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In Situ Modeling of the Enhanced Brønsted Acidity in Zeolites

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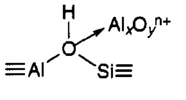
Abstract: Enhanced Brønsted acidity is experimentally modeled by a low-temperature adsorption of a Lewis acid (BF_3) on the hydrogen form of EMT zeolite. The increase in acid strength is detected in FTIR studies of a low-temperature adsorption of carbon monoxide on the samples pretreated with BF_3. The proton affinity of Brønsted hydroxyls decreases linearly with increase in the surface coverage with BF_3. A structure for a surface complex, zeolite−Lewis acid, is proposed, and local and cooperative views on the mechanism of enhancing the acid strength of Brønsted hydroxyls are discussed.

Introduction

High catalytic activity of steamed forms of Y zeolite, mordenite, and ZSM-5 in catalytic cracking is usually attributed to the Brønsted sites of enhanced acidity.[1] Recent FTIR studies of US-Y zeolites allowed their direct spectroscopic observation.[2−5] These sites are believed to be a result of the interaction between Brønsted sites and Lewis sites created during steaming procedures, since both are present, and since it is known that, in solution, enhanced Brønsted acidity can be generated by adding Lewis acid to Brønsted acid.[1] The proposed structure of the sites, therefore, is



Theoretical calculations show that such hydroxyls should be more acidic and, for example when $Al_xO_y^{n+}$ is $Al(OH)_3$, their proton affinity is decreased by 30 kJ·mol^{-1}.[6]

However, to date no direct proof that Lewis sites participate in the enhancement of Brønsted acidity has been forthcoming. The present study reports on the model system, H-EMT zeolite/BF_3, which demonstrates enhanced acidity. Adsorption of BF_3 is reversible and does not modify zeolite lattice/structure.

Experimental Section

Carbon monoxide was supplied by BOC (R grade) and boron trifluoride by Aldrich (99.95%+).

A sample of H-EMT (Si/Al = 4.0, Na/Al < 0.01) was synthesized in the laboratories of Elf France (Solaize). ^{29}Si MAS NMR and ^{27}Al MAS NMR proved the absence of dislodged aluminium.

The FTIR spectroscopic technique was described in detail elsewhere.[7] Briefly, an infrared cell facilitated high-temperature pretreatment of the samples *in situ* and was on-line with the adsorption rig. A self-supporting disk (m = 5.1 mg, ρ = 2.9 mg·cm^{-2}) was heated at 1 °C·min^{-1} to 350 °C under vacuum and held at this temperature overnight (pressure of 10^{-5} Torr). Additional experiments on pyridine adsorption proved the absence of Lewis acidity after such a pretreatment. For spectroscopic/adsorption measurements, the IR cell was lowered into a quartz Dewar filled with liquid nitrogen and small increments of BF_3 or CO (0.4−1.0 μmol) were admitted to the cell. Adjustment of the sample position within the cell permitted the placement of the sample in regions of different temperature. Thus, the temperature of the sample during adsorption/desorption of BF_3 was between −40 and −100 °C; during the CO adsorption and for the spectra registration it was between −100 and −120 °C.

The spectra were collected using a Cygnus-100 Mattson FTIR spectrometer, at a scanning rate of 100 and a resolution of 2 cm^{-1} in the wavenumber interval of 2500−4000 cm^{-1}.

The fractional coverages with the sorbates were determined from the spectroscopic results as follows: θ_{BF_3} refers to the decrease in I(HF) (intensity of the high frequency band) due to BF_3 adsorption divided by I(HF) before any adsorption; θ_{CO} refers to the decrease in I(HF) due to BF_3 and CO adsorption divided by I(HF) after BF_3 adsorption only: θ_{BF_3+CO} refers to the decrease in I(HF) due to BF_3 and CO adsorption divided by I(HF) before any adsorption.

Consequently, $\theta_{CO} = (\theta_{BF_3+CO} - \theta_{BF_3})/(1 - \theta_{BF_3})$

The shifts, $\Delta\nu_{OH}$, due to the perturbation with carbon monoxide were determined as peak-to-peak distances in difference spectra obtained by subtraction of the spectra of the samples before adsorption from their spectra after adsorption.

Results and Discussion

Low-Temperature Adsorption of BF_3 on H-EMT. Slow adsorption of BF_3 at temperatures close to that of liquid nitrogen gives rise to two different types of adsorbed complexes, designated as a strong complex (**I**) and a weak complex (**II**). Low-temperature pumping removes complex **II**, leaving complex **I** unchanged on the surface.

Using FTIR spectroscopy, these two species can be clearly distinguished. A difference spectrum which is a result of subtraction of the initial spectrum of the sample before adsorption from the spectrum after a low-temperature adsorption followed by a low-temperature pumping corresponds to complex **I** (Figure 1). It indicates that formation of complex **I** affects the hydroxyls in both super- and β-cages (negative peaks at 3638 and 3544 cm^{-1}). A new broad line at ~3267 cm^{-1} can be assigned to the vibrations from the perturbed OH groups in the complex. A difference spectrum between the spectrum after low-temperature adsorption of BF_3 and the spectrum following

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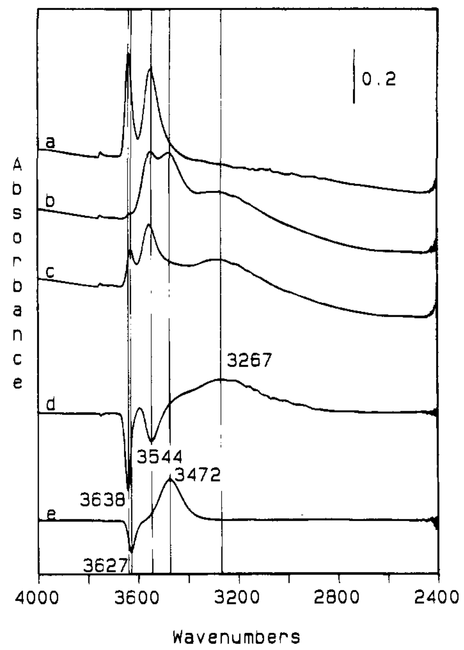
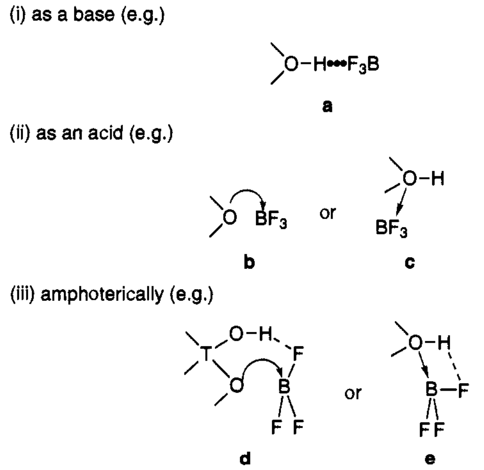


Figure 1. FTIR spectra for H-EMT zeolite in the course of adsorption/desorption of BF_3: (a) initial sample, (b) after a low-temperature adsorption of excess BF_3, (c) after following low-temperature evacuation, (d) part c minus part a, and (e) part b minus part c.

low-temperature pumping can be ascribed to complex **II**. The presence of only one negative peak at 3627 cm^{-1} indicates that only Broensted hydroxyls in larger cages take part in the interaction. A new peak at 3472 cm^{-1} is obviously due to these hydroxyls engaged in hydrogen bonding to the sorbate. The adsorption is reversible and prolonged pumping at room temperature completely removes the adsorbed species restoring the spectrum of the initial sample.

In principle, a BF_3 molecule can interact with zeolite



Ab initio HF/SCF molecular orbital calculations have been performed, in order to investigate the stability of the possible complexes, using a finite molecular cluster to represent the zeolite. Preliminary calculations reported here were obtained using the 3-21G basis set in the GAUSSIAN92 software suite.[8] A more thorough study is in progress.

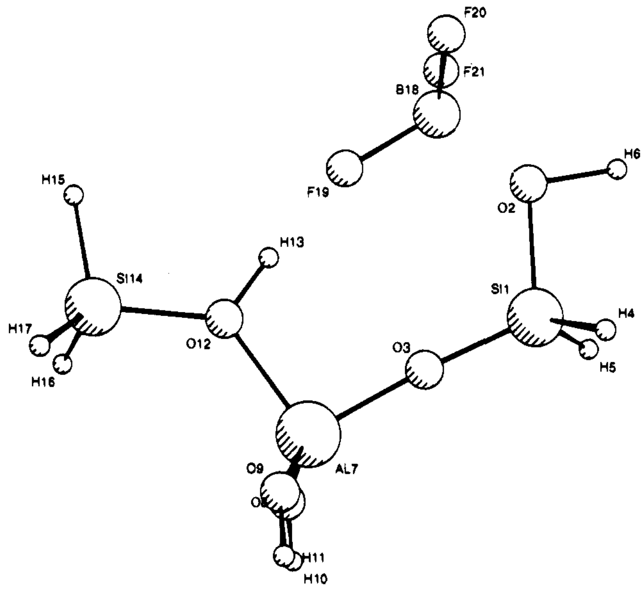


Figure 2. Optimized geometry of the strong adsorption complex of BF_3 on the zeolite acid site model. Distances between the acid site model and the BF_3 molecule are O2−B18 1.59 Å and H13−F19 1.56 Å.

Calculations show that a structure similar to complex **d** is predicted to be the most stable. For the model cluster used, this structure is shown in Figure 2 and the energies from SCF-MO calculations are summarized in Table 1. It is characterized by a two-point interaction: a strong H bond between one F atom of BF_3 and the Brønsted hydrogen and a strong B−O bond, approximately 0.2 Å larger than the bond lengths observed in boron trioxide and $B(OH)_3$.[9] It is interesting to note that no stable complex exists when the B atom interacts with the framework oxygen immediately adjacent to the aluminium atom. This is in contrast to calculations involving other bases that are predicted to coordinate via two points, such as methanol and ammonia.[10,11] A complex of this type is not stable for this system due to repulsion effects between the framework and the out-of-plane F atoms. The interaction energy of the complex in Figure 2 is calculated to be approximately 238 kJ/mol. Other starting geometries were adopted, to investigate other modes of bonding the BF_3 to this acid site. All resulted in either hardly-bound stationary points or no stationary point at all.

The small basis set used for these calculations is subject to a considerable Basis Set Superposition Error (BSSE).[12] This BSSE artificially increases the interaction energy. An estimate of this error is calculated as 102 kJ/mol, according to the method detailed in ref 13. Thus the estimate of the interaction energy is reduced to 136 kJ/mol.

The effects of electron correlation are included via single point Møller−Plesset calculations, truncated at second-order terms (MP2), at the SCF optimized geometries. Inclusion of electron correlation decreases the interaction energy by 5 kJ/mol. This is in contrast to previous calculations employing larger basis sets, which have shown that electron correlation stabilizes the complexes between a Brønsted acid site with CO and a Brønsted acid site with methanol by 9 and 23 kJ/mol, respectively.[13,10]

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Table 1. Energies from SCF-MO Calculations for Complex **I**[a]

	HF/3-21G//HF/3-21G	HF/3-21G//MP2/3-21G
acid site$-BF_3$ complex	−1514.7847036 hartrees	−1515.9039133 hartrees
acid site	−1193.2280347 hartrees	−1193.9425745 hartrees
BF_3	−321.4658449 hartrees	−321.8723781 hartrees
interaction energy	−238.4 kJ/mol	−233.6 kJ/mol
BSSE correction (see ref 13)	+102.1 kJ/mol	
fixed SiOH angle calcn energy		
acid site$-BF_3$ complex	−1514.7532753 hartrees	
acid site	−1193.2120146 hartrees	
BF_3	−321.4658449 hartrees	
new interaction energy	−198.0 kJ/mol	

[a] HF/3-21G//MP/3-21G means a HF-optimized geometry using the 3-21G basis set, followed by a single point MP2-energy calculation using the 3-21G basis set and the HF-optimized geometry.

Finally, we note that the framework oxygen acting as a Lewis base to BF_3 is within 4° of sp^2 hybridization, thus maximizing electron donation. In the case of a "real" zeolite, the hybridization at this oxygen is likely to be intermediate between sp (180°) and sp^2 (120°), thus reducing the efficiency of electron donation. To estimate the size of this artefact of the cluster model used, calculations have been performed with this $\angle$SiOH angle fixed at 150°. A reduction in SCF interaction energy of 20% is observed.

On the basis of these calculation results, we tentatively assign a structure of type **d** to complex **I** and estimate the interaction energy of this complex to be approximately 100 kJ/mol, based on the corrections described above. We also assign a structure of type **a** to complex **II**.

Spectroscopic results are in agreement with this choice. Hydroxyls in complex **I** are strongly perturbed (their characteristic vibrations are shifted from their original position by $\sim$300 cm^{-1}) and are insensitive to a probe such as CO. As regards complex **II**, the shape of the perturbed band and the value of the shift ($\Delta\nu_{OH}$ = 155 cm^{-1}) are typical for hydroxyls involved in a hydrogen-bonded interaction with CHF_3[14] or saturated hydrocarbons in the row $CH_4-C_6H_{12}$.[15]

Acidity of Brønsted Hydroxyls in the H-EMT/BF_3 System. Since only structure **d** involves participation of BF_3 as a Lewis acid, we will further concentrate on the study of complex **I** and the effect of its formation on zeolitic acidity. The question to be discussed is how the interaction with Lewis acids affects the remaining Brønsted acid sites in the material. Figure 3 shows a set of infrared spectra for different coverage with BF_3 (complex **I** only). The growth of the wide band at 3267 cm^{-1} corresponds to the simultaneous decrease in the HF band, accompanied by minor changes in the LF component. A thorough consideration of the position of the HF band shows that it shifts slightly to lower wavenumbers with increase in coverage with BF_3 (Figures 3 and 4). On the contrary, during interaction with weak bases such as CO[16] or strong bases such as NH_3,[17] the position of the unperturbed hydroxyls shifts to higher wavenumbers, reflecting the fact that the stronger hydroxyls react first. The results due to CO adsorption, obtained in the present work, are given in Figure 4 for reference.

Possible explanations for the minor low-frequency shift are given below: (1) Formation of the complex **I** involves the weaker hydroxyls leaving the stronger ones unperturbed. It might be that the weaker hydroxyls are the neighbors of the stronger basic sites and such a double adsorption site has a bigger stabilization energy in structure **d**. (2) The electron density withdrawal to BF_3 results in the increase in acidity of the remaining Brønsted hydroxyls.

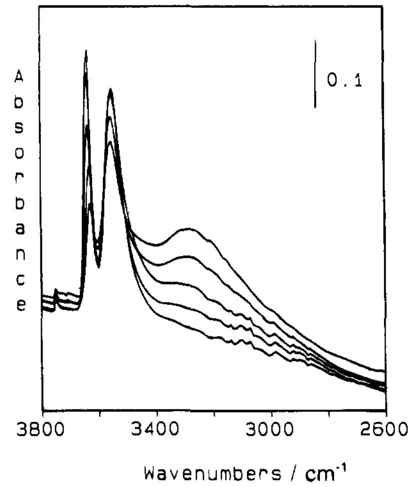

Figure 3. FTIR spectra for different coverages of H-EMT with BF_3 as a result of low-temperature adsorption followed by low-temperature evacuation.

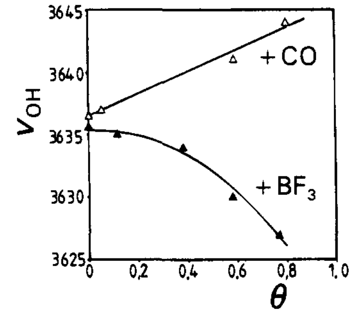

Figure 4. Position of the HF band vs the fractional coverage of the HF hydroxyls with different sorbates.

Low-temperature adsorption of carbon monoxide provides further information on the likelihood of these two possibilities. The method is based on a stepwise low-temperature adsorption of CO.[18-20] Briefly, the bigger the shift in the position of the hydroxyl band due to the perturbation, $\Delta\nu_{OH}$, the less the protons are constrained and the more acidic, therefore, are the hydroxyls. The values of $\Delta\nu_{OH}$ at different surface coverage with carbon

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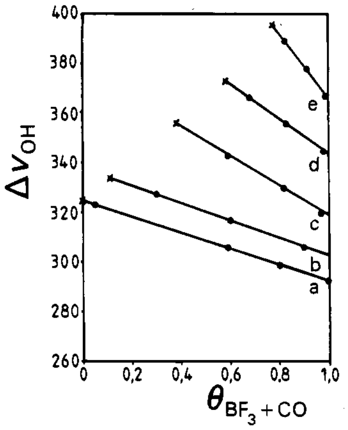


Figure 5. Shift in the position of the HF hydroxyls due to perturbation with carbon monoxide vs the fractional coverages of the HF hydroxyls with both sorbates, BF_3 and CO. Lines a—e represent five series of titrations of HF hydroxyls with CO, differing in the amount of preadsorbed BF_3. Fractional coverages of HF hydroxyls with preadsorbed BF_3 (complex **I** only) for these series are (a) 0, (b) 0.11, (c) 0.38, (d) 0.58, and (e) 0.77.

monoxide, θ_{CO}, provide information on the heterogeneity in the acid site strength. The shift determined at the limit $\theta_{CO} = 0$ reflects the acid strength of the strongest Brønsted hydroxyls whereas the extrapolation of $\theta_{CO} = 1$ corresponds to the average acidity in the sample. The following correlation links the experimental results for $\Delta\nu_{OH}$ with the proton affinities of Brønsted hydroxyls:

$$PA^{OH}/kJ{\cdot}mol^{-1} = 2254.8 - 442.5 \log (\Delta\nu_{OH}/cm^{-1})$$

Each coverage with BF_3 spectroscopically presented in Figure 3 has been used as an initial stage for a stepwise CO adsorption. Only the HF hydroxyls are perturbed by CO, and there is no interaction between CO and the LF band which agrees with previous studies.[16] Also, there are no changes in the wide band at 3267 cm^{-1} indicating no interaction between the hydroxyls in complex **I** and CO molecules.

Mathematical treatment of the experimental results on CO adsorption in terms of plots of $\Delta\nu_{OH}$ vs θ_{BF_3+CO} for different starting θ_{BF_3} is given in Figure 5. Different lines correspond to different starting θ_{BF_3} and crosses at the end of each line correspond to their values in the series of adsorptions of CO. The shifts due to CO perturbation, $\Delta\nu_{OH}$, become bigger as more BF_3 is preadsorbed in the form of complex **I**. This is direct evidence for the enhancement of the strength of Brønsted hydroxyls resulting from the interaction of zeolite with BF_3 (the second option discussed above).

The presentation of the results in terms of plots of $\Delta\nu_{OH}$ vs θ_{CO} (Figure 6) reveals that the range of heterogeneity of the acid sites at each level of enhancement of acidity is the same, since all the lines are parallel. This could mean that BF_3 forms complex **I** randomly and this equally affects the weakest and the strongest Brønsted sites. It seems to be likely that the formation of complex **I** affects all the Brønsted sites, not only those in the immediate vicinity, i.e., it is a cooperative effect; otherwise the range of heterogeneity of the sites would increase with adsorption of BF_3.

As mentioned above, $\Delta\nu_{OH}(\theta = 0)$ and $\Delta\nu_{OH}(\theta = 1)$ reflect the acid strength of the strongest hydroxyls and an average acidity, respectively. Figure 7 represents these values derived from the correlations in Figure 6 against the fractional coverage with BF_3, θ_{BF_3}, and indicates that (i) an increase in the acid strength of Brønsted hydroxyls is proportional to the amount of BF_3 adsorbed in the form of the complex **I**, (ii) the maximum possible acid strength for the system H-EMT/BF_3 ($\theta_{BF_3} = 1$, $\theta_{CO} = 0$) is PA = 1096 kJ·mol^{-1} corresponding to $\Delta\nu_{OH}$ = 416 cm^{-1}, and (iii) the maximum average acid strength which is possible to reach in the system H-EMT/BF_3 ($\theta_{BF_3} = 1$, $\theta_{CO} = 1$) is PA = 1112 kJ·mol^{-1} corresponding to $\Delta\nu_{OH}$ = 382 cm^{-1}.

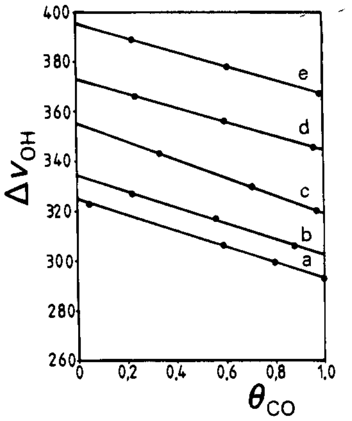


Figure 6. Shift in the position of the HF hydroxyls due to perturbation with carbon monoxide vs the fractional coverage of the HF hydroxyls with CO, for different fractional coverage of the HF hydroxyls with BF_3 (lines a—e correspond to the lines in Figure 5).

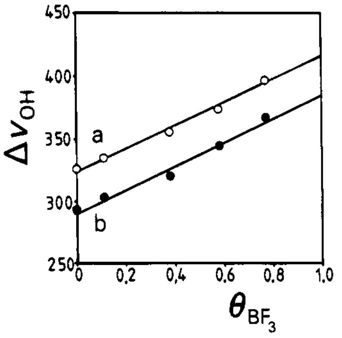


Figure 7. Approximate shift in the position of the HF hydroxyls due to perturbation with carbon monoxide in the limits $\theta_{CO} = 0$ (a) and $\theta_{CO} = 1$ (b) for different fractional coverages of the HF hydroxyls with BF_3.

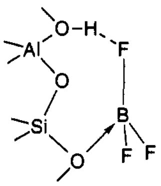
It is interesting to note that the shift observed in ref 20 for the hydroxyls having enhanced acidity in US-Y zeolites (and therefore, their proton affinities) is exactly the same, 382 cm^{-1} ($\theta_{CO} = 1$).

Finally, we admit that there are some questions which require clarification in further studies: (1) firm justification of the assignment of structure **d** to complex **I**, (2) an evaluation of local versus cooperative effects in the zeolitic framework—Lewis acid interaction, and (3) understanding of the difference between the enhanced acidity in the model system described and in commercial catalysts such as US-Y.

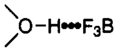
Nevertheless, to our knowledge, this is the first report in the literature on the creation of enhanced Brønsted acidity in zeolites in a model system without destruction of the zeolitic lattice. In general, it proves for the first time the hypothesis that enhanced Brønsted acidity can be formed by the interaction of Brønsted sites with Lewis acids or Lewis acid sites.

Conclusions

Low-temperature adsorption of BF_3 on H-EMT zeolite may result in the formation of a stronger complex **I** or a weaker complex **II**. Their structures proposed on the basis of initial theoretical calculations for a specific cluster are



complex **I**, amphoteric interaction



complex **II**, acid–base interaction

Formation of a complex of type **I** enhances the acidity of the remaining, uncomplexed Brønsted hydroxyls. A possible mechanism for enhancement of acidity could involve electron density withdrawal from appropriate zeolite oxygen.

The present study proves that the enhanced Brønsted acidity can result from the interaction of an acid zeolite with a Lewis acid. Further work is in progress.

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