Does the Cal-Ad Method Distinguish Differences in the Acid Sites of H-MFI?

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Abstract: Recent claims that calorimetric measurements of solid acidity can be performed more effectively in the presence of a solvent, the “cal-ad” method, were examined using vapor-phase measurements for the coadsorption of pyridine and *n*-hexane in H-MFI. The results indicate that equilibrium is not achieved for pyridine titration measurements in a solvent at room temperature. Therefore, the ability of the cal-ad method to distinguish Brønsted-acid sites of widely different strengths in H-MFI is unproven.

Introduction

Zeolites are crystalline aluminosilicates which are used as acid catalysts for a number of industrially important reactions, including hydrocarbon cracking and toluene alkylation reactions. H-MFI, also known as H-ZSM-5, is the acidic form of a particularly important zeolite structure that has interconnecting channels, approximately 0.6 nm in diameter. While controversies remain regarding how one should describe and characterize acidity in zeolites,[1] the concentration of Brønsted sites in H-MFI is usually considered to be equal to the framework Al concentration. Basic adsorbates tend to form well-defined complexes with the Brønsted sites in H-MFI. Indeed, evidence for equivalent, 1:1, stoichiometric adsorption complexes in H-MFI has come from NMR,[2,3] IR,[4−6] microcalorimetry,[7−11] and temperature programmed desorption (TPD).[6,12] In IR of adsorbed pyridine, only pyridinium ions were present at a coverage of one/site.[6] In microcalorimetry, differential heats of adsorption for pyridine at 480 K were shown to be 200 kJ/mol up to a coverage of one/Al for adsorption in a vacuum on a series of H-MFI samples with varying Al contents.[7] For coverages above one/Al, the differential heats are significantly lower. These observations, along with the fact that the catalytic activity of H-MFI increases linearly with Al content for a large number of reactions,[14] has led to the conclusion that the Brønsted sites associated with framework Al in H-MFI are essentially equivalent.

However, this conclusion has recently been questioned.[15] Using a new technique called the cal-ad method, heats were measured when dilute solutions of pyridine in *n*-hexane were added to a solid acid, which is itself in a slurry with *n*-hexane. Contrary to earlier calorimetric results for H-MFI in a vacuum,[7] the cal-ad method suggests the presence of two, energetically different types of sites, with only the strong sites capable of transferring a proton to the adsorbed base. For a sample containing an acid-site concentration of 0.6 mmol/g, it was reported that only 5% of the sites are strong sites with differential heats of ∼176 kJ/mol, while the remaining 95% of the sites exhibit differential heats of 36 ± 16 kJ/mol. These observations have very important implications for the characterization of solid acidity. If only 5% of the sites are actually involved in catalysis, as suggested by the authors of that study, many theoretical and spectroscopic studies would be cast into doubt.

The cal-ad experiment measures the enthalpy change $\Delta H_{\mathrm{cal-ad}}$ associated with the following reaction:

$$\mathrm{Py(dil)} + \mathrm{ZOH(hex)} \rightarrow \mathrm{Hpy{\cdots}ZO(hex)} + \mathrm{(hexane)} \quad (1)$$

ZOH refers to H-MFI zeolite and Hpy···ZO(hex) refers to the zeolite after titration with pyridine, in both cases saturated with *n*-hexane solvent. Py(dil) represents a dilute solution of pyridine in liquid *n*-hexane, and (hexane) is shown explicitly to account for solvent displaced from the zeolite by the adsorption of pyridine. Since the thermodynamic quantities depend only on the initial and final states of the reaction, it is possible to relate the heats of adsorption measured with and without *n*-hexane. Furthermore, because pore filling to liquid density of *n*-hexane in MFI occurs at a pressure of a few Torr at room temperature, the presence of bulk liquid is unnecessary. We investigated

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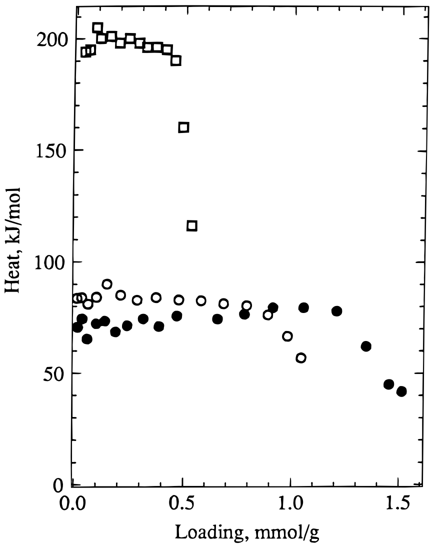

Figure 1. Differential heats of adsorption for the following adsorbates on an H-MFI sample containing 0.50 mmol/g of Brønsted acid sites: pyridine on H-MFI at 480 K (□); *n*-hexane on H-MFI at room temperature (●); and *n*-hexane on H-MFI containing 0.50 mmol/g of pyridine (○).

the cal-ad experiment indirectly by measuring the isosteric heat of adsorption (Q_{st}) of gaseous pyridine. ΔH_{cal-ad} was then calculated from Q_{st} for *n*-hexane and the known enthalpies of vaporization of liquid pyridine and liquid *n*-hexane. Changing the order of contact with the zeolite, *n*-hexane followed by pyridine or pyridine followed by *n*-hexane, should have no effect upon the overall change in enthalpy, which is a state function.

Experimental Section

The H-MFI sample used in this study was obtained in the Na form from Chemie Uetikon AG (Zeocat-Pentasil-PZ-2/54Na) and exchanged into the protonic form as described elsewhere.[3] It had a Brønsted acid site concentration of 0.50 mmol/g, in reasonable agreement with the bulk Al content, 0.63 mmol/g. The pore volume for the sample in the hydrogen form was 0.174 cm^3/g, close to the ideal pore volume of 0.19 cm^3/g for the MFI structure.

Two different calorimeters were used for our measurements. Because TPD measurements for pyridine in H-MFI demonstrated that even physisorbed pyridine lacks sufficient mobility to diffuse to the Brønsted sites below 400 K,[6] calorimetric measurements for pyridine were usually performed on a high-temperature instrument at 480 K to ensure equilibration.[7] We note that the differential heat for pyridine at room temperature should not differ significantly from the value at 480 K. Even if one assumes the difference in heat capacities of the adsorbed and gas phases is as large as the gas-phase heat capacity of gaseous pyridine, the differential heats at room temperature must be within approximately 25 kJ/mol of the value at 480 K.

The second calorimeter was used in the *n*-hexane measurements. It was optimized for room-temperature operation,[16,17] and previous results showed excellent agreement between heats measured by microcalorimetry and by adsorption isotherms.

Results and Discussion

The results for the measurements required to complete the calculations in the Introduction are shown in Figure 1. The measurements for pyridine adsorption on H-MFI in a vacuum at 480 K were reproduced from a previous paper.[18] The differential heats are essentially constant at 200 kJ/mol up to a coverage of 0.50 mmol/g, corresponding to one molecule per acid site, after which the heats fall dramatically. The pressure above the sample was not measurable for coverages less than 0.50 mmol/g, but rose significantly for pyridine exposures greater than this value. As discussed elsewhere, these results are consistent with the H-MFI sample having energetically equivalent sites.[7]

Table 1. Isosteric Heats of Adsorption from Gas Phase (Q_{st}^{gas}) and Latent Heat of Vaporization of the Liquid (ΔH^{vap}) at 25 °C

adsorbate	adsorbent	Q_{st}^{gas}, kJ/mol	ΔH^{vap}, kJ/mol
C_5H_5N	ZOH	200.	40.2
n-C_6H_{14}	ZOH	75.0	31.6
	ZOH with preadsorbed C_5H_5N	80.0	

For *n*-hexane on H-MFI at room temperature, the differential heats start at 70 kJ/mol and rise with coverage to 80 kJ/mol at a coverage of 1.0 mmol/g. This rise in the differential heat with coverage has been observed for other adsorbates in MFI and is due to van der Waals interactions between adsorbate molecules.[16,17] The differential heat falls significantly at a coverage of 1.3 mmol/g, the point at which the pressure above the sample also rises significantly. If one assumes a liquid density for the adsorbed *n*-hexane, a coverage of 1.3 mmol/g corresponds to 0.17 cm^3/g, the pore volume of the sample. These observations agree very well with what is found in the literature for *n*-hexane in MFI. While one group has reported slightly higher differential heats (80kJ/mol) for *n*-hexane in H-MFI,[19] Stach and co-workers reported initial heats for *n*-hexane identical to our value for low coverage, 70 kJ/mol.[20] We note that Stach et al. also reported the differential heat of adsorption for ethane in MFI to be 29 kJ/mol, the same value that we found calorimetrically and from isotherms.[16]

To form the 1:1 complexes for pyridine on H-MFI, we first dosed the evacuated sample with just enough pyridine to match the Al content; we then heated the sealed sample to 500 K in the sealed cell to equilibrate adsorption. Because the pressure in the sealed cell did not rise significantly, this procedure also ensured that Brønsted sites had been present in the sample. If some sites had been lost in the calcination procedure, molecules in excess of one/site would have desorbed at this temperature. After the sample was cooled to room temperature, the differential heats for *n*-hexane were again measured. As shown in Figure 1, the initial heats for *n*-hexane were now higher, 80 kJ/mol, and remained essentially constant to a coverage of 0.9 mmol/g, the point at which pore filling likely occurred. Because 80 kJ/mol is identical to the differential heats for *n*-hexane on H-MFI at high loadings, the additional energy associated with adsorption on the pyridine complex is almost certainly due to van der Waals interactions. The difference in the saturation coverage, 0.9 mmol/g compared to 1.3 mmol/g, is explained by 0.50 mmol/g preloading of pyridine and the higher density of liquid pyridine (0.98 cm^3/g) compared to *n*-hexane (0.66 cm^3/g).

The calorimetrically measured, isosteric heats of adsorption of pyridine and *n*-hexane from the gas phase on H-MFI are reported in Table 1 with enthalpies of vaporization for the saturated liquids taken from the *CRC Handbook*, 75th ed. The tabulated heat of adsorption of *n*-hexane (75 kJ/mol) is the average of the experimental values (70−80 kJ/mol).

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Taking as a basis 1 g of H-MFI zeolite, the reactants in the cal-ad reaction 1 are the following: liquid pyridine in hexane solvent (0.5 mmol) and hexane adsorbed on ZOH (1.3 mmol). The products in the cal-ad reaction 1 are the following: pyridine adsorbed on ZOH (0.5 mmol), hexane adsorbed on ZOH (0.9 mmol), and liquid hexane (0.4 mol). The enthalpy change corresponding to reaction 1 is the sum of the following steps:

1.	unmix liquid pyridine from hexane solvent	$-(0.5)(5)$
2.	vaporize liquid pyridine	$(0.5)(40.2)$
3.	desorb hexane from ZOH	$(1.3)(75.0)$
4.	adsorb pyridine on clean ZOH	$-(0.5)(200)$
5.	adsorb hexane on ZOH with preadsorbed pyridine	$-(0.9)(80)$
6.	liquefy rest of desorbed hexane	$-(0.4)(31.6)$

$$\Delta H_{\mathrm{cal-ad}} = -69.5$$

Therefore, $\Delta H_{\mathrm{cal-ad}} = -69.5$ J/0.5 mmol $= -139$ J/mmol $= -139$ kJ/mol of pyridine.

The value of 139 ± 15 kJ/mol obtained by us for the heat of adsorption of pyridine in *n*-hexane solvent disagrees with the measurements of Drago and co-workers,[15] who measured the heat of adsorption for pyridine in *n*-hexane solvent on an H-MFI sample containing 0.6 mmol/g of acid sites. They reported the presence of two types of sites: a small (5%) concentration of strong sites with heats of 176 kJ/mol and a larger (95%) concentration of weak sites with heats of 36 kJ/mol. Therefore, the average heat of adsorption of pyridine associated with the Brønsted sites from their measurements is $(0.05)(176) + (0.95)(36) = 43$ kJ/mol.

Our value of 139 kJ/mol for $\Delta H_{\mathrm{cal-ad}}$ contains some uncertainty associated with the fact that the heat of adsorption at room temperature may differ slightly from 200 kJ/mol, the value at 480 K. Another source of error is the estimated partial molar enthalpy of dilute pyridine in liquid *n*-hexane (−5 kJ/mol). However, neither of these uncertainties is comparable to the discrepancy of nearly 100 kJ/mol in the integral heat of adsorption of liquid pyridine on H-MFI in the presence of *n*-hexane solvent.

Clearly, the results of our study are inconsistent with those determined by the cal-ad method. Because *n*-hexane adsorption at room temperature is reversible, while pyridine adsorption is not, we favor the values obtained in our experiment. Furthermore, our results are reasonable if one considers the isosteric heat of adsorption for pyridine from the gas phase to be the sum of two terms, a proton-transfer term (∼120 kJ/mol) and a van der Waals term (∼80 kJ/mol). As we have discussed in past publications,[8−10] these terms are not independent and any exact treatment of adsorption combines both. Still, one can gain insights into the relative energetics for adsorption of a series of similar molecules by using these arguments.

Summary

We have demonstrated that results from the cal-ad method for H-MFI are inconsistent with results obtained from microcalorimetric measurements in which the order of adsorption of *n*-hexane and pyridine is reversed. Because the mobility of pyridine is too low to ensure adsorption equilibrium at room temperature, we believe that results from the cal-ad method are unreliable. The conclusion that the sites in H-MFI are energetically equivalent remains valid.

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