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Cooperativity of adjacent Brønsted acid sites in MFI zeolite channel leads to enhanced polarization and cracking of alkanes

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ABSTRACT

The spatial proximity between Brønsted acid sites (BAS) in HZSM-5 zeolites is demonstrated by ^{1}H double quantum (DQ) MAS NMR measurements. This proximity results in more pronounced polarization of adsorbed acetone and alkanes in zeolites, evident from ^{13}C MAS NMR spectra. The adjacent BAS with synergistic interactions on alkane reactants (propane, *n*-butane, and *n*-pentane) cooperatively catalyze alkane cracking at higher turnover rates than on isolated BAS. Apparent activation energies are similar on HZSM-5 catalysts with different concentrations of isolated and adjacent BAS, while apparent activation entropies become less negative at higher BAS concentrations. Kinetic experiments in conjunction with adsorption measurement and DFT calculations prove that cracking rates at these Al-site pairs are mainly due to more positive intrinsic activation entropies, suggesting that the protonation transition state occurs later along the reaction coordinate on adjacent BAS. Adjacent Brønsted acid sites favor cracking over dehydrogenation and favor central cracking over terminal cracking.

1. Introduction

As a family of important solid catalysts, zeolites have been extensively employed in petroleum refining, petrochemicals production, and pollution control [1–4] to catalyze a variety of reactions, such as fluid catalytic cracking, hydrocracking, paraffin isomerization, aromatic alkylation, xylene isomerization, and toluene disproportionation [5,6]. The properties of acid sites, associated with framework Al atoms, in zeolites have crucial impacts on catalytic performances [7–14]. Generally, the transformations of reactants start with polarization and protonation by the acid sites in zeolites. Thus, the charge distribution and its subtle change in zeolite channels could influence adsorption and reaction energetics.

The effect of framework Al and proton location in zeolites has been explored in reactions such as alkylation and protonation of olefins [7,8]. A stronger kinetic preference for 8-membered ring H^+ was shown for C_2H_4 dimerization than for CH_4–C_2H_4 alkylation [9]. The spatial volume of the zeolite cavity and the dimensionality of the pore structure were also been proposed to influence the product selectivity for 1-pentene conversion [10]. Gounder and Iglesia proved that propane cracking rates were higher on acid sites in the 8-membered ring than in the 12-membered ring in H-MOR, mainly because transition states are only partially confined within smaller pockets [11]. Similarly, Janda and Bell also reported that protons located in less confined portions of the MFI zeolite pore system; e.g., the channel intersections also contribute to the increased cracking rate of *n*-butane because of the less confinement on them [14].

The effect of Al site proximity is also frequently found to affect alkane conversion catalysis. For 1-butene transformation, Sazama and Gábová claimed that the close “Al pairs” in HZSM-5 zeolites were responsible for the enhanced rate of the hydride transfer reactions which account for the higher yield of aromatics, while the olefin cracking reaction was preferred over an isolated Al site [12]. Bell et al. reported that the turnover rate of propene oligomerization decreased but the selectivity to dimer increased with the site proximity in the MFI zeolite [13].

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A variety of chemical and spectroscopic methods have been reported to detect the Al distribution in Si-rich zeolites, which ultimately reflects the electrostatic field distribution in zeolite channels. Using Co^{2+} ions as the probe, which are controlled to exchange with the zeolitic protons, the occurrence of "Al pairs" (defined as Al–O–$(Si–O)_{1,2}$–Al sequences in one ring that are to coordinate with Co^{2+} ions) in the framework of MFI and their spatial distribution have been investigated [15–17]. In addition, double quantum (DQ) MAS NMR spectroscopy has also been successfully applied to monitor the vicinity of extra-framework Al species and framework Al atoms in dealuminated, formerly Al-rich zeolites. The proximity of two corresponding nuclei, e.g., H and H or Al and Al, can be detected [18–20]. Diphosphine probe molecules have also been used to detect the proximity between acidic sites in zeolite HY by ^{31}P MAS NMR [21]. Quantitatively probing the Al distribution in zeolite has recently been achieved using extended X-ray absorption spectroscopy to evaluate the longer range interatomic distances around Al T sites [22]. The advantages of NMR-based methods in investigating proximity between acidic sites in bifunctional Lewis/Brønsted acid catalysts and distribution of acid sites within the pores of zeolites have been shown [23]. Recently, Perea et al. precisely determined the short-range distribution of Al over the different T-sites and the most probable Al–Al neighboring distance within parent and steamed HZSM-5 crystals, as well as the long-range redistribution of Al upon zeolite steaming using atom probe tomography technique [24].

These investigations represent important progress in the elucidation of the effect of zeolite channel size and the location of framework Al atoms and have important implications for understanding the structure–activity relations in the transformation of organic molecules. For monomolecular cracking, the mechanism is generally thought to be based on carbonium-ion-like intermediate and transition states [25–29]. A subtle change in the electron field around the Brønsted acid sites (BAS) contained in molecular-sized pores can influence the cracking reaction of the alkanes. For instance, proximal polarization of C–H bonds of alkanes by La^{3+} cations and the strong BAS appears to enhance the catalytic reactions of isomerization, cracking, and alkylation [30]. This can be explained by the stronger positive partial charge induced in the secondary and tertiary carbon atoms on alkanes (e.g., isobutane) by La^{3+} cations [31]. The previous work from our group also implies that the enhanced cracking rate of methylcyclohexane is caused by the additional polarization of reactants by a Lewis acid site (LAS) adjacent to a BAS [32]. Polarization of alkanes is a universal phenomenon in zeolite channels, and acid sites in proximity (BAS-BAS and/or BAS-LAS) could in principle exert different extents of polarization and thus affect energetics for activating and converting the molecule [33]. While a large number of studies have been published, the consequences of spatially close BAS in confined zeolite pores have hardly been investigated in alkane cracking, partly because interfering structural factors (e.g., LAS in the vicinity, distribution of BAS among locations with different spatial constraints) may be at play.

In this report, a series of HZSM-5 zeolites with varying concentrations of isolated and adjacent BAS have been used as catalysts for monomolecular alkane cracking. ^{1}H DQ MAS NMR and UV–vis measurements of Co^{2+}-exchanged zeolites [16,17,34–38] were used to estimate the relative numbers of Al pairs and single Al atoms in zeolites. Adsorption of *n*-alkanes and acetone in these zeolites has been investigated by solid state ^{13}C MAS NMR, adsorption isotherm and calorimetry measurements, and DFT calculations. This integrated approach enables us to identify the underlying causes for enhanced rates of alkane cracking on adjacent BAS.

2. Experimental

2.1. Materials

HZSM-5 zeolites were purchased from Zeolyst International and denoted as HZSM-5-*x*, where *x* represents the Si/Al ratio determined by ^{29}Si MAS NMR measurement. Samples were heated in synthetic air with a flow rate of 80 mL min^{-1} to 773 K at a rate of 2 K min^{-1} and maintained for 6 h to convert zeolites from NH^{4+} to H^{+} form. Then samples were pressed and crushed into particles of 60–80 mesh for characterization and catalytic tests. Ammonium hexafluorosilicate (denoted as AHFS) treated zeolites were performed according to the procedure [39] and named as HZSM-5-*x*-AHFS.

2.2. Characterization

2.2.1 ^{29}Si and ^{27}Al MAS NMR

^{29}Si and ^{27}Al MAS NMR experiments were performed on a Bruker Avance III spectrometer at resonance frequencies of 79.5 and 104.3 MHz, respectively. ^{29}Si MAS NMR spectra were recorded using a 7 mm MAS probe with a $\pi/2$ length of 4.5 μs and a recycle delay ranging from 10 to 40 s at a spinning rate of 6 kHz. The chemical shift was referenced to 4,4-dimethyl-4-silapentane-1-sulfonic acid (DSS) at 1.534 ppm. ^{27}Al MAS NMR spectra were recorded using a 4 mm MAS probe and a spinning rate of 14 kHz with a $\pi/6$ pulse length of 1.4 μs and a recycle delay of 0.1 s for all the hydrated samples. The chemical shift was referenced to $Al(NO_3)_3$ (0.1 mol L^{-1}) solution.

2.2.2. ^{1}H and ^{1}H DQ MAS NMR

^{1}H and ^{1}H DQ MAS NMR experiments were performed on a Bruker Avance III spectrometer at a resonance frequency of 400.1 MHz using a 3.2 mm probe with a spinning rate of 20 kHz. Prior to the NMR measurements, samples were packed into a quartz tube and evacuated at 383 K for 7 h, and then heated to 673 K at a rate of 1 K min^{-1} and maintained for 12 h at a pressure below 1×10^{-1} Pa to remove adsorbed water in the zeolites. After cooling to room temperature, samples were packed into a 3.2 mm ZrO_2 rotor in the glove box. The chemical shift was referenced to tetramethylsilane (TMS at 0.0 ppm). The DQ coherences were excited and reconverted with the BABA (back to back) dipolar recoupling sequence [40].

2.2.3. ^{13}C MAS NMR

^{13}C MAS NMR experiments were performed on a Bruker Avance III spectrometer in a magnetic field strength of 9.4 T at a resonance frequency of 100.6 MHz. Prior to NMR measurements, samples were heated to 383 K at a rate of 1 K min^{-1} and maintained for 6 h, and then heated to 673 K at a rate of 1 K min^{-1} and maintained for 10 h at a pressure below 1×10^{-1} Pa. After cooling to room temperature, the samples were exposed to adsorbates (propane, *n*-pentane, or acetone-$^{13}C_3$). For the ^{13}C MAS NMR spectra of adsorbed alkanes, after a certain amount of alkanes were introduced (final content: 290 μmol g^{-1} for HZSM-5-16; 190 μmol g^{-1} for HZSM-5-25; 120 μmol g^{-1} for HZSM-5-40; 40 μmol g^{-1} for HZSM-5-140) to the zeolite, the zeolite was in situ packed into a 7.0 mm rotor. The spectra were recorded with a $\pi/2$ pulse length of 3.6 μs, and the recycle delay was 4 s at a spinning rate of 6 kHz. For the ^{13}C MAS NMR of adsorbed acetone, after a certain amount of acetone is introduced (100 μmol g^{-1} for HZSM-5-16, HZSM-5-25 and HZSM-5-40; 50 μmol g^{-1} for HZSM-5-140; 0.10, 0.16, 0.25, and 0.42 acetone/Al_F ratio for HZSM-5-16, HZSM-5-25, HZSM-5-40, and HZSM-5-140, respectively) to the dehydrated zeolite, the zeolite was packed into a 7.0 mm rotor in the glove box.