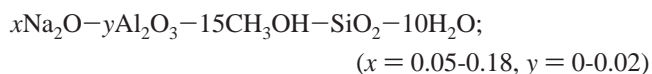
NMR characterization²⁰ and FT-IR studies of the adsorption of different alkanes²¹ have been carried out to investigate the

isomerization mechanism. IR data concerning CO adsorption at 77 K on the protonic form of Theta-1 zeolite are available,²² but a comprehensive study of Brønsted and Lewis acidic properties is lacking. This is attempted in the present paper by a systematic use of FTIR spectroscopy. Brønsted acidity is the ability to give proton-transfer to suitable molecules: an indirect measure of acidity, without actually transferring the proton, is provided by the study of the hydrogen-bonding between hydroxyl groups and molecules with weakly basic property (such as N₂, CO, unsaturated hydrocarbons, etc.), which may also provide information about Lewis sites.^{23,24}

In the present work the molecules employed are N₂, CO, and propene. Results are compared to the literature data concerning H-ZSM-5,^{21,25–27} H-mordenite,^{28–30} and H-MCM-22.^{31,32} The zeolite has been synthesized through an innovative procedure using methanol instead of bulky organic molecules (such as 1-ethylpyridinium bromide) to direct the synthesis. The choice of methanol has two advantages: it lowers drastically the costs and enables the formation of Theta-1 zeolite in a wide range of Si/Al ratios. Two samples with different Si/Al ratio have been considered.

2. Experimental Section

The samples studied had a Si/Al ratio 25 and 50. Reported results basically concern the sample with higher Al content. Synthesis involved mixtures of the following type:



kept in a magnetically stirred stainless steel reactor, at the temperature of 140 °C under autogenous pressure. After quenching the autoclave in cold water, the solid product was filtered, washed, and dried at 105 °C overnight.

* Author to whom correspondence should be addressed. Phone: +39-011-5644661. Fax: +39-011-5644699. E-mail: edoardo.garrone@polito.it.

[†] Politecnico di Torino.

[‡] Università della Calabria.

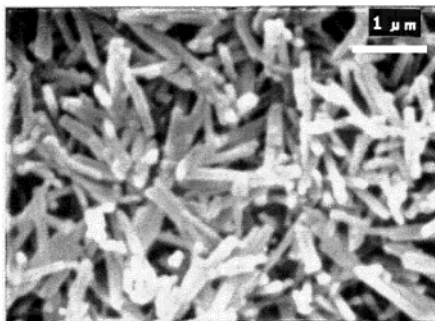


Figure 1. Scanning electron micrograph of Theta-1 sample (Si/Al = 25) synthesized from alcohol–water system.

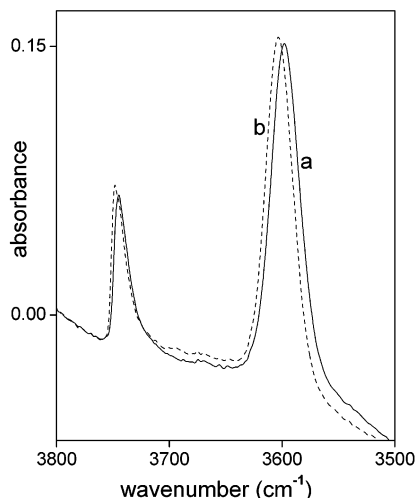


Figure 2. IR spectra of the OH stretching region of Theta-1 sample (Si/Al = 25) after activation at 773 K. Curve a: ambient temperature; curve b: at a nominal 77 K temperature.

XRD analysis showed the sample to be completely crystalline: scanning electron microscopy (JEOL JTSM 330°) confirmed the absence of amorphous phase and showed needlelike crystallites with length ranging from 0.6 to 1.0 μm and width from 0.06 to 0.10 μm (Figure 1).

The template was removed in a vacuum first heating at 773 K for 2 h, then treating in 250 hPa of O_2 at the same temperature for an additional 2 h. To obtain the H-form of the zeolite, the calcined sample was exchanged in a 1 M aqueous solution of NH_4NO_3 at about 320 K for 48 h, then calcined again.

For IR measurements, thin self-supporting wafers were prepared and activated under dynamic vacuum (10^{-2} Pa) for 2 h at 773 K and finally outgassed at the same temperature for 1 h. Spectra were collected on a Bruker FTIR Equinox 55 equipped with a MCT cryodetector working at 2 cm^{-1} resolution.

The interaction with N_2 and CO has been followed at the nominal temperature of 77 K by using liquid nitrogen as coolant. The actual temperature of the sample is about 100 K, due to the heating effect of the IR beam. Adsorption of propene was studied at ambient temperature.

3. Results and Discussion

Figure 2 shows the OH stretching region after activation at 773 K, both at the ambient temperature (curve a) and at a nominal 77 K temperature (curve b). Bands are observed at 3745 and at 3598 cm^{-1} . The former is the $\nu(\text{OH})$ mode of the isolated silanol, mainly located at the external surface of the zeolite crystals; the band at 3598 cm^{-1} is ascribed to the $\nu(\text{OH})$ mode

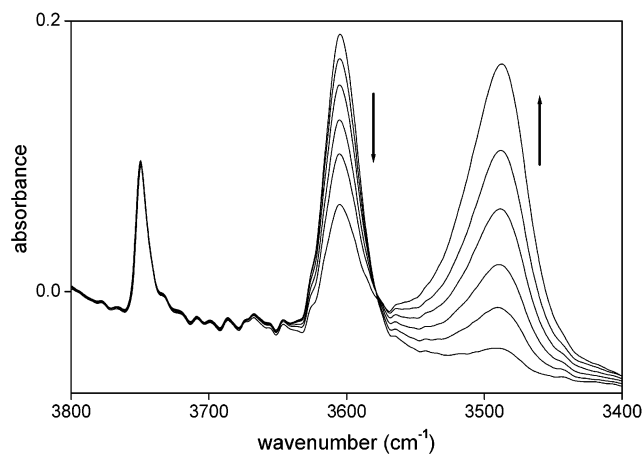


Figure 3. Adsorption of N_2 at nominal 77 K on Theta-1 sample (Si/Al = 25; IR spectra in the OH stretching region).

of the bridged OH groups, $\text{Si}(\text{OH})\text{Al}$. The absence of any absorption around 3500 cm^{-1} suggests a negligible presence of hydroxyl nests,³¹ caused by structural imperfections.

The value of 3598 cm^{-1} is unusually low for the OH stretching vibrations of free $\text{Si}(\text{OH})\text{Al}$ groups: for instance, the values observed for ZSM-5, H-MOR, and H-MCM-22 are 3610, 3609, and 3626 cm^{-1} , respectively.^{27–28,30–31} Unusually low frequencies in the region 3560–3580 cm^{-1} have been observed for OH species in constrained environments, like the sodalite cavities of faujasites^{33,34} or in SAPO-40,³⁵ because of the electrostatic interactions with surrounding oxygen atoms.³⁴ These interactions are close in nature to hydrogen-bonding, and indeed the bands shift to lower frequencies when the temperature is lowered, in contrast with free hydroxyl species, which undergo small hypsochromic shifts with decreasing temperature.³⁵ The TON structure does not exhibit any small cavity, and the value of 3598 cm^{-1} is comparatively low but still in the range of free $\text{Si}(\text{OH})\text{Al}$ species, so that this low frequency is to be ascribed to some other reason. Indeed, comparison of curves a and b in Figure 2 shows that the 3598 cm^{-1} band shifts by 6 cm^{-1} to higher frequencies as a consequence of lowering the temperature to about 100 K, confirming that the $\text{Si}(\text{OH})\text{Al}$ species behaves as an unperturbed species.

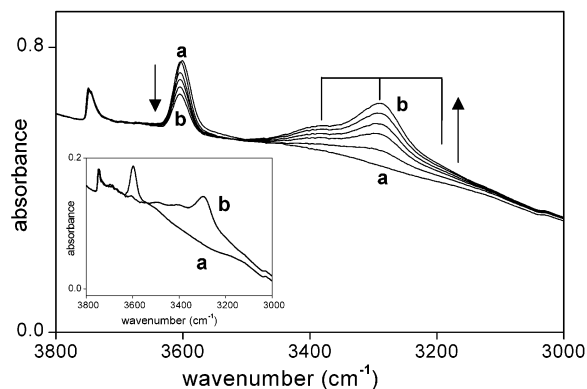
As a rule of thumb, it is often assumed that the lower the frequency, the more acidic the Brønsted site: it may be therefore be expected that the species absorbing at 3598 cm^{-1} has a strong acidic nature. This empirical rule has recently received support from calculations from Lewis and Sastre within the same structure.³⁶

Figure 3 shows the effect of dosing increasing amounts of N_2 at nominal 77 K on the OH stretching region. The 3598 cm^{-1} band is gradually eroded and a new band at around 3483 cm^{-1} is observed ($\Delta\nu = -117 \text{ cm}^{-1}$) due to the formation of hydrogen-bonded $\text{OH} \cdots \text{N}_2$ species. The corresponding N_2 stretching mode (figure not shown) gives rise to a peak at 2333 cm^{-1} .^{28,30} The observed shift is similar to that observed with H-ZSM-5,²⁶ H-MOR,^{28,30} and H-MCM-22³¹ (Table 1). As the value of $\Delta\nu(\text{OH})$ is a measure of the strength of the hydrogen bond, which in turn is roughly correlated with the acidity of the OH species, the shift observed with Theta-1 indicates Brønsted acidity not too different from the reference zeolites. Even at relatively high pressure, N_2 does not deplete the 3598 cm^{-1} band, so indicating that not all Brønsted sites interact with the molecular probe.

Figure 4 illustrates the adsorption of CO at the nominal temperature of 77 K: increasing the equilibrium pressure leads

TABLE 1: Shifts (in cm^{-1}) of the OH Stretching Mode of Si(OH)Al Observed with Basic Probes on Different Systems

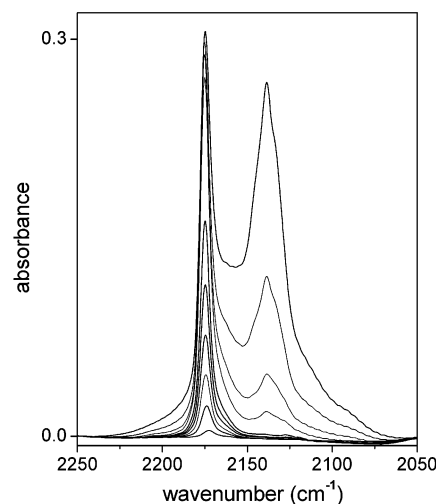
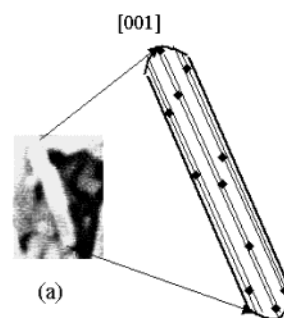
probe molecule	Theta-1	ZSM5 ^a	MOR ^b	MCM-22 ^c	Aerosil
propene	450	540	510	500	152
N ₂	117	125	109	120	40
CO	316	330	294	320	90

^a Refs 21,25–27. ^b Refs 28–30. ^c Refs 31,32.**Figure 4.** Adsorption of CO at nominal 77 K on Theta-1 sample (Si/Al = 25) (IR spectra in the OH stretching region). Inset: the same for the sample (Si/Al = 50). Curve a: samples outgassed at 773 K; curve b: high pressure of CO. The fork represents the coupling of the ν -(OH) mode with an intermolecular ν (OH- -CO) mode.

to a progressive erosion of the band at 3598 cm^{-1} and the parallel formation of the broad band at ca. 3284 cm^{-1} . The bathochromic shift ($\Delta\nu \sim -316\text{ cm}^{-1}$) and the increase in both width and intensity of the growing band are due to the OH- -CO interaction.^{24–26} The shift is intermediate between those observed for ZSM-5 and MOR, $\sim 330\text{ cm}^{-1}$ ^{21,25,26} and 294 cm^{-1} ,²⁹ respectively (Table 1), suggesting a corresponding intermediate Brønsted acidity.²² This result, in accord with the corresponding one concerning N₂, shows that the unusually low $\nu_{\text{O-H}}$ value for Si(OH)Al species H-Theta-1 is not to be attributed to any higher Brønsted acidity with respect to the reference zeolites.

A definite shoulder of the band at 3282 cm^{-1} is seen at ca. 3400 cm^{-1} . A similar component at higher frequency accompanying a band due to hydrogen-bonded Si(OH)Al species has been reported in other cases, and attributed either to the presence of weaker sites,³⁷ or to the combination between the OH stretching mode and a low-lying intermolecular mode OH- -CO.³⁵ In the present case, a third component is seen at about 3170 cm^{-1} , roughly displaced to low frequency by as much as the component at 3400 cm^{-1} is displaced to higher frequencies. This shows fairly clearly that coupling is taking place between the OH stretching mode and an intermolecular mode with frequency $\nu(\text{OH- -CO}) \approx 130\text{ cm}^{-1}$, so that not only the summation band $\nu_s = \nu(\text{OH}) + \nu(\text{OH- -CO})$ is seen at 3400 cm^{-1} , but also the difference band $\nu_d = \nu(\text{OH}) - \nu(\text{OH- -CO})$ at 3170 cm^{-1} . The intensity ratio between ν_s and ν_d is expected to be of the order of $\exp[-h\nu(\text{OH- -CO})/kT]$, with $T \sim 100\text{ K}$, i.e., about 0.30: the ratio between the intensity of the two modes is in fair agreement with this estimate. An intermolecular mode of this kind has been observed by Tsyganenko and co-workers for the CO/SiOH case.^{38,39}

Figure 5 shows that the stretching mode of hydrogen-bonded CO molecules occurs at 2173 cm^{-1} at any coverage. This suggests the absence of heterogeneity among Si(OH)Al species, in agreement with the absence of any preferential erosion of

**Figure 5.** Adsorption of CO at nominal 77 K on Theta-1 sample (Si/Al = 25) (IR difference spectra in the CO stretching region).**CHART 1**^a Enlarged detail of scanning electron micrograph of Theta-1 sample: a crystallite. ^b Sketch of the blocking of monodimensional pores by extraframework debris (■).

the 3598 cm^{-1} band. The pressure-dependent band at about 2138 cm^{-1} is related to liquidlike CO in the zeolite channels.²²

In the region around 2220 cm^{-1} , where bands due to CO adsorbed on extraframework Al³⁺ species are expected to fall, no signal is observed. This apparently indicates that the amount of Al extraframework species present in the sample is negligible, but further considerations lead to a different conclusion.

As with N₂, even at substantial CO pressures the erosion of the 3598 cm^{-1} band is not complete (curve b, Figure 4). Some zeolitic systems (e.g., faujasite and mordenite) do show inaccessible OH species, located in cavities too small to be reached by the molecular probes. No such cavities are present in the TON structure. A possible explanation takes into account the peculiar morphology of the needlelike crystallites (Figure 1), where all channels run in the same direction for the whole length⁸ without intersections between the pores. Any obstruction can easily lead to the isolation of portions of the channel and therefore to the exclusion of Brønsted sites from interaction. Dealumination is very likely to be the origin of these obstructions: thermal treatments of zeolites bring about some expulsion of structural Al atoms with the formation of nonstructural aluminum oxide clusters within the zeolite pores, that can partially occlude the channels. This interpretation is illustrated in Chart 1.

The absence of absorptions due to CO interacting with extraframework Al³⁺ species, which might appear to suggest that dealumination was negligible, is instead in accord with the blockage of the channels by small aluminum oxide clusters, where debris is located. Accessible Al sites only are at ends of

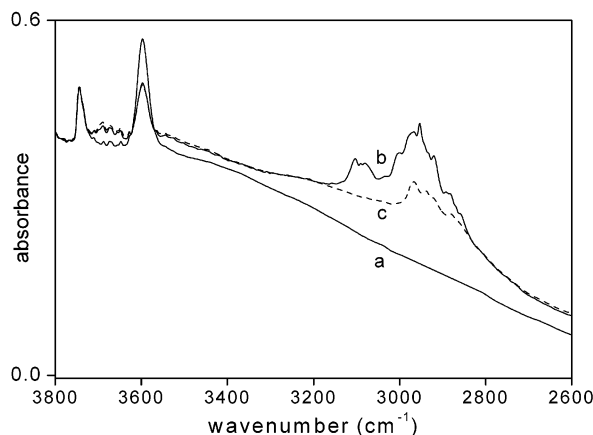


Figure 6. Adsorption of propene on Theta-1 sample (Si/Al = 25) at 300 K (IR spectra). Curve a: sample outgassed at 773 K; curve b: after 30 min contact with propene (initial pressure = 30 hPa); curve c: after short outgassing at room temperature.

the blocked portions and are therefore a minority of the total dealuminated amount.

A lower Al content corresponds to a more limited extent of dealumination. The inset in Figure 4 illustrates CO adsorption on the sample with a Si/Al = 50; in this case the depletion of the 3598 cm^{-1} band was observed.

The other probe, propene, is in principle able both to engage in hydrogen-bonding with the acidic species and to cause proton transfer, with the formation of carbocationic species, giving then rise to oligomers. This has been observed both with H-ZSM-5⁴⁰ and H-MOR;⁴¹ the case of H-MCM-22 is discussed below. Figure 6 shows that upon contact with 30 hPa of propene, the Si(OH)Al band is only partially eroded, for the same reason discussed above for the CO and N_2 cases, while a broad band appears at around 3150 cm^{-1} , due to Si(OH)Al species hydrogen-bonded with propene molecules in a π complex ($\Delta\nu \approx -450 \text{ cm}^{-1}$). The absorption at 3080–3060 cm^{-1} is due to the stretching modes of unsaturated CH groups in molecular propene. Oligomerization does not occur: the band at 3150 cm^{-1} is stable even after several hours of contact, in contrast with H-ZSM-5 and H-MOR, where the formation of oligomers at room temperature is so fast that the π complex is only observed either by drastically lowering the temperature or by operating fast scans. Short outgassing at room temperature leads to spectrum c, which reveals indeed only minute amounts of residual CH species, i.e., negligible activity toward oligomerization. Because of difficult diffusion along the narrow one-dimensional pores, the 3150 cm^{-1} lowering does not decrease upon short outgassing as well as does not increase the intensity of free Si(OH)Al species. In the CH bending region (1700–1350 cm^{-1} , figure not reported), bands are seen at 1633 and 1645 cm^{-1} : the former is due to the C=C stretch of the molecule involved in the π complex, while the latter is due to the same mode of physisorbed species.

The shift value observed for propene with Theta-1 is considerably lower than those observed with H-ZSM-5, H-MOR and H-MCM-22 (Table 1), in contrast with the CO and N_2 cases discussed above. This is probably due to the fact that C_3H_6 forms a π -bonded adduct at a right angle with the acidic hydroxyl, and has therefore a substantial cross-section, so that secondary (van der Waals) interactions with the surrounding walls may take place.⁴² Optimization of the overall energy of interaction may lead to a decrease in the purely hydrogen-bonding contribution. As hydrogen-bonding is rather sensitive to the geometry of the complex, small variations from the conforma-

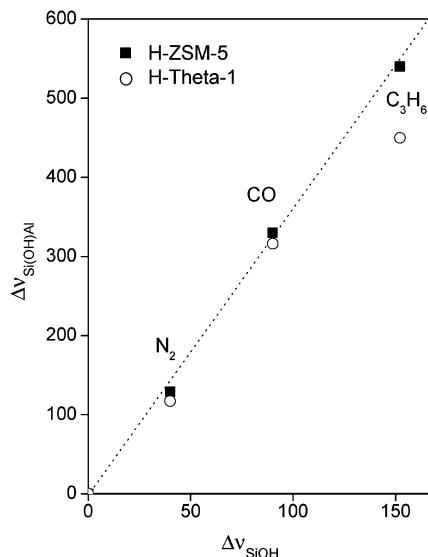


Figure 7. Bellamy-Hallam-Williams plot for H-ZSM-5 and H-TON; abscissa: $\Delta\nu$ values for the isolated silanol of Aerosil; $\Delta\nu$ values for the Si(OH)Al groups of ZSM-5 (squares) and the same for Theta-1 (slots).

tion optimizing the hydrogen-bonding energy alone may result in a smaller shift value.

Support to this interpretation comes from the plot in Figure 7, which reports the data in Table 1, regarding Theta-1 and H-ZSM-5, against those concerning the isolated OH species in dehydrated Aerosil (also reported in Table 1), in the form of the so-called BHW (Bellamy-Hallam-Williams) plots. Because of the nonporous nature of the Aerosil the isolated SiOH species may be assumed as relatively free from secondary interactions with the walls, and therefore the corresponding values afford a reasonable set of independent variables. With H-ZSM-5, all three points line up with the origin, showing proportionality with the data for Aerosil: the same takes places with mordenite and MCM-22 (plots not reported). With Theta-1, the points corresponding to CO and N_2 line up with the origin: that for propene, instead, lies outside, showing the occurrence of hindrance at the Brønsted site.

The proximity of the walls to the Brønsted sites, imparting steric constraints, which we assume to cause deviations in the BHW plots, might provide an explanation also for the rather surprising absence of oligomerization. As Theta-1 seems to be as acidic as other zeolites with comparable Al content on the basis of the propensity to form hydrogen-bonds, the lack of activity in the oligomerization of propene has to be ascribed to other reasons. Probably, the activated state is sterically demanding and therefore inhibited by the presence of close walls. Also in the case of MCM-22, propene has been observed to oligomerize with difficulty,³² and this fact has been related to the observation that the propene shift is smaller than those observed with H-ZSM-5 and H-MOR.

The environment of the Brønsted site may also be the reason for the exceptionally low frequency of the OH stretching mode of the Si(OH)Al species (to which does not correspond any high acidity), without, however, the walls being so close to the Si(OH)Al moiety to yield hydrogen-bonding-like interactions.

4. Conclusions

Although the Brønsted acidity of Si(OH)Al groups in Theta-1, as evaluated from the adsorption of dinitrogen and carbon monoxide, is close to that of H-ZSM-5 or H-MOR, oligomer-

ization of propene does not take place. The explanation advanced is that the acidic center is surrounded by relatively close-lying walls, which impart steric constraints: evidence is provided by the hydrogen-bond interaction between the acidic OH and propene itself, yielding shifts notably lower with respect to those measured with H-ZSM-5, H-MOR, and H-MCM-22. The assumption of sterically constrained Si(OH)Al species is also in agreement with the unusually low value of the OH stretching frequency.

With the sample richer in Al, dealumination takes place, revealing itself not through the appearance of new sites, but through the blocking of monodimensional pores by the debris, which excludes sizable portions of the sites from interactions.

References and Notes

- (1) Rabo, J. A.; Gajda, G. J. *Catal. Rev.—Sci. Eng.* **1989**, *31*, 385.
- (2) Karge, H. G. *Stud. Surf. Sci. Catal.* **1991**, *65*, 133.
- (3) Vedrine, J. C. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 2544.
- (4) Karge, H. G.; Dondur, V. *J. Phys. Chem.* **1990**, *94*, 765.
- (5) Ward, J. W. In *Zeolite Chemistry and Catalysis*; Rabo, J. A., Ed.; ACS Monograph 171; American Chemical Society: Washington, DC, 1976; pp 118–284.
- (6) Kokotailo, G. T.; Schelenker, J. L.; Dwyer, F. G.; Vallycsik, E. W. *Zeolites* **1985**, *5*, 349.
- (7) Borade, R. B.; Adnot, A.; Kaliaguine, S. *Zeolites* **1991**, *11*, 710.
- (8) Hogan, P. J.; Whittam, T. V.; Birtill, J. J.; Stewart, A. *Zeolites* **1984**, *4*, 27.
- (9) Simon, M. W.; Suib, S. L.; O'Young, C. L. *J. Catal.* **1994**, *147*, 484.
- (10) Martens, J. A.; Parton, R.; Uytterhoeven, L.; Jacobs, P. A. *Appl. Catal.* **1991**, *76*, 95.
- (11) Jacobs, P. A.; Martens, J. A. *Pure Appl. Chem.* **1986**, *56*, 1329.
- (12) Dwyer, F. G. U.S. Patent 4,556,477, 1985.
- (13) Kumar, R.; Ratnaswamy, P. *J. Catal.* **1989**, *116*, 440.
- (14) Hogen, P. J.; Whittam, T. V.; Birtill, J. J.; Stewart, A. *Zeolites* **1989**, *4*, 275.
- (15) Mark, W.; Simon, S. L.; Chi, L. *J. Catal.* **1994**, *147*, 484.
- (16) Kumar, N.; Lindsforts, L. E. *Stud. Surf. Sci. Catal.* **1995**, *94*, 325.
- (17) Jianhua, Y.; Le van Mao, R.; Louise, D. *Appl. Catal.* **1990**, *65*, 175.
- (18) Minachev, K. M.; Degarchev, A. A. *Catal. Today* **1992**, *13*, 645.
- (19) Kasture, M.; Krysiak, J.; Mataschowski, L.; Machej, T.; Derewinski, M. *Stud. Surf. Sci. Catal.* **1999**, *125*, 579.
- (20) Barri, S. A.; Smith, G. W.; White, D.; Young, D. *Nature* **1984**, *312*, 533.
- (21) Pieterse, J. A. Z.; Veeffkind-Reyes, S.; Seshan, K.; Lercher, J. A. *J. Phys. Chem. B* **2000**, *104*, 5715.
- (22) Garrone, E.; Chiappetta, R.; Spoto, G.; Ugliengo, P.; Zecchina, A.; Fajula, F. In *R. Proceedings of the 9th International Zeolite Conference*, Montreal, 1992; Von Ballmoos, R., et al., Eds.; Butterworth-Heinemann, Woburn, MA, 1993; p 297.
- (23) Zecchina, A.; Otero Areán, C. *Chem. Soc. Rev.* **1996**, *25*, 187.
- (24) Knözinger, H.; Huber, S. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 2047.
- (25) Pel'menshchikov, A. G.; Paukshtis, E. A.; Stepanov, V. G.; Pavlov, V. I.; Yurchenko, E. N.; Ione, K. G.; Zhidomirov, G. M.; Beran, S. *J. Phys. Chem.* **1989**, *93*, 6725.
- (26) Kustov, L.; Kasansky, V.; Beran, S.; Kubelková, L.; Jiru, P. *J. Phys. Chem.* **1987**, *91*, 5247.
- (27) Zecchina, A.; Bordiga, S.; Geobaldo, F.; Spanò, G.; Scarano, D. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4863.
- (28) Geobaldo, F.; Lamberti, C.; Ricchiardi, G.; Bordiga, S.; Zecchina, A.; Turnes Palomino, G.; Otero Areán, C. *J. Phys. Chem.* **1995**, *99*, 11167.
- (29) Bordiga, S.; Lamberti, C.; Geobaldo, F.; Zecchina, A. *Langmuir* **1995**, *11*, 527.
- (30) Wakabayashi, F.; Kondo, J.; Wada, A.; Domen, K.; Hirose, C. *J. Phys. Chem.* **1993**, *97*, 10761.
- (31) Onida, B.; Geobaldo, F.; Testa, F.; Crea, F.; Garrone, E. *Microporous Mesoporous Mater.* **1999**, *30*, 119.
- (32) Onida, B.; Geobaldo, F.; Testa, F.; Aiello, R.; Garrone, E. *J. Phys. Chem. B* **2002**, *106*, 1684.
- (33) Jacobs, P. A.; Uytterhoeven, J. B. *J. Chem. Soc., Faraday Trans.* **1973**, *69*, 359.
- (34) Jacobs, P. A.; Mortier, W. J. *Zeolites* **1982**, *2*, 226.
- (35) Onida, B.; Gabelica, Z.; Lourenco, J.; Garrone, E. *J. Phys. Chem.* **1996**, *100*, 11072.
- (36) Sastre, G.; Lewis, D. W. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 3049.
- (37) Otero Areán, C.; Turnes Palomino, G.; Geobaldo, F.; Zecchina, A. *J. Phys. Chem.* **1997**, *100*, 66678.
- (38) Smirnov, K. S.; Nikolskaya, M. A.; Tsyganenko, A. A. *Opt. Spectrosc. (USSR)* **1987**, *62*, 743.
- (39) Tsyganenko, A. A. *Russ. J. Phys. Chem.* **1982**, *56*, 1428.
- (40) Spoto, G.; Bordiga, S.; Ricchiardi, G.; Scarano, D.; Zecchina, A.; Borello, E. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 2827.
- (41) Geobaldo, F.; Spoto, G.; Bordiga, S.; Lamberti, C.; Zecchina, A. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1243.
- (42) Onida, B.; Bonelli, B.; Borello, L.; Fiorilli, S.; Geobaldo, F.; Garrone, E. *J. Phys. Chem.* **2002**, *106*, 10518.