



Trace water amounts can increase benzene H/D exchange rates in an acidic zeolite



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ABSTRACT

Reactions between benzene and the zeolite HZSM-5, carried out at low pressure and room temperature, revealed that controlled addition of sub-stoichiometric amounts of water increases the rate of isotopic ¹H/²H exchange between benzene-d₆ and the surface acid site by almost an order of magnitude relative to the control case in which no water is added. Single-ring aromatics like benzene have been identified as an active form of the hydrocarbon pool in methanol-to-hydrocarbon chemistries, but their role as reactive centers for alkylation and dealkylation chemistry is general to all of solid-acid catalysis. Maximum reaction rates were observed for water loadings of ca. 0.1 equivalents for catalysts with Si/Al equal to 15. No beneficial water effect was observed in benzene/zeolite reactions using a much lower acid-density catalyst HZSM-5 with Si/Al equal to 40. In-situ experiments strongly suggest that the origin of the water enhancement effect for the high-acid density catalyst arises from an increase in the “vehicle hopping” proton-transfer mechanism, which cannot occur when acid sites are sufficiently far apart as in the Si/Al equal to 40 catalyst. When the water loading is too high, water’s competitive adsorption and excluded volume reduces the benzene adsorption probability due to the increased proton affinity of a water cluster.

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1. Introduction

Solid-acid catalysts are valuable in many existing industrial hydrocarbon conversion processes, the majority of which occur in the gas-phase, but are also promising for new applications in biomass utilization and environmental remediation [1–3]. Microporous zeolites with pore diameters in the sub-nanometer range are the most commonly employed solid-acid catalysts, although variations in hydrocarbon distributions from currently available petroleum sources have generated interest in mesoporous aluminosilicates possessing Brønsted acid sites [4–6]. In addition, new solid-acid catalyzed upgrading of renewable feedstocks in the liquid-phase demonstrates the catalytic diversity of zeolite structures [7,8]. Water can be incorporated in the reaction system in the feed or evolved as a side product inside the solid acid catalyst during reaction. For example, in biomass conversion processes, water is a major component of the feedstock and in reactions involving oxygenates (alcohols, aldehydes, acids) water may be produced stoichiometrically in-situ [2,9]. Such reactions include

methanol-to-hydrocarbon, aldol condensation, ketonization, and alkylation catalyzed by zeolites and other solid acids [10–14]. Multiple reports discuss the difficulty in completely removing water from acidic zeolites [15–17].

Water is generally considered deleterious in solid-acid chemistry. First, water is a competitive base that strongly adsorbs at the acid site, thereby inhibiting proton availability for hydrocarbon reagents [18–20]. Second, at high-temperatures, the presence of water may lead to lattice dealumination and loss of acidity. Finally, in the case of zeolites, the presence of condensed water causes severe losses in crystallinity and catalytic activity [21]. There are a few instances in which water has been found to exhibit a positive effect on selectivity by virtue of its ability to prevent secondary reactions by strongly adsorbing at Brønsted acid sites and reducing product readsorption events. For example, selectivity enhancements for methanol-to-hydrocarbon conversions through water co-addition have been reported for many years [22,23], and even very recently the origin of this effect has been attributed to water’s competitive adsorption properties [24]. Interestingly, for an alcohol reagent like methanol, which generates water in the condensation step to dimethyl ether, addition of even more water leads to increased selectivity to primary products like small olefins. Recent work on another alcohol system, propanol, indicated that propanol actually adsorbs more strongly than water, but water helped stabilize

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adsorbed intermediate, i.e. pre-transition, states relative to stabilization of the transition state itself such that reduced reaction rates were observed [25].

All of the cases cited above demonstrate that catalyst activity is generally reduced when additional water is introduced, which may be used to improve selectivity, not intrinsic activity. More interesting, and only recently recognized, are cases in which the catalytic activity is actually promoted by the presence of water. For example, in a gas-phase Fischer-Tropsch study involving Ru catalysts, Hibbitts et al. showed that CO activation is increased through water-mediated hydrogen transfer [26]. Similarly, Yoon et al. [27] demonstrated that activity in Rh-catalyzed biphasic conversions of lignin-derived molecules increased in the presence of co-fed water by enhancing a key hydrodeoxygenation step on the bifunctional catalyst. Water's role in each of these cases proceeded *only* through interaction with the metal, not a solid acid function. A few reports in the literature suggest that introduction of small amounts of water can increase reactions rates in purely solid-acid catalysts. For example, Zhao et al. reported an enhancement in rates over zeolite catalysts, showing increased methylpentane isomerization rates upon introduction of small amounts of water over HY zeolites [18]. More recently, Motokura et al. demonstrated that addition of water in the range of 1–5 wt% relative to the mass of the proton-exchanged montmorillonite catalyst increased reaction rates between bulky alkenes by over an order of magnitude [28]. In a study utilizing the industrially-important HZSM-5 catalyst, Chen et al. demonstrated a one-order of magnitude increase in the reaction rate, relative to the completely dry catalyst, for isobutane isotopic exchange with Brønsted acid sites when ca. one equivalent of water was introduced to the reaction mixture [29]. Finally, computational studies suggest that water might enhance ring alkylation/dealkylation steps in the critical hydrocarbon pool mechanism in MTH chemistry through stabilizing the transition state [30].

In this contribution, benzene activation in acidic HZSM-5 catalysts was investigated in the presence of controlled water addition. Benzene was chosen due to the fact that single-ring aromatics are germane to so many hydrocarbon processes in zeolites, for its critical role in the carbon pool mechanism in MTH chemistry [13,14], and perhaps most significantly its role as a precursor to large polycyclic aromatics that ultimately lead to zeolite deactivation at high temperature. Reactions between benzene and the zeolite HZSM-5, carried out at low pressure, room temperature, and equimolar benzene-to-acid site stoichiometry, revealed that controlled addition of sub-stoichiometric amounts of water, i.e., less than one equivalent, increases the rate of isotopic $^1\text{H}/^2\text{H}$ exchange between benzene- d_6 and the surface acid site by almost an order of magnitude relative to the control case in which dry zeolite is used. This result is unexpected, given that water is typically viewed as lowering zeolite activity and is utilized in that manner to help improve selectivity to primary reaction products. *Importantly, water's activity promotion effect was only observed with high acid density catalysts, i.e., at Si/Al = 15, but was not observed for catalysts with Si/Al = 40.* The fact that sub-stoichiometric water addition significantly increased reaction rates for aromatic hydrocarbons in acidic zeolites is not anticipated from the literature, and potential mechanisms to explain these surprising results as well as their dependence on the acid site density are discussed.

2. Experimental

2.1. Zeolites

Zeolite ZSM-5 samples with different aluminum content (Si/Al = 15 CBV 3024E and Si/Al = 40 CBV 8014) were obtained from

Zeolyst in the ammonium-exchanged form. As reported by the vendor, the average crystallite size of all these samples was 1 μm , the BET surface areas vary from 379 to 386 m^2/g independent of Si/Al ratios. SEM experiments indicated that the average particle size was closer to 0.6–0.7 μm . Calcined and dehydrated zeolite samples were prepared from the ammonium form in a glass reactor body via a stepwise vacuum procedure to a final temperature of 723 K, as previously reported. High vacuum conditions with pressures of 2×10^{-5} torr during the activation were achieved with an Edwards EO4 K diffusion pump. Dry catalyst samples were sealed and immediately placed in a dry argon glove box following activation in order to facilitate transfer to zirconia MAS rotors for the in-situ experiments. Complete calcination and dehydration of samples was verified by ^1H MAS NMR. HZSM-5 (Si/Al = 15) catalyst has a high acid site density, with a maximum of 6 acid sites per unit cell, while the Si/Al = 40 catalyst contains 2.34 acid sites per unit cell.

2.2. Water and C_6D_6 adsorption method

A vacuum line equipped with a CAVERN type apparatus was used for quantitative adsorption, following previously published procedures [31]. Typically, a fixed quantity of catalyst was placed in a 7-mm zirconia MAS NMR rotor in the CAVERN, evacuated and sealed, and the adsorbate vapor introduced in the vacuum line to an initial pressure. A desired pressure drop is used to control the adsorption quantity after exposure to the catalyst. For example, to adsorb C_6D_6 (≥ 99.6 atom% deuterium, Aldrich) onto ZSM-5 with Si/Al = 15, 40 mg of catalyst was loosely packed into the rotor in the CAVERN device. For example, 10 torr of initial pressure and 3.2 torr of pressure drop were used to determine when 1 eqv of benzene was adsorbed. The rotor was capped using the CAVERN device. Brønsted acid site densities are calculated from Si/Al ratios (e.g. acid density = 1.04 mmol/g for Si/Al = 15). Reports have shown that the acid site concentration is typically lower than the Al content in zeolites [32], with the H^+/Al ratio equal to 0.8 for this particular ZSM-5 catalyst [33]. In all stack plots shown, spectral traces in a single stack plot are from the same sample unless otherwise noted. For reference and to aid the reader, one equivalent of adsorbate corresponds to 6 and 2.25 molecules per unit cell for Si/Al = 15 and 40, respectively.

2.3. H/D exchange experiments

In-situ solid state ^1H MAS NMR methods were used to follow reactions. For dry-catalyst experiments, 1 eqv of C_6D_6 molecules were adsorbed into both ZSM-5 (15) and ZSM-5 (40) as described above and then tested by ^1H NMR. The H/D exchange took place immediately after adsorptions, while the adsorption processes usually took 3–5 min for completion. The initial H/D exchange spectra were typically acquired 8–11 min following the initial exposure. The following spectra were then taken with 2–3 min intervals to follow the reaction, as shown in Figs. 2–4. For experiments involving water, catalysts with water loadings ranging from 0.06 to 1.0 eqv were prepared via exposure to controlled amounts of water vapor on a vacuum line. Each catalyst with water loading was sealed overnight to allow water diffusion and equilibration within the catalysts, and then characterized by ^1H MAS NMR to confirm the water loadings as shown in Fig. 1. After NMR characterization, they were opened inside the glove box to avoid exposure to any additional water, immediately inserted to the CAVERN body, sealed, and transferred to the vacuum line for subsequent C_6D_6 adsorption.

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