

Calorimetric Investigation of CO and N<sub>2</sub> for Characterization of Acidity in Zeolite H–MFI

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Microcalorimetric measurements were performed at 195 K for CO and N<sub>2</sub> on zeolite H–MFI and on a siliceous MFI in order to characterize the interaction of these molecules with the Brønsted acid sites. On the siliceous MFI, the differential enthalpies of adsorption (isosteric heats) for CO and N<sub>2</sub> were found to be essentially constant with coverage at a value of  $16 \pm 1$  kJ/mol. While the isosteric heats for N<sub>2</sub> were slightly higher on H–MFI at coverages below one per site, the additional interaction with the Brønsted sites is less than 3 kJ/mol. For CO on H–MFI, microcalorimetry provides evidence for a 1:1 adsorption complex with the acid sites in that the isosteric heats are higher on H–MFI at low coverages and approach the values for the siliceous material at higher coverages. Because the calorimetric data can be fit to a two-site, Langmuir model in which the hydrogen-bonded CO interacts with an additional 10.5 kJ/mol, the results suggest that the Brønsted acid sites in H–MFI are essentially identical in regard to how they interact with CO.

## Introduction

While Brønsted acidity in zeolites is commercially very important, there is still considerable uncertainty about how one should describe the acid sites in these solids and which are the best methods for characterizing them.<sup>1</sup> In our laboratory, we have focused primarily on the high-silica zeolite H–MFI as a model system because there is considerable evidence that this material has essentially equivalent sites in a concentration equal to the framework Al content.<sup>2</sup> For example, rates for a number of reactions in H–MFI increase linearly with Al content over a wide range of Si/Al ratios.<sup>3</sup> Furthermore, well-defined adsorption complexes, with a stoichiometry of one molecule per Brønsted site, have been observed for a large number of organic molecules in H–MFI using NMR,<sup>4,5</sup> IR,<sup>6–8</sup> microcalorimetry,<sup>9–12</sup> and temperature-programmed desorption (TPD).<sup>8,13</sup>

However, the relationship between catalytic activities for hydrocarbons and the adsorption properties of relatively strong bases is unclear.<sup>14</sup> A number of groups have studied the adsorption of very weak bases, including CO and N<sub>2</sub>, using infrared and NMR spectroscopies at low temperatures to better discriminate sites.<sup>15–25</sup> These molecules, which have proton affinities even lower than many organic reactants ( $PA_{CO} = 582$  kJ/mol;  $PA_{N_2} = 476$  kJ/mol),<sup>26</sup> form hydrogen bonds with the Brønsted sites so that proton transfer is not complete as it is in the case for strong bases. A theoretical model has been developed to quantify the strength of these interactions on the basis of changes in the  $\nu(O-H)$  stretching frequency of the Brønsted hydroxyl.<sup>27</sup> Experimental support for the validity of this model comes from the observation that frequency shift increases monotonically with the proton affinity of the probe molecules.<sup>24</sup>

In the present study, we examined the interaction of CO and N<sub>2</sub> with the Brønsted acid sites in H–MFI using microcalorimetry. Results in H–MFI were compared to results in a siliceous MFI so that the van der Waals component of the heats could be estimated and subtracted from the total energy to give the energetics of the hydrogen bonding. To avoid possible

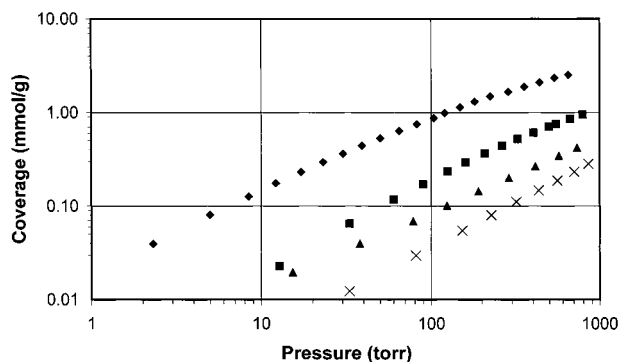
contributions from defect sites, the two MFI samples were synthesized in a fluoride medium with low Na content, conditions that previous work has shown lead to low concentrations of defects. Finally, the calorimetric measurements were performed at a relatively low temperature, 195 K, to achieve high adsorbate loadings at low pressures and to help localize adsorption to the acid sites.

## Experimental Section

The two MFI samples used in this study were prepared using a fluoride-based process to achieve low defect concentrations.<sup>28</sup> For example, the synthesis procedure for H–MFI began by mixing distilled water (46 g), TPA-Br (3.0 g), NH<sub>3</sub>OH (29 wt %, 5.9 g), NH<sub>4</sub>F (3.0 g), NH<sub>4</sub>Cl (8.8 g), Catapal (0.17 g), and Ludox (HS-30, 12.4 g). The mixture was placed in an autoclave and maintained at 180 °C for 11 days. After being filtered, the solid from the autoclave was calcined to 500 °C in flowing air to remove the template. Finally, the calcined sample was ion-exchanged twice in 1 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> for 2 h at 85 °C with intermediate calcination. The two samples will be designated H–MFI for the acidic sample and MFI(sil) for the silicalite.

Both the H–MFI and MFI(sil) samples appeared highly crystalline and uniform under normal light microscopy. The crystals were rectangular, approximately 100  $\mu$ m long and 20  $\mu$ m wide. XRD patterns of the samples were indicative of pure MFI, with negligible amounts of amorphous material. On the basis of *n*-hexane uptakes at room temperature and 10 Torr, the pore volumes of both samples were 0.17 cm<sup>3</sup>/g, which is less than the ideal pore volume of 0.19 cm<sup>3</sup>/g but close to what we observe for commercial-type materials. Simultaneous temperature-programmed-desorption and thermogravimetric-analysis (TPD–TGA) measurements with isopropylamine were used to measure the Brønsted acid site densities. The TPD–TGA technique, which is based on the fact that amine molecules protonated by the Brønsted sites react to propene and ammonia prior to desorption,<sup>8</sup> indicated that the H–MFI and MFI(sil) samples had Brønsted site concentrations of 0.42 and 0.04 mmol/g, respectively. (While no Al was intentionally added during the synthesis of MFI(sil), a small amount of Al was obviously

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**Figure 1.** Isotherms for N<sub>2</sub> on H-ZSM-5: (◆) 195 K; (■) 236 K; (▲) 273 K; (×) 295 K.

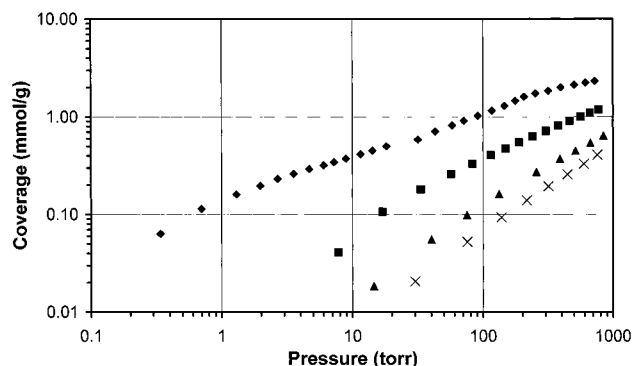
incorporated.) Of additional interest from our TPD-TGA measurements, we found that essentially all of the physisorbed isopropylamine in the MFI(sil) sample could be removed by evacuation at room temperature. Even though most silicalite samples that we have studied are made up of smaller crystallites, it is usually necessary to heat above 450 K in a vacuum to remove physisorbed isopropylamine.<sup>8</sup> Since the physisorbed molecules are likely hydrogen-bonded to silanol defects in the MFI structure, the virtual absence of these molecules in MFI(sil) suggests that the sample contains a low defect concentration.

The calorimeter used in this study has been described elsewhere,<sup>29</sup> and only slight modifications were necessary to perform the measurements at 195 K. For these measurements, the Al-block heat sink was placed in a Styrofoam container with dry ice. Calibration of the thermopiles, using current passed through a Pt wire placed between the sample cell and the thermopiles, indicated that the calibration factor was not affected by lowering the temperature from 298 K.<sup>8,9</sup> The only additional change to the apparatus was that the tube connecting the sample cell to the gas-handling system was lengthened so that the dosing volumes could be maintained at room temperature. Because adsorbate loadings were determined volumetrically, He expansion was carried out both at room temperature and 195 K to determine the sample volumes. Because the number of moles that adsorbed was always large compared to the number of moles in the gas phase of the sample cell, corrections due to temperature differences in the sample volume were negligible.

Prior to the calorimetric measurements, adsorption isotherms were measured for N<sub>2</sub> and CO on the H-MFI sample, both to demonstrate mobility of the adsorbates at 195 K for ensuring that thermodynamic equilibrium could be achieved and to estimate the differential heats. These measurements were performed in the calorimetric apparatus while holding the sample in the following constant-temperature baths: dry ice/acetone (195 K); frozen anisole (236 K); ice water (273 K); room temperature (295 K). Data were taken following both adsorption and desorption, demonstrating complete reversibility of the process.

## Results

Adsorption isotherms for N<sub>2</sub> and CO in H-MFI at 195, 236, 273, and 295 K are shown in Figures 1 and 2, respectively. At 295 K, the data for N<sub>2</sub> are essentially identical to what has been reported elsewhere for silicalite, which is to be expected given that the interactions between N<sub>2</sub> and the Brønsted sites should be very weak. Of more interest for this study, we find that adsorption is reversible, even at 195 K, and that loadings as high as 2.0 mmol/g can be achieved at atmospheric pressures. Using the density of liquid N<sub>2</sub> at 78 K, a coverage of 2.0 mmol/g



**Figure 2.** Isotherms for CO on H-ZSM-5: (◆) 195 K; (■) 236 K; (▲) 273 K; (×) 295 K.

corresponds to  $\sim 0.07$  cm<sup>3</sup>/g, which is a significant fraction of the available pore volume, 0.17 cm<sup>3</sup>/g. Finally, one can use the isotherm data to estimate the differential enthalpy of adsorption (isosteric heat). For an ideal gas, the isosteric heat at a fixed loading is given by

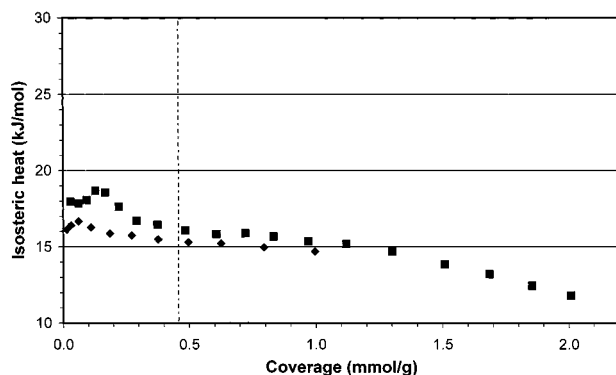
$$\Delta H = R[d \ln(p)/d(1/T)] \quad (1)$$

Using the data at 195 and 295 K for maximum accuracy, we calculate that the isosteric heat for N<sub>2</sub> on H-MFI at a coverage of 0.1 mmol/g is 18.3 kJ/mol. This is in excellent agreement with the zero-coverage isosteric heat reported previously for N<sub>2</sub> in silicalite, 17.6 kJ/mol.<sup>29</sup>

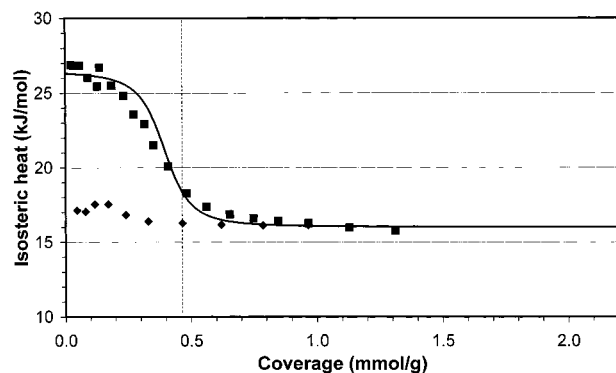
The analogous isotherm data for CO, shown in Figure 2, again indicate that adsorption is reversible under our conditions. The isotherms for CO are very similar to those for N<sub>2</sub>, which should be expected on the basis of the fact that the molecules have the same molecular weight and a very similar critical temperature ( $T_c$  is 133 K for CO and 126 K for N<sub>2</sub>). However, the shape of the curves for CO, particularly the isotherm at 195 K, suggests that one cannot adequately describe adsorption in terms of a single type of site. The isotherm at 195 K shows an inflection point at a loading of approximately 0.5 mmol/g, close to the Brønsted site density. It is clear that both sites are populated in the same pressure range, even at 195 K, so that one cannot choose conditions in which the molecules will interact only with the Brønsted sites. Using the isotherms at 195 and 295 K, we estimate that the differential enthalpy of adsorption for CO on H-MFI is 26.5 kJ/mol at a loading of 0.1 mmol/g. Again, this value agrees very well with that determined from microcalorimetry, to be discussed next.

The differential isosteric heats measured calorimetrically on both H-MFI and MFI(sil) are shown in Figures 3 and 4. The data for N<sub>2</sub> in Figure 3 show that there is little difference between the results for MFI(sil) and for H-MFI, implying that N<sub>2</sub> interacts very weakly with the Brønsted sites. On MFI(sil), the initial heats are between 16 and 17 kJ/mol and remain relatively constant with coverage, decreasing to about 15 kJ/mol at 1.0 mmol/g. On H-MFI, the initial heats are between 18 and 19 kJ/mol. The heats decrease with coverage to the MFI(sil) value at high coverages, but there is no sharp demarcation at a coverage equal to the Brønsted site density, 0.4 mmol/g.

The calorimetric results for CO exhibit much clearer evidence for interactions with the Brønsted sites, as shown in Figure 4. On MFI(sil), the differential heats are again constant, between 17 and 18 kJ/mol at low coverages and decreasing to approximately 16 kJ/mol at higher coverages. However, on H-MFI, the initial heats are between 26 and 27 kJ/mol, falling to the MFI(sil) value above 0.8 mmol/g. The differential-heat



**Figure 3.** Isosteric heats for N<sub>2</sub> on H-MFI (■) and MFI(sil) (◆) measured at 195 K. The dashed line at 0.42 mmol/g shows the Brønsted acid site density for H-MFI measured using TPD-TGA of isopropylamine.



**Figure 4.** Isosteric heats for CO on H-MFI (■) and MFI(sil) (◆) measured at 195 K. The solid line through the data for H-MFI shows the best fit for a two-site Langmuir model at 195 K. The dashed line at 0.42 mmol/g shows the Brønsted acid site density for H-MFI measured using TPD-TGA of isopropylamine.

curve has a sigmoidal shape, centered around the Brønsted-site density of 0.4 mmol/g. This is clear evidence for hydrogen bonding between CO and the Brønsted sites.

The data are also consistent with all of the Brønsted sites being energetically equivalent. Along with the data in Figure 4, we include the calculated profile for a two-site Langmuir model. The only fitted parameters in the model are the energies of the two sites, which were chosen to be 26.5 and 16 kJ/mol, respectively. The concentration of weak sites was chosen to be 10 times the concentration of the strong sites, based roughly on the measured ratio of Brønsted sites, 0.42 mmol/g, to the concentration of molecules needed to fill the pore volume at liquid density, 4.9 mmol/g. We also assume that there are no entropic differences between the two adsorbed states. The sigmoidal shape in the curve comes from the Boltzmann distribution for the adsorbed molecules at 195 K.

## Discussion

The calorimetric results for CO and N<sub>2</sub> provide complementary evidence to that obtained from earlier spectroscopic studies for the interaction of weak bases with the Brønsted acid sites in H-MFI. The fact that even weak bases, especially CO, form relatively uniform 1:1 complexes confirms that there is a significant energetic distinction between the Brønsted acid sites and other siliceous parts of the MFI structure. For N<sub>2</sub>, the additional interaction with the acid sites is small, less than 3 kJ/mol. For CO, those molecules associated with the Brønsted sites are bound by an additional 10.5 kJ/mol over that for

molecules on silicalite. The stronger interaction for CO compared to N<sub>2</sub> should be expected on the basis of its higher proton affinity.<sup>24</sup>

The results for CO also provide additional evidence that the Brønsted acid sites in H-MFI are nearly energetically equivalent. One might expect heterogeneity to arise from two sources. First, Al incorporation into the various lattice positions of the MFI structure could result in different proton affinities for the sites. Second, the effective cavity dimension surrounding the sites in the channel intersections should be larger than that for sites that are completely in the 10-membered rings. Given that the van der Waals interaction can change significantly with channel size,<sup>30</sup> the magnitude of this component could be important. However, on the basis of the excellent fit of the data to the two-site Langmuir model, we suggest that the sites in H-MFI are energetically homogeneous and that Boltzmann factors are primarily responsible for the fact that the isosteric heats do not exhibit a sharp drop at coverages above one per site. This conclusion is consistent with that from previous adsorption<sup>2,9</sup> and reaction<sup>3</sup> work.

If the interaction between the adsorbate molecules and the Brønsted sites can be assumed to be a simple sum of the van der Waals attraction and the hydrogen-bonding interaction, the hydrogen bond is calculated to be worth 10.5 kJ/mol for CO and  $\leq 3$  kJ/mol for N<sub>2</sub>. While these values are very reasonable given the range of energies typically observed for hydrogen bonds,<sup>31</sup> they should probably be considered to be a lower limit on the actual value. It seems likely that molecules associated with the Brønsted sites may not be able to optimize their interactions with the siliceous walls in the same way as other molecules in the zeolite cavity. For example, if the hydrogen-bonded CO molecule forms a linear complex that extends into the center of the channels, the van der Waals component will be less than its optimum value. However, we suggest that the actual hydrogen-bond strengths cannot be more than a few kJ/mol above the values given here.

Because IR spectroscopy has been widely used to characterize hydrogen-bonded complexes, it is interesting to compare the hydrogen-bond energies we have obtained to those calculated spectroscopically. In IR, it is usually assumed that a linear complex is formed with the base, O—H...B.<sup>27</sup> The formation of this complex will cause a shift in the hydroxyl stretching frequency,  $\nu(\text{OH})$ . Quantum calculations indicate that the change in the hydroxyl stretching frequency,  $\Delta\nu(\text{OH})$ , correlates with the hydrogen-bond strength,  $-\Delta H_{\text{int}}$ , according to the following relation:

$$-\Delta H_{\text{int}} = 1.347\{\Delta\nu(\text{OH}) - 40\}^{1/2} \quad (2)$$

The shifts in  $\nu(\text{OH})$  in H-MFI have been reported to be 300 cm<sup>-1</sup> for CO and 100 cm<sup>-1</sup> for N<sub>2</sub>,<sup>20</sup> resulting in calculated hydrogen-bond strengths of 22 and 12 kJ/mol. This is considerably larger than what we have measured in our calorimetric study. As we discussed above, the hydrogen-bond strength may be larger than the difference between the isosteric heats for the 1:1 complex and the heats on MFI(sil). However, we believe it is unlikely that the hydrogen-bond strengths for CO and N<sub>2</sub> could be as large as the values calculated from the spectroscopic measurements. Obviously, a number of assumptions go into eq 2, and the numbers we have obtained in this study may prove helpful in refining the theory.

Whether the hydrogen-bond strength for CO or N<sub>2</sub> will correlate with the ability of the solid to donate protons to typical hydrocarbon reactants has yet to be determined. As discussed in a previous study of CD<sub>3</sub>CN in H-MFI and H-[Fe]MFI,<sup>32</sup>

there may be no correlation between the hydrogen-bond strength determined using either IR or microcalorimetry and the catalytic activity for alkane cracking or olefin oligomerization. It will be interesting to see whether weaker bases such as CO and N<sub>2</sub> will prove to be more effective.

## Conclusion

The microcalorimetry data provide evidence for the formation of 1:1 complexes between CO and the Brønsted acid sites in H-MFI at 195 K. The strength of the hydrogen bond appears to be approximately 10.5 kJ/mol. By contrast, the interaction between N<sub>2</sub> and the Brønsted acid sites is too weak to be easily measured at 195 K.

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