Modification of Acid Sites in ZSM-5 by Ion-exchange: An *in-situ* FTIR Study

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Abstract

A study of the acid sites in M^{n+} -ZSM-5 zeolites ($M^{n+} = H^+$, Al^{3+} , Ca^{2+} , and Ba^{2+}), synthesized by ion-exchange from the NH_4^+ form, has been carried out using X-ray diffraction, ^{27}Al MAS NMR, and *in-situ* FTIR spectroscopy. X-ray diffraction data indicate that the crystalline structure of ZSM-5 is maintained on ion-exchange. ^{27}Al MAS NMR spectroscopy confirms that Lewis acid sites in all of the M^{n+} -ZSM-5 zeolites are mainly located on the tetrahedral aluminum atoms in the zeolite framework. However, octahedral extra-framework aluminum is another source of Lewis acid sites in H^+ -ZSM-5 and Al^{3+} -ZSM-5. Brønsted acid sites are identified as originating from the hydroxyl groups that bridge Al and Si atoms. The acid sites in M^{n+} -ZSM-5 have been characterized by *in-situ* FTIR spectroscopy with pyridine as the probe molecule. FTIR spectroscopy demonstrated that the number of accessible acid sites and ratio of Lewis to Brønsted acid sites in M^{n+} -ZSM-5 can be effectively modified by ion-exchange. The number of acid sites in M^{n+} -ZSM-5 increases in the same order as the acidity of cations with $Ba^{2+} < Ca^{2+} < NH_4^+ < Al^{3+} < H^+$. Though the strength of both Lewis and Brønsted acid sites is virtually identical for all M^{n+} -ZSM-5 zeolites, the ratio of Brønsted to Lewis acid sites varies as a result of the loaded cation. In addition, modification of acid sites in M^{n+} -ZSM-5 by loading different cations is discussed in terms of the accessibility of the surface of the zeolite channels and the reactivity of the cations with Brønsted acid hydroxyls. We conclude that larger cations can effectively constrict the zeolite channels and impede the ability of pyridine to access acid sites on the surface of the channels.

1. Introduction

Brønsted and Lewis acid sites in the framework of zeolite-based catalysts play an important role as active sites for various processes in refining and petroleum processing.[1-4] For example, Brønsted acid sites of ZSM-5 have been widely exploited for paraffin isomerization,[5] conversion of methanol to gasoline and olefins,[6, 7] ethylbenzene production,[4] and the Chichibabin condensation.[8] Lewis acid sites of hydrothermally pretreated ZSM-5 control the catalytic activity for hydroxylation of aromatics to their corresponding phenols.[9] Lewis acid sites in zeolite Y have also been shown to be efficient for the isomerization of glucose to fructose in alcohols and aqueous media.[10] Nevertheless, for some applications a high degree of zeolite acidity can produce undesired reactions such as cracking.[11] For this reason it is highly desirable to be able to control zeolite acidity. Methods that have been widely explored involve modifying the Si/Al ratio through dealumination[12-15] or ion-exchange.[16-19] It has been reported that these procedures can be used to control the formation and rearrangement of carbonium ions in many hydrocarbon reactions.[20, 21]

Since zeolite acid sites are involved in acid-catalyzed hydrocarbon reactions, characterization and measurement of the acidity of zeolites, including the number, type, origin, and strength of the acid sites, is of scientific and practical interest. There are many methods that have been used to characterize the acidity of solid acid catalysts, of which temperature-programmed desorption (TPD)[2, 12, 22-24] and FTIR spectroscopy [2, 12, 25-27] have been widely used. Information on the strength of solid acid sites, as determined by the strength of the probe molecule – acid site bond, can be readily derived from TPD data. However, TPD cannot intrinsically distinguish between Brønsted and Lewis acid sites. Additionally, extraction of quantitative information from TPD data in an explicit form depends on a valid interpretation of the TPD data in terms of a correlation between the TPD profiles and different acid sites. There is an excellent review about TPD method that explores these issues.[28]

FTIR spectroscopy has proved to be a very powerful tool for identifying the nature (type and strength) of acid sites.[2, 29-32] By employing probe molecules, such as ammonia, acetonitrile and pyridine, FTIR spectroscopy can be used to easily discriminate

between Brønsted and Lewis acids. Acid strength can be estimated from the intensity profile of desorbed molecules versus temperature. An experimental determination of the integrated molar extinction coefficients of bound pyridine can be used to provide a reliable estimate the number of acid sites.[29, 30] FTIR spectroscopy with probe molecules has been used in the determination of the number of acid sites for cation modified ZSM-5.[33-35] For instance, Sachtler et al. synthesized Zn/Ga/Fe-ZSM-5 loaded with acidic cations (Zn,Ga, and Fe) and investigated the effect of these metal cations on Brønsted acid sites of ZSM-5.[27] Coelho et al. explored the influence of basic sodium ions on the number and strength of acid sites.[18] TPD with FTIR spectroscopy have been combined to provide comprehensive information on acidity. For example, Niwa and co-workers reported that IR combined with NH₃-TPD simultaneously provides information on the strength and quantity of acid sites of zeolites[23, 24, 36, 37] and ZrO₂. [38]

Studies that explore how the cations affect the acidity of ion-exchanged zeolites are rare. To our knowledge, there have been no systematic quantitative studies of the effect of cation acidity on the acid sites of zeolites, i.e., the number of total acid sites, the distribution (or ratio) of Brønsted and Lewis acid sites, and the strength of the acid sites. In this work, a series of Mⁿ⁺-ZSM-5 (Mⁿ⁺= H⁺, NH₄⁺, Al³⁺, Ca²⁺, and Ba²⁺), where the cations have different Lewis acidities has been synthesized via ion-exchange methods and characterized by XRD, ²⁷Al MAS NMR, and *in-situ* FTIR spectroscopy. We also prepare H⁺-ZSM-5 via *in-situ* calcination of the ammonia form of ZSM-5 which allows us to compare this material to H⁺-ZSM-5 produced by ion exchange. Employing *in-situ* FTIR spectroscopy with a pyridine probe molecule, the individual Brønsted and Lewis acid sites in Mⁿ⁺-ZSM-5 have been identified and quantified. We also discuss the mechanism by which the number of accessible acidic sites is modified as a function of the nature of the cation and propose a model by which loaded cations affect the acidity of zeolites. We anticipate that this work will provide insights into the fabrication of new Mⁿ⁺-ZSM-5 catalysts with desirable levels of the appropriate type of acid sites (Brønsted or Lewis) for a given reaction.

2. Experimental

2.1. Synthesis and *in-situ* pretreatments

NH_4^+ -ZSM-5 (Si/Al=80) was purchased from Sigma-Aldrich and used without further purification. A series of metal cation-functionalized M^{n+} -ZSM-5 ($\text{M}^{n+} = \text{Al}^{3+}$, Ca^{2+} , and Ba^{2+}) and H^+ -ZSM-5 zeolites were prepared by a standard ion-exchange procedure using aqueous solutions of the each nitrate salt or nitric acid.[39] Typically, 1.5 g of NH_4^+ -ZSM-5 was suspended in 50 mL of 2.0 M aqueous solution of each nitrate salt (nitric acid for H^+ -ZSM-5) and was stirred at 80 °C for 4 h, followed by washing with deionized water until no free ions remained, centrifugation, and then drying in vacuum at 120 °C for 5 h. The absence of free ions was determined for Ca^{2+} and Ba^{2+} ions by titration with a sulfate and for Al^{3+} ions by reaction with NaOH. Prior to *in-situ* FTIR studies all the samples were heated in the reaction cell under vacuum to 120 °C with a temperature ramp of 5°C min⁻¹, which was maintained for 2 h, followed by cooling to the room temperature and degassing under vacuum for 0.5 h. In addition, the acidic ZSM-5, H^+ -ZSM-5 has been prepared by the *in-situ* calcination of NH_4^+ -ZSM-5 at 500 °C for 3 h under vacuum.[40] H^+ -ZSM-5 prepared by ion-exchange and *in-situ* calcination of NH_4^+ -ZSM-5 exhibit the identical acid sites as shown in Section 3.

2.2. Characterization

XRD patterns were recorded on Rigaku Dmax powder diffractometer using a continuous scan of Cu K α radiation (operational parameters of 4 kV and 22.5 mA) equipped with a scintillation type detector which registered Bragg's angles (2 θ) between 5 and 50°.

²⁷Al MAS NMR spectra were recorded at room temperature at 104.3 MHz on a Varian-400 spectrometer equipped with a magic angle spin probe at a spin rate of 5 kHz. $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ was used as a reference.

Metal ion ($\text{Al}^{3+}/\text{Ca}^{2+}/\text{Ba}^{2+}$) content was measured using inductively couple plasma techniques with a Varian Vista MPX ICP-OES combustion analyzer. Metal ion standards in the range of 2-50 ppm used for instrument calibration were prepared from a 1000 mg

L⁻¹ (1000 ppm) ICP standard solution (Sigma Aldrich) for each of the metal ions. Mⁿ⁺-ZSM-5 zeolites were dissolved in 35% hydrofluoric acid and diluted with deionized water.

2.3. *In-situ* FTIR spectroscopy

In-situ FTIR spectra were recorded with a Nicolet 6700 (Thermo Scientific) infrared spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride (MCT) detector. Each spectrum was obtained by averaging 128 scans at 2 cm⁻¹ resolution. The samples were mounted in a custom fabricated IR cell which was specifically designed to study highly scattering powder samples in a transmission mode. The IR cell and the preparation of the Mⁿ⁺-ZSM-5 (Mⁿ⁺ = H⁺, NH₄⁺, Al³⁺, Ca²⁺, and Ba²⁺) samples, which are supported on a highly transmissive tungsten mesh (~ 2 cm² area), have been described previously.[41-43] In brief, Mⁿ⁺-ZSM-5 powders were pressed onto a tungsten grid. The sample was then mounted inside the IR cell which is connected to a turbo pumped gas manifold with a base pressure of ~ 5 × 10⁻⁷ Torr. The cell is sealed with CaF₂ windows, which can be used for IR transmission studies down to ~1000 cm⁻¹. The sample can be resistively heated to a set temperature, which is measured by a K-type Chromel-Alumel thermocouple attached to center of the grid. After *in-situ* pretreatment, the background spectra were recorded. Pyridine (Sigma-Aldrich, >99.9%) was chemisorbed at 110 °C by admitting the vapor to the cell with the pressure monitored with a capacitance manometer. IR spectra of adsorbed pyridine were recorded after exposure to vacuum at 110, 150 and 250 °C, respectively.

3. Results and Discussion

3.1. Structural properties of the ion-exchanged M^{n+} -ZSM-5 zeolites

The X-ray diffraction data for the series of M^{n+} -ZSM-5 zeolites, displayed in Fig. 1, show that all the M^{n+} -ZSM-5 zeolites exhibit virtually identical XRD patterns. These patterns are ascribed to the pentasyl type framework structure characteristic of ZSM-5.[32, 44] The diffraction patterns confirm that the crystalline structure of ZSM-5 remains the same after the chemical and thermal treatment used in the ion-exchange process. There is no evidence for the presence of a new phase implying that there is no observable formation of metal oxides and no observable incorporation of the loading ions into the ZSM-5 framework. The ^{27}Al MAS NMR spectra of M^{n+} -ZSM-5 are shown in Fig. 2. All the M^{n+} -ZSM-5 samples display a resonance at $\delta \approx 54$ ppm, which is ascribed to framework tetrahedral Al, Al_{Td} . [9, 12, 17] The resonance at $\delta \approx 0$ ppm corresponds to octahedral extra-framework aluminum, $\text{Al}_{\text{Td-Oh}}$, which has been observed in Al^{3+} -ZSM-5 and in H^+ -ZSM-5. In the case of Al^{3+} -ZSM-5, the Al^{3+} ions loaded on the ZSM-5 coordinate to water ligands in a reversible process resulting in octahedral coordination, which is observed as a resonance around 0 ppm. This resonance has been reported to be associated with H^+ counter ions that can coordinate to water ligands.[45, 46] However, the framework aluminum in H^+ -ZSM-5 is tetrahedrally coordinated. Based on our data, the ratio of $\text{Al}_{\text{Td-Oh}}$ to total aluminums in Al^{3+} -ZSM-5 and H^+ -ZSM-5 is ~ 8 and 15%, respectively.

In-situ FTIR spectra provide additional information about the structure of the M^{n+} -ZSM-5 zeolites. Prior experimental and theoretical results clearly indicate there are two types of local structures for NH_4^+ -ZSM-5 --unperturbed and hydrogen-bonded. The latter includes monodentate-, bidentate-, and tridentate- NH_4^+ -ZSM-5.[47] Scheme 1 displays the representative structures of NH_4^+ -ZSM-5. It has been demonstrated that hydrogen-bonding interactions of the ammonium ion with the charged atoms in the channels play a critical role in stabilizing these ionic structures.[48] Therefore, the hydrogen-bonded structures, such as monodentate-, bidentate-, and tridentate- NH_4^+ -ZSM-5 are expected to be the major species rather than the unperturbed ammonium form.[48] This is confirmed by the IR spectrum of NH_4^+ -ZSM-5, which is shown in Fig.

3(a). The broad absorption bands from 2400 to 3300 cm^{-1} have been attributed to the N-H stretch of the hydrogen-bonded ammonium ion while the sharp band at 3375 cm^{-1} is attributed to the N-H stretch of the unperturbed ammonium ion.[30] The absorption bands around 1450 and 1484 cm^{-1} are attributed to N-H bending vibration modes of the NH_4^+ moieties with different bonding interactions.[24] The IR bands around 1875 and 2000 cm^{-1} are assigned to combination bands or overtones of the Si-O stretch in the framework of ZSM-5.[49] The O-H bending mode at 1640 cm^{-1} is observed for ZSM-5 pretreated at 120 $^{\circ}\text{C}$ for 2 h under vacuum indicating that some water is still present even after heating at 120 $^{\circ}\text{C}$ under vacuum for 2 h.[24] The absorption bands from 3400–3800 cm^{-1} originate from the various types of O-H stretches.[2, 44, 50] The broad band around 3500 cm^{-1} is attributed to hydrogen-bonded hydroxyls, including those in water. The absorption band around 3610 cm^{-1} is ascribed to the Brønsted acid OH groups bridging a Si and an Al in the zeolite framework $[\text{Si}(\text{OH})\text{Al}]$. The absorption bands at 3685 and 3737 cm^{-1} are assigned to unperturbed O-H stretches of bridging and silanol hydroxyls.[2, 44, 50, 51]

After ion-exchange the corresponding cations are substituted for ammonium ions. ICP data show that approximately $1.5 \times 10^{-4} \text{ mol g}^{-1} \text{ Al}^{3+}$ ions, $2.8 \times 10^{-4} \text{ mol g}^{-1} \text{ Ca}^{2+}$ ions, and $1.6 \times 10^{-4} \text{ mol g}^{-1} \text{ Ba}^{2+}$ ions have been exchanged into the ZSM-5. The exchange level of H^+ with NH_4^+ ions is determined by a comparison of the intensity of the IR absorption band around 1450 cm^{-1} , which is assigned to the bending mode of the bound ions, with the assumption that extinction coefficients are identical in all M^{n+} -ZSM-5. The procedure is: (a), integrate the absorption band around 1450 cm^{-1} for each M^{n+} -ZSM-5; (b) calculate the change of the integral of the absorption band around 1450 cm^{-1} of M^{n+} -ZSM-5 relative to the same band for NH_4^+ -ZSM-5; (c) divide the change of the integral of the absorption band by the sample weight; (d) estimate the degree of exchange of H^+ ions by using the measured concentration of the exchanged cation in a given ZSM-5. About $5.5 \times 10^{-4} \text{ mol g}^{-1} \text{ H}^+$ ions are estimated to be exchanged. As shown in Fig. 3(b)–3(d), ion-exchange between NH_4^+ and the cations is further confirmed by the complete disappearance of the absorption band of the unperturbed ammonium ions at 3375 cm^{-1} . In addition, the absorption band due to the ammonia bending mode around 1450 cm^{-1} and the absorption band due to hydrogen-bonded ammonium ions in the 2400–3300 cm^{-1}

region become weaker after ion-exchange. However, the change in the broad absorption in the 2400–3300 cm^{-1} region varies with different cations. Compared to NH_4^+ -ZSM-5, the intensities of the absorption bands in the 2400–3300 cm^{-1} region decrease significantly after ion-exchange with H^+ , Al^{3+} , and Ca^{2+} ions while the intensity of this absorption band in Ba^{2+} -ZSM-5 is still relatively high. Combined with data on the ion content, as determined by ICP, it is concluded that the ion-exchange for H^+ , Al^{3+} , and Ca^{2+} ions is efficient, but it is less efficient for Ba^{2+} ions. It is worthwhile to note that the ion-exchange process does not destabilize the ZSM-5 framework. ZSM-5 with high Si/Al ratios is basic and is stabilized by Lewis acidic cations. Thus, it is not surprising that the ZSM-5 we use, with a Si/Al ratio of 80/1, is stabilized under acidic conditions. [33, 34, 52] [33, 34, 51] Correspondingly, ZSM with a low Si/Al ratio is expected to be stabilized under basic condition. In the present study, as verified by the identical XRD patterns for NH_4^+ -ZSM-5, Ca^{2+} -ZSM-5 and Ba^{2+} -ZSM-5, ZSM-5 is still stable after ion-exchange with basic Ca^{2+} and Ba^{2+} ions. One reasonable explanation is that the Ca^{2+} and Ba^{2+} ions occupy the same position as occupied by the NH_4^+ ions and do not incorporate into the crystal lattice of ZSM-5. Thus they have a negligible effect on the stability of the structure of ZSM-5.

We now discuss the absorption band around 3610 cm^{-1} that is assigned to the O-H stretch of Brønsted acid hydroxyls. As shown in Fig. 3, it is obvious that this absorption band disappeared after ion-exchanged with Ca^{2+} and Ba^{2+} ions whereas this absorption is still present at a relatively high intensity after ion-exchange with H^+ and Al^{3+} . The disappearance of this absorption is due to the reaction of Brønsted acid hydroxyls with Ca^{2+} and Ba^{2+} ions during the ion-exchange process.[27, 53] Additionally, the absorption bands of silanol hydroxyls at 3685 and 3737 cm^{-1} decreased slightly implying that silanol hydroxyls participate in the reactions of Ca^{2+} and Ba^{2+} ions with Brønsted acid hydroxyls. The interaction between the metal cations and ZSM-5 is shown schematically in Scheme 2. We note that the diagram in Scheme 2 should not be viewed as an attempt to present a unique mechanism for the structure of the metal loaded ZSM-5. We simply present a plausible mechanism for the processes under consideration.

3.2. Acid sites in M^{n+} -ZSM-5 zeolites

3.2.1. Type and number of acid sites in the M^{n+} -ZSM-5 zeolites

Studies of pyridine adsorption and desorption on the M^{n+} -ZSM-5 zeolites were performed using *in-situ* FTIR spectroscopy with the goal of: (1) determine the types of acid sites; (2) quantify the number of acid sites; (3) estimate the strength of the acid sites.

Fig. 4 shows spectra of pyridine adsorbed on M^{n+} -ZSM-5 zeolites taken at 110 °C in the 1700-1400 cm^{-1} region. The spectra in this region probe the vibrational modes of pyridine adsorbed on the M^{n+} -ZSM-5 surfaces (shown in Table 1). Heating to 110 °C prior to pyridine adsorption significantly decreases the influence of adsorbed water and effectively reduces the amount of physisorbed pyridine. All the M^{n+} -ZSM-5 zeolites show IR bands due to hydrogen-bonded pyridine (1447 and 1599 cm^{-1}) adsorbed on Lewis acid sites (1455 and 1623 cm^{-1}), pyridine adsorbed on Brønsted acid sites (1547 and 1640 cm^{-1}), and a band at 1490 cm^{-1} associated with an interaction of pyridine with both Lewis and Brønsted acid sites.[12, 27, 30, 50, 54] As shown in Fig. 5, H^+ -ZSM-5 prepared by calcinations of NH_4^+ -ZSM-5 and ion exchange shows the identical spectrum for adsorbed pyridine as seen for H^+ -ZSM-5 prepared by ion exchange which suggests that these two methods for preparation of H^+ -ZSM-5 lead to very similar materials. The Lewis acid sites originate mainly from the framework aluminum species, A_{Td} . In addition, extra-framework Al^{3+} ions present on Al^{3+} -ZSM-5 also act as Lewis acid sites. The Brønsted acid sites mainly originate from the hydroxyls bridging between Si and Al as shown in Scheme 1.[25, 32]

In-situ transmission FTIR spectroscopy can be used to quantify the number of acid sites based on the absorption coefficients for these sites reported in the literature. The reported average integrated molar extinction coefficients ϵ ($\text{cm} \mu\text{mol}^{-1}$) are 1.73 at 1445 cm^{-1} (Lewis acid sites), 1.23 at 1547 cm^{-1} (Brønsted acid sites) and 1.46 at 1490 cm^{-1} (associated with both Lewis with Brønsted acid sites), respectively.[30, 31] The approximate number of acid sites can therefore be determined based on the Lambert-Beer equation

$$C_w = \frac{A \times S}{W \times \epsilon}$$

Where C_w , ($\mu\text{mol g}^{-1}$), A (is the length of the x axis for the absorption band in cm^{-1}), W (g), and S (cm^2) denotes number of acid sites, IR absorption intensity, sample weight, and sample area, respectively. As is shown in Fig. 6 (a), when the NH_4^+ ions in ZSM-5 are replaced by the acidic H^+ ions, the number of the acid sites increases from 230 to 320 $\mu\text{mol g}^{-1}$. Correspondingly, the number of acid sites decreases from 230 to 90 $\mu\text{mol g}^{-1}$ as a result of incorporation of basic Ba^{2+} ions. The number of acid sites on Al^{3+} -ZSM-5 and Ca^{2+} -ZSM-5 has been determined as 280 and 160 $\mu\text{mol g}^{-1}$, respectively. Thus, the trend in the number of acid sites for M^{n+} -ZSM-5 is: H^+ -ZSM-5 > Al^{3+} -ZSM-5 > NH_4^+ -ZSM-5 > Ca^{2+} -ZSM-5 > Ba^{2+} -ZSM-5. Interestingly, this ordering is consistent with the acidity of the ions $\text{H}^+ > \text{Al}^{3+} > \text{NH}_4^+ > \text{Ca}^{2+} > \text{Ba}^{2+}$. The reasons for this ordering will be discussed in more detail in Section 3.3.

In addition, as shown in Fig. 6(b), the ion-exchange procedure alters the distribution of Lewis and Brønsted acid sites. The ratio of Lewis to Brønsted acid sites increases in the same order as the Lewis acidity for the metal ions: $\text{Al}^{3+} > \text{NH}_4^+ > \text{Ca}^{2+} > \text{Ba}^{2+}$. However, H^+ -ZSM-5 is an exception. The influence of the loaded cations on the total Brønsted and Lewis acid sites and ratio of Brønsted to Lewis acid sites will be discussed in detail in Section 3.3.

3.2.2. Strength of acid sites in the M^{n+} -ZSM-5 zeolites

As discussed in the Introduction, the number and type of acid sites are of primary importance in the acid-catalyzed reactions of zeolites. In addition, the strength of acid sites has been shown to influence reaction rates and mechanisms.[55, 56] For instance, the reaction of methanol to other hydrocarbons was studied over two isostructural zeolite catalysts with different acid strengths, H-SAPO-5 and H-SSZ-24. It was found that acid strength can potentially be used to tune the selectivity of zeolite catalyst towards aromatics and alkanes versus alkenes.[56]

The strength of acid sites in zeolite type catalysts has been subject to both theoretical and experimental investigations.[55, 57-59] Among the methods proposed so

far, temperature programmed desorption (TPD) is probably most popular. Niwa et al employed IRMS-TPD with ammonia as a probe molecule to estimate the strength of Brønsted acid site in zeolite type catalysts.[60-62] Here, we adopted the IR-TPD method with pyridine as a probe molecule. It has been shown that pyridine molecules are effectively bonded to both Lewis and Brønsted acid sites and therefore the strength of both Lewis and Brønsted acid sites can be determined simultaneously by IR-TPD with pyridine as the probe molecule. Fig. 7 shows the representative spectra of Al^{3+} -ZSM-5 and Ca^{2+} -ZSM-5 at different desorption temperatures. The absorption band at 1447 cm^{-1} decreases significantly when the sample is heated to $150\text{ }^{\circ}\text{C}$ indicating that the hydrogen-bonded pyridine that has an absorption at this frequency is the least strongly bound pyridine moiety. The number of Lewis acid sites increases slightly, which could be due to generation of the more accessible Al sites as a result of breaking of hydrogen bonds as the temperature is increased to achieve desorption of pyridine. Consistent with this hypothesis, we observed a decrease in the absorption of hydroxyls in the 3500 cm^{-1} region that correlates with the increase in Lewis acid sites. It has been reported that surface Lewis acid sites are hydrogen-bonded to the adjacent hydroxyls on hydroxyl-rich alumina surfaces.[63] Similar to alumina, the M^{n+} -ZSM-5 is also rich in surface hydroxyls. Therefore, the Lewis acid sites are probably hydrogen-bonded to the adjacent hydroxyls. Heating the sample to $150\text{ }^{\circ}\text{C}$ breaks the hydrogen bond between Al and the hydroxyls and exposes surface Al as active Lewis acid sites.

The hydrogen bonded pyridine desorbs between 150 and $200\text{ }^{\circ}\text{C}$. Pyridine adsorbed on both Brønsted and Lewis acid sites is significantly more stable. There are still strong absorption bands due to pyridine on these latter types of sites that are present even after the Al^{3+} -ZSM-5 and Ca^{2+} -ZSM-5 zeolites are heated to $250\text{ }^{\circ}\text{C}$. In addition, as shown in Fig. 7, as the temperature increases, more pyridine remains bonded to Brønsted acid sites than to Lewis acid sites. This result implies that the Brønsted acid sites form stronger bonds to pyridine than do the Lewis acid sites and thus the Brønsted acid sites are stronger acids. It is worth noting that the respective strength of both Brønsted and Lewis acid sites is virtually identical in all M^{n+} -ZSM-5 (other spectra not shown). Therefore, the modification of ZSM-5 with different cations only affects the number of

acid sites and the ratio of Brønsted to Lewis acid sites, but the strength of the acid sites does not change significantly.

3.3. Influence of cation loading on the number of acid sites in M^{n+} -ZSM-5 zeolites

The acid sites detected in this study are located on the surface of the channels that are *accessible* to the pyridine.[17] Clearly, acid sites that the pyridine cannot access will not be detected. Therefore, the accessibility of the surface of the channels to the pyridine probe molecule is an important factor in the observed variation of the acid sites among the different zeolites studied. The accessibility of the surface of the channels in M^{n+} -ZSM-5 is affected by the size of loaded cations. In addition, as discussed in Section 3.1, the loaded cations have different reactivity with Brønsted acid hydroxyls resulting in a variation in the number of acid sites. In the following text, the effect of different cations on the number of acid sites in M^{n+} -ZSM-5 will be discussed in terms of the accessibility of the surface of the channels and the possible reactions of the loaded cations with Brønsted acid hydroxyls.

Our reference point for the discussion of the change in the number of acid sites is NH_4^+ -ZSM-5. As shown in Fig. 6(a), the number of Brønsted acid sites in NH_4^+ -ZSM-5 is $\sim 70 \mu\text{mol g}^{-1}$. When NH_4^+ ions on the surface of the channels are substituted by H^+ ions, the number of Brønsted acid sites increases to $\sim 130 \mu\text{mol g}^{-1}$, which is due to the recovery of Brønsted acid sites on the surface of the channels. This is expected since H^+ ions now occupy the sites that were occupied by NH_4^+ ions in the NH_4^+ -ZSM-5 resulting in these sites becoming Brønsted acid sites.[47] The number of Lewis acid sites also increases, from 90 to $110 \mu\text{mol g}^{-1}$. When the larger radius NH_4^+ ($r = 1.4 \text{ \AA}$) ions on the surface of the ZSM-5 channels are replaced by a smaller radius H^+ ions, more aluminum Al_{Td} on the surface of channels are exposed, yielding additional accessible Lewis acid sites. Data in Fig. 6(a) demonstrates that substitution of NH_4^+ ions by Al^{3+} ions does not lead to an increase in the number of the Brønsted acid sites in the framework of ZSM-5. The number of Brønsted acid sites in Al^{3+} -ZSM-5 and NH_4^+ -ZSM-5 are both $\sim 80 \mu\text{mol g}^{-1}$. However, Al^{3+} ions loaded on the surface of the channels yield more extra-framework Lewis acid sites. Additionally, the smaller size of the Al^{3+} ions ($r = 0.7 \text{ \AA}$) compared to the NH_4^+ ions favors exposure of additional accessible Lewis acid sites on the surface of

the channels. These two factors acting together lead to an increase in the number of accessible Lewis acid sites for the Al^{3+} -ZSM from 100 to 130 $\mu\text{mol g}^{-1}$.

There is a significant change in the number of acid sites that results from loading basic Ca^{2+} and Ba^{2+} ions versus the ammonium starting material. As is shown in Fig. 6, there is a loss of both Brønsted and Lewis acid sites in Ca^{2+} -ZSM-5 and Ba^{2+} -ZSM-5 compared to NH_4^+ -ZSM-5. Scheme 2 depicts the fact that the loss of Brønsted acid sites originates mainly from reactions between Ca^{2+} and Ba^{2+} ions with Brønsted acid site hydroxyls.[27] This is supported by the disappearance of the absorption band at 3610 cm^{-1} , which is assigned to these sites, upon substitution of Ca^{2+} and Ba^{2+} ions for NH_4^+ ions. The decrease in Lewis acid sites arises mainly as a consequence of the steric effect of these ions. In the Cs^+ -exchanged zeolite β , it is reported that Cs^+ ions are located on the surface of the channels of the zeolite β and that before Cs^+ substitution these positions are accessible to pyridine.[39] However, it is logical that the Cs^+ ions cause a constriction in the diameter of the channels leading to decreased accessibility of these sites to the probe molecules such as pyridine, and thus there is a decrease in both accessible Brønsted and Lewis acid sites measured by pyridine adsorption.[17] Since the Ba^{2+} and Cs^+ ions have comparable ionic radii, 1.5 versus 1.7 Å,[64] the Ba^{2+} ions on the surface of the channel are also expected to lead to a constriction of the channels in Ba^{2+} -ZSM-5. Alternatively, the accessibility of the surface of the channels to probe molecules can be described by the effective radius of the open portion of the channel (micropore).[35] The exchanged cations such as Ca^{2+} and Ba^{2+} narrow the effective radius of the micropores by sticking out from the channels of ZSM-5 leading to a significant decrease in the effective channel radius and thus the accessibility of the channels to the pyridine probe molecule. However, another factor could contribute to the change in the number of accessible sites for Ba^{2+} and Ca^{2+} loaded zeolites. When the basic Ba^{2+} and Ca^{2+} ions react with Brønsted acid hydroxyls, we believe it is plausible that a weakly bonded framework is formed in the channel leading to a larger effective ionic radius which results in greater steric hindrance and therefore makes the surface of the channels even less accessible to probe molecules. This effect would contribute to the observed decrease in the number of accessible Lewis acid sites. The significant decrease in the number of acid sites is verified by the data in Fig. 6(a), where the number of both Brønsted and Lewis acid sites decreases from 70 and

100 $\mu\text{mol g}^{-1}$ to 30 and 40 $\mu\text{mol g}^{-1}$ respectively. The steric effect of Ca^{2+} ions is not as large as for Ba^{2+} ions, consistent with its smaller radius of 1.1 Å.

3.4. Implications

Zeolites have been widely used as acid catalysts for hydrocarbons for over 50 years.[2, 25] Due to the importance of their acid sites in many catalytic reactions, strategies have been developed for the direct synthesis of zeolite frameworks with specific number of Brønsted and Lewis acid sites. However, most of these direct synthetic methods are relatively complex. The present work demonstrates that loading acidic or basic cations through ion-exchange not only changes the number of total acid sites on zeolites but also alters the ratio of Brønsted to Lewis acid sites. In the “acid” catalyzed reactions, controlling the ratio of Brønsted to Lewis acid sites can be of great importance for a given reaction in order to obtain higher conversion and selectivity. For example, a higher ratio of Brønsted to Lewis acid sites on HY zeolites is desirable for the efficient aqueous phase dehydration of carbohydrates to furfural;[3] a high ratio of Lewis to Brønsted acid sites on zeolite Y favors the isomerization of glucose to fructose.[10]

We also note that the loaded cations could potentially increase interactions between reactive molecules and the zeolite support enhancing their reactive behavior.[39, 65-72] For example, Kuwahara et al. designed a new class of heterogeneous catalytic systems utilizing this effect: cation– π interactions (π from potential reactive molecules) in microporous titanosilicate molecular sieves for cyclohexene epoxidation.[39] Possibly the heavier alkali metal cations (K^+ , Rb^+ , and Cs^+) have an increased interaction with the cyclohexene molecules as a result of a weak cation– π interaction, which results in an enhancement of their catalytic activity and selectivity for epoxidation.

4. Conclusion

The acid sites on the surface of M^{n+} -ZSM-5 modified by exchange with H^+ , Al^{3+} , Ca^{2+} and Ba^{2+} ions have been systematically investigated using X-ray diffraction, ^{27}Al MAS NMR, and *in-situ* FTIR spectroscopy. The XRD and ^{27}Al MAS NMR results demonstrate the stability of the ZSM-5 structure after the ion-exchange procedure. *In-situ* FTIR spectroscopy, with pyridine as a probe molecule, was used to determine the type, number, and strength of the acid sites. The number of acid sites in M^{n+} -ZSM-5 varies in the order Ba^{2+} -ZSM-5 < Ca^{2+} -ZSM-5 < NH_4^+ -ZSM-5 < Al^{3+} -ZSM-5 < H^+ -ZSM-5, which parallels the acidity of the loaded cations: Ba^{2+} < Ca^{2+} < NH_4^+ < Al^{3+} < H^+ . Pyridine desorption data demonstrate that the majority of the pyridine remains bound to both Brønsted and Lewis acid sites even after heating to 250 °C and that the strength of acid sites in all M^{n+} -ZSM-5 zeolites is virtually identical. The change in the number of acid sites of M^{n+} -ZSM-5 is discussed in terms of the accessibility of the surface of the channels and the reactivity of the loaded cations with Brønsted acid hydroxyls. Loading small acidic cations, such as H^+ ions, leads to the recovery of Brønsted acid sites. Additionally, the small ionic radius of H^+ ions compared to the large ionic radius of NH_4^+ ions make the surface of the channels more accessible and results in an increase in number of both Lewis and Brønsted acid sites. Though loading with Al^{3+} ions does not lead to recovery of Brønsted acid sites, the loaded Al^{3+} ions generate more extra-framework Al^{3+} ions, resulting in an increase in the number of Lewis acid sites in ZSM-5. In addition, the Al^{3+} ions, with a small ionic radius, make the surface of the channels in ZSM-5 more accessible than the NH_4^+ reference zeolite. The situation is different for Ca^{2+} -ZSM-5 and Ba^{2+} -ZSM-5. Loading basic Ca^{2+} and Ba^{2+} ions significantly reduces the acidity of ZSM-5. Basic Ca^{2+} and Ba^{2+} ions react with Brønsted acid hydroxyls, leading to the loss of the Brønsted acid sites. These large Ca^{2+} and Ba^{2+} ions lead to a constriction of the zeolite channels and make acid sites less accessible to pyridine (and other small molecules). Additionally, we propose that a weakly bonded framework is formed between Ca^{2+} and Ba^{2+} ions and surface hydroxyls leading to even larger effective radii for Ca^{2+} and Ba^{2+} ions. This decrease in accessibility appears as a loss of acid sites but is really a decrease in the number of Lewis and Brønsted acid sites that are accessible to the pyridine probe molecule.

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Scheme 1. Schematic of Possible Structures of NH_4^+ -ZSM-5

Scheme 2. Schematic of Possible Mechanisms for the Formation of M^{n+} -ZSM-5

Table1. Vibration frequencies of the CC bond in pyridine bound to different sites in M^{n+} -ZSM-5

Absorption bands/ cm^{-1}	Vibration modes	Linkage of pyridine
1640	$\nu_{\text{CC(N)}}$	Brønsted acid sites
1623	$\nu_{\text{CC(N)}}$	Lewis acid sites
1599	$\nu_{\text{CC(N)}}$	Hydrogen-bonded
1547	$\nu_{\text{CC(N)}}$	Brønsted acid sites
1490	$\nu_{\text{CC(N)}}$	Brønsted and Lewis acid sites
1455	$\nu_{\text{CC(N)}}$	Lewis acid sites
1447	$\nu_{\text{CC(N)}}$	Hydrogen-bonded

Fig. 1. X-ray diffraction patterns of M^{n+} -ZSM-5: (a) NH_4^+ -ZSM-5; (b) Al^{3+} -ZSM-5; (c) H^+ -ZSM-5; (d) Ba^{2+} -ZSM-5; (e) Ca^{2+} -ZSM-5.

Fig. 2. ^{27}Al MAS NMR spectra of $\text{M}^{\text{n}+}$ -ZSM-5: (a) NH_4^+ -ZSM-5; (b) Al^{3+} -ZSM-5; (c) H^+ -ZSM-5; (d) Ca^{2+} -ZSM-5; (e) Ba^{2+} -ZSM-5.

Fig. 3. IR spectra of M^{n+} -ZSM-5: (a) NH_4^+ -ZSM-5, (b) Al^{3+} -ZSM-5, (c) H^+ -ZSM-5, (d) Ca^{2+} -ZSM-5; (e) Ba^{2+} -ZSM-5.

Fig. 4. IR spectra of pyridine adsorbed on M^{n+} -ZSM-5 at 110 °C: (a) NH_4^+ -ZSM-5; (b) Al^{3+} -ZSM-5; (c) H^+ -ZSM-5; (d) Ca^{2+} -ZSM-5; (e) Ba^{2+} -ZSM-5.

Fig. 5. IR spectra of pyridine adsorbed on H^+ -ZSM-5 at 110 °C: (a) prepared by calcinations of NH_4^+ -ZSM-5; (b) prepared ion-exchange with aqueous nitric acid.

Fig. 6. Comparison of the total number of Lewis and Brønsted acid sites (a), and ratio of a given type of acid site to the total number of acid sites (b) in M^{n+} -ZSM-5.

Fig. 7. IR spectra after pyridine desorption from M^{n+} -ZSM-5 at different temperatures:
 (a) Al^{3+} -ZSM-5; (b) Ca^{2+} -ZSM-5.

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