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Acid strength and solvation in catalysis by MFI zeolites and effects of the identity, concentration and location of framework heteroatoms

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ABSTRACT

The effects of heteroatom identity (Al^{3+}, Ga^{3+}, Fe^{3+}, or B^{3+}), concentration and location on catalysis by MFI zeolites are examined and interpreted mechanistically using methanol dehydration rate constants and density functional theory estimates of acid strength (deprotonation energies, DPE). In doing so, we shed light on the concomitant effects of confinement and acid strength on catalytic reactivity. Rate constants (per H^+ from pyridine titrations during catalysis) in the first-order and zero-order kinetic regimes decreased exponentially as the DPE of MFI with different heteroatoms increased. These trends reflect a decrease in the stability of ion-pair transition states relative to the relevant precursors (H-bonded methanol and methanol dimers, respectively, for these two regimes) with decreasing acid strength and resemble those in mesoporous solid acids (e.g., polyoxometalates). Confinement effects, weaker in mesoporous solids, give larger rate constants on MFI than on POM clusters with similar DPE. Such reactivity enhancements reflect the effects of MFI voids that solvate transition states preferentially over smaller precursors via van der Waals interactions with the confining voids. Both dehydration rate constants on MFI with 0.7–2.4 H^+ per unit cell volume (5.2 nm^3) are independent of Al or H^+ densities, indicating that neither H^+ location nor acid strength depend on acid site concentration. Higher site densities (3.6 H^+ per unit cell) lead to larger first-order rate constants, but do not influence their zero-order analogs. These data reflect, and in turn provide evidence for, the initial siting of H^+ in less constrained channel intersections and their ultimate placement within the more solvating environments of the channels themselves. Thus, the higher reactivity of Al-rich samples, often attributed to the stronger acid sites, arises instead from the ubiquitous role of zeolites as inorganic solvents for the relevant transition state, taken together with H^+ siting that depends on Al density. We find that heteroatom composition, but not Al density, influences acid strength in MFI, consistent with experiment and theoretical estimates of DPE, and that methanol dehydration rate constants, properly interpreted, provide relevant insights into the combined effects of acid strength and confinement on the reactivity of solid Brønsted acids.

1. Introduction

Zeolites are inorganic silica-based solids with microporous void structures and Brønsted acid sites that catalyze chemical reactions with unique reactivities and selectivities [1–4]. The isomorphous substitution of framework Si-atoms with trivalent atoms (e.g., Al^{3+}, Ga^{3+}, Fe^{3+} or B^{3+}) creates anionic charges that can be compensated by protons located on bridging O-atoms (e.g., Al–O(H)–Si). The acid strength of X-MFI samples (where X indicates the isomorphous substitution of Si^{4+} by Al^{3+}, Ga^{3+}, Fe^{3+} or B^{3+}) depends on the identity of the trivalent framework heteroatom, as shown by deprotonation energy (DPE) estimates from density functional theory (DFT); these DPE values are much smaller for Al-MFI than for Ga-MFI, Fe-MFI or B-MFI (by 11, 23, 72 kJ mol^{-1} [5]). Absolute and relative DPE values differ among X-MFI samples [5–9], however, depending on the type and size of the zeolite model used. These differences reflect how cluster and periodic models account for longer-range electrostatic interactions that stabilize the anionic framework after deprotonation [10,11]. Therefore, it is necessary to compare and validate calculated DPE values with experimental estimates of acid strength.

Probes of solid Brønsted acid strength include adsorption enthalpies of amines [12], alkane cracking and dehydrogenation turnover rates [13], Hammett indicators [14], ^{13}C NMR chemical shifts of adsorbed acetone [15] and Brønsted $\nu(OH)$ frequency shifts upon interactions with weak bases [16]. These probes often

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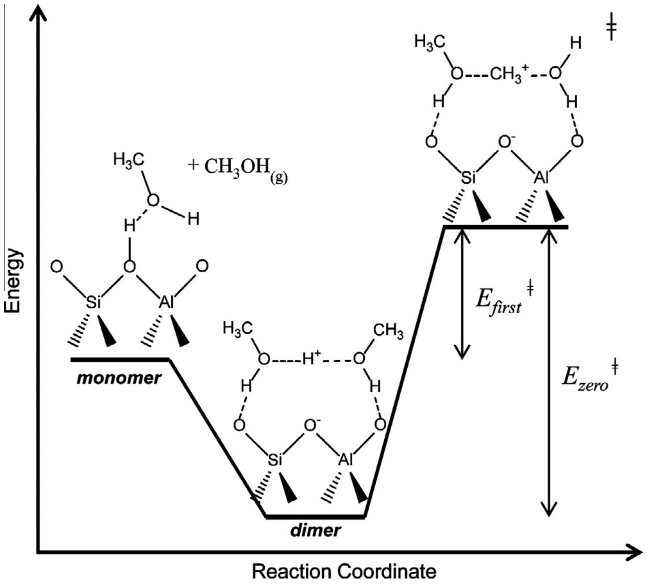
lead to conflicting conclusions about the acid strength of X-MFI, at least in part, because measured properties depend on the identity of the probe molecules and on the location of protons within the microporous voids, which leads, in turn, to differences in the dispersive stabilization of adsorbed probes because of local variations in void shape and size within a given framework structure [17]. For instance, differential adsorption enthalpies of NH_3 measured calorimetrically on Al-MFI and Fe-MFI zeolites are similar (-145 ± 5 kJ mol^{-1}), but these samples differ markedly in their n-hexane cracking turnover rates (1.3×10^{-3} vs. 0.048×10^{-3} n-C_6H_{14}·(H^+·s)$^{-1}$, 700 K) [18] leading to contradictory conclusions about their acid strength differences.

CH_3OH dehydration (to dimethyl ether, DME) rate constants on SiO_2-supported Keggin polyoxometalate (POM) clusters decrease exponentially with DFT-derived DPE estimates of the clusters [19]. First-order (k_{first}) CH_3OH dehydration rate constants reflect the free energy of the DME formation transition state relative to an uncharged adsorbed CH_3OH and a gaseous CH_3OH molecule (Scheme 1). Zero-order rate constants (k_{zero}) reflect the free energy of the same transition state, but in this instance relative to that of a cationic CH_3OH dimer (Scheme 1). The differences in charge and size between this transition state and the two reactive intermediates (H-bonded CH_3OH monomers, k_{first}; protonated CH_3OH dimers, k_{zero}) cause these two rate constants to depend differently on acid strength and solvation by van der Waals interactions with the surrounding void environment. Therefore, such measurements on X-MFI samples may allow the independent assessment of their acid strengths and of their heteroatom siting among the diverse local environments provided by channels and intersections within MFI frameworks. Here, we report these rate constants on X-MFI, normalized by the number of protons and their DPE values, estimated by DFT methods through extrapolation to large MFI clusters.

2. Methods

2.1. Catalyst synthesis and characterization

Al-MFI was synthesized by dissolving $Al(OH)_3$ (53% Al_2O_3, Reheis F-2000 dried gel, 0.02–0.08 g) in a solution containing demineralized H_2O (6 g), tetra-n-propyl ammonium hydroxide (TPAOH, 40 wt%, Aldrich, 1.5 g) and NaOH (1 M solution in demineralized H_2O, Fisher, 1.5 g). Amorphous SiO_2 (Cab-o-sil M-5, 15 mmol) was added to the mixture, which was treated in a rotating sealed Teflon-lined vessel (43/60 Hz; Parr, 23 cm^3) held at 433 K for 6 days in a convection oven (Blue M). Solids were collected by vacuum filtration, washed with H_2O to reduce the pH to ~9 and treated in vacuum overnight at ambient temperature. Ga-MFI and B-MFI were synthesized by the same protocols using $Ga(NO_3)_3$ (nonahydrate, 99.9%, Aldrich, 0.03 g) and $Na_2B_4O_7$ (decahydrate, >99.5%, Aldrich, 0.06 g) instead of $Al(OH)_3$. The same procedure was used to prepare Fe-MFI, using $Fe(NO_3)_3$ (nonahydrate, >99.9%, Baker, 0.12 g), TPAOH (40 wt%, Aldrich, 2.4 g), NaOH (1 M solution in demineralized H_2O, Fisher, 0.5 mMoles), demineralized H_2O (4 g) and Cab-o-sil M-5 (20 mmol). Other Al-MFI samples were obtained from a commercial source (Table 1).



Scheme 1. Illustration of the relationships between the energies of H-bonded CH_3OH monomers, protonated dimers and cationic DME formation transition states reflected in measured first-order ($E^{\neq}_{first}$) and zero-order ($E^{\neq}_{zero}$) CH_3OH dehydration rate constants.

Samples were analyzed by scanning electron microscopy (JEOL JSM-6700F) and X-ray diffraction (Siemens D-500; Cu K$_\alpha$ radiation) to determine their size and framework identity. Si, Al, Ga, Fe, B and Na contents were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES; Galbraith Laboratories; Supporting information). The fraction of Al-atoms in tetrahedral and octahedral coordination was determined from ^{27}Al magic angle spinning NMR lines at 55 ppm and 0 ppm, respectively (details in Section S.2 of the Supporting information).

2.2. Catalytic rate measurements

MFI samples were pressed, crushed using a mortar and pestle, and sieved (to retain 180–250 μm aggregates), and then diluted with SiO_2 (Cab-o-sil HS-5, washed with 1.0 M HNO_3, 180–250 μm pellets) to maintain a sample mass larger than >0.025 g. Samples were held on a coarse quartz frit within a tubular packed-bed quartz reactor (7.0 mm i.d.) and their mass (5–220 mg) was adjusted to conversions below 5%. The bed temperature was kept constant using a resistively heated three-zone furnace (Applied Test Systems Series 3210) and Watlow controllers (EZ-ZONE PM Series); it was measured using a K-type thermocouple in contact with the outer surface of the quartz tube at the center of the catalyst bed.

All samples were treated in flowing 5% O_2/He mixture (83.3 cm^3 g^{-1} s^{-1}, 99.999%, Praxair) by heating to 773 K (at 0.025 K s^{-1}), holding at 773 K for 2 h and cooling to 433 K before catalytic measurements. Liquid CH_3OH (99.8%, Sigma–Aldrich) was introduced via heated lines (>373 K) into He flow (99.999%, Praxair) using a syringe pump (Cole-Palmer 780200C series). Reactant, product and titrant concentrations were measured by gas chromatography (Agilent 6890N GC) using a DB-Wax capillary column (0.320 mm ID × 30 m × 0.50 μm film; J&W Scientific) and

Table 1
Zeolite sample information.

Zeolite	Provenance	Si/T[a]	H^+/T[b]	H^+/T[c]	%T_{Td}[d]
H-[Al]-MFI-1	Commercial	16.6	0.65	0.52	88
H-[Al]-MFI-2	This work	22.8	0.27	0.33	85
H-[Al]-MFI-3	Commercial	29.2	0.77	0.72	89
H-[Al]-MFI-4	Commercial	43.8	1.03	0.89	89
H-[Al]-MFI-5	This work	51.9	0.59	–	87
H-[Al]-MFI-6	This work	117.6	0.86	–	96
H-[Ga]-MFI	This work	108.7	1.09	–	–
H-[Fe]-MFI	This work	61.1	0.85	0.68	–
H-[B]-MFI	This work	75.3	0.25	–	–

[a] Determined from elemental analysis (ICP-OES; Galbraith Laboratories).

[b] Determined from pyridine titrations during CH_3OH dehydration reactions at 433 K.

[c] Determined from NH_4^+ decomposition.

[d] Fraction of Al in tetrahedral coordination (%T_{Td}) determined from ^{27}Al MAS NMR.