Available online at www.sciencedirect.com

Journal of Catalysis 218 (2003) 155–162

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Quantifying the *n*-hexane cracking activity of Fe- and Al-based acid sites in H-ZSM-5

Haiming Liu,[a,1] Guenter H. Kuehl,[a] Istvan Halasz,[b] and David H. Olson[a,*]

[a] *Department of Chemical and Biomolecular Engineering, University of Pennsylvania, 311A Towne Building, 220 S. 33rd St., Philadelphia, PA 19082, USA*
[b] *PQ Corporation Research and Development Center, 280 Cedar Grove Road, Conshohocken, PA 19428, USA*

Received 8 November 2002; revised 11 February 2003; accepted 18 February 2003

Abstract

The relative *n*-hexane cracking activity of Brønsted acid sites in H-[Al]-ZSM-5, H-[Fe]-ZSM-5, and H-[Al,Fe]-ZSM-5 zeolites has been investigated as a function of temperature, Cs-exchange level, and aging. Similar to H-[Al]-ZSM-5, acid sites in H-[Fe]-ZSM-5 are homogeneous. Per Brønsted acid site the reaction rate constant over H-[Fe]-ZSM-5 was found to be 15% of that of H-[Al]-ZSM-5. The acid sites in H-[Fe,Al]-ZSM-5 show inhomogeneity as expected for the coexistence of strong Al-based acid sites and weaker Fe-based acid sites. In Cs-exchanged materials, an equilibrium relationship has been found for the distribution of Cs between the two different Brønsted acid sites. Using equilibrium constants 6.6 and 75, the activity-decreasing effect of replacing protons with Cs^+ ions can be described both for H-[Fe,Al]-ZSM-5 and for mildly steamed H-[Al]-ZSM-5, respectively. FTIR results also indicated preferred Cs poisoning on the more active acidic sites. The peaks representing the stronger and weaker acid sites in H-[Fe,Al]-ZSM-5 are not resolved in either FTIR or temperature-programmed ammonia desorption. The aging of H–Fe sites appears to influence that of H–Al sites in [Fe,Al]-ZSM-5.

Keywords: H-ZSM-5; H-[Al,Fe]-ZSM-5; Ferrosilicate; Brønsted acid sites; Acid strength; Acid site homogeneity; *n*-Hexane cracking activity; Cs poisoning; Cs distribution; Aging

---

1. Introduction

Aluminosilicate zeolites are widely used in the petroleum and petrochemical industry as acidic catalysts [1–4] of which H-[Al]-ZSM-5 having the MFI structure has been an outstanding representative with unique shape selectivity [5].

The concentration of Brønsted acid sites in H-[Al]-ZSM-5 is determined by the content of framework Al, as one hydrogen atom per Al balances the negative charge generated by an Al^{3+} ion substituting for a Si^{4+} ion in the framework. These sites are denoted as Al-Brønsted acid sites or H–Al hereafter. For a large variety of reactions the catalytic activity correlates linearly with the concentration of Brønsted acid sites. For example the rate constant of *n*-hexane cracking was found to be strictly proportional to the number of acid sites [6,7]. In carefully prepared H-[Al]-ZSM-5 all the Al sites have equal activity, and thus equal acid strength. This can be deduced from (1) the linear decline in activity with decreasing aluminum content and (2) the linear decline in activity as protons are replaced by Cs^+ ions via ion exchange [5,8].

The Brønsted acid strength and catalytic activity of H-MFI zeolites isomorphously substituted by trivalent elements have attracted increasing academic and industrial interest [9–15]. The Brønsted acid strength appears to decrease in the order H-[Al], [Ga], [Fe], [B]-ZSM-5 based on the increasing OH-stretching frequency in FTIR of the acidic Si–OH–M groups, decreasing peak temperature in TPAD (temperature-programmed ammonia desorption) [9] and as predicted by a recent density functional study of isomorphous substitution [14]. However, arguments [12] exist that neither the hydroxyl-stretching frequency nor the TPAD peak temperature alone could justify the ranking of relative acid strength. The catalytic activity of H-[B]-ZSM-5 for hexane cracking may be solely due to the small amount of Al impurity [10]. H-[Fe]-ZSM-5, in particular, may be of interest for catalysis requiring high selectivity, in-

---

[*] Corresponding author.
E-mail address: dholson@seas.upenn.edu (D.H. Olson).

[1] Current address: Atofina Chemicals, Inc., 900 First Ave., King of Prussia, PA 19406, USA.

0021-9517/03/$ – see front matter © 2003 Elsevier Inc. All rights reserved.
doi:10.1016/S0021-9517(03)00068-X

cluding olefin oligomerization [16], de-NO_x reactions [17], and benzylation of benzene [15]. The differences between H-[Fe]-ZSM-5 and H-[Al]-ZSM-5 in Si–OH–M-stretching frequency (3630 and 3610 cm^{-1}, respectively) and in TPAD peak temperature (∼ 300 and 360 °C, respectively) have been found to be considerable [9]. H-[Fe]-ZSM-5 appears to have much lower hexane cracking activity than H-[Al]-ZSM-5 since Brønsted acid sites associated with framework Fe, noted as Fe-Brønsted acid sites or H–Fe hereafter, are reported to have no measurable activity, and that the observed low activity in H-[Fe]-ZSM-5 may be due to Al impurities [12]. Rapid aging of the n-hexane cracking activity of H-[Fe]-ZSM-5 also hampered the earlier study [12]. So far there has been a lack of quantification of cracking activity of H-[Fe]-ZSM-5 and examination of its acid strength homogeneity.

In this paper we investigate, employing hexane cracking and Cs-poisoning tests, the relative activity of H-[Al]-ZSM-5, H-[Fe]-ZSM-5, and H-[Al,Fe]-ZSM-5 zeolites and examine their acid site homogeneity. The cracking activity is measured as a function of temperature and Cs-exchange level. The equilibrium distribution of Cs ions at the different types of T-sites is described and quantified and related to their relative cracking activity. The aging during n-hexane cracking is also compared.

2. Experimental methods

2.1. Materials

[Al]-ZSM-5 was prepared according to the method of Argauer and Landolt [18].

[Fe]-ZSM-5 was synthesized as described elsewhere [16], using Cab–O–Sil as the silica source to minimize Al impurity. The product is a white crystalline powder shown by X-ray diffraction to be of the MFI structure type and of high purity. This ferrosilicate contains 85 ppm, i.e., 0.003 mmol/g, of Al impurity measured by elemental analysis.

[Fe,Al]-ZSM-5 was synthesized as follows: 2.50 g $Fe(NO_3)_3 \cdot 9H_2O$ and 2.07 g $Al_2(SO_4)_3 \cdot 18H_2O$ were dissolved in 33.3 g of deionized water, and 5.33 g concentrated H_2SO_4 was added dropwise with stirring. Then the salt solution was mixed with a solution of 8.00 g of tetrapropylammonium bromide dissolved in 13.33 g of deionized water. Next, a solution of 66.66 g sodium silicate (PQ N-Clear) diluted in 66.66 g deionized water was added to the mixture solution with rigorous stirring, forming a gel. Finally the gel was sealed in a 300 ml Parr autoclave equipped with a stirrer and heated to 170 °C for 3 days. The product is a white, high-purity, crystalline powder having the MFI structure as indicated by XRD.

The as-synthesized ferrosilicates were calcined in flowing dry N_2 at 500 °C (heated from 25 to 500 °C at a ramping rate of 3 °C/min) for 8 h, cooled to 300 °C, and then further heated in flowing dry air at 500 °C for 4 h (ramped up from 300 °C at 3 °C/min to minimize the loss of framework Fe). The typical flow rate for N_2 or air is 100 cm^3/min. The calcined zeolites were ammonium-exchanged two times with 1.0 M NH_4Cl solution by stirring at room temperature with the pH of the slurry adjusted to 7.3 by addition of NH_4OH solution. The product was then heated in deionized water at 80–90 °C for 1 h to remove physisorbed ammonia. H-ferrosilicates were obtained by heating NH_4-ferrosilicates at 500 °C for 1 h under flowing N_2. The samples' off-white color indicated that most Fe remained in the framework.

The n-hexane sorption capacities for the three H-ZSM-5 materials, measured at 90 °C and 90 Torr n-hexane partial pressure, are all close to 100 mg/g, which further confirmed their high crystallinity.

In a typical preparation of a Cs-exchanged sample, 2 g of H-[Fe,Al]-ZSM-5 or H-[Fe]-ZSM-5 in 100 ml of water was contacted with a stoichiometric volume of 0.1 M CsOH solution with stirring for 1 h. The product is a partially Cs-exchanged Cs_xH_{1-x}-[Fe,Al]-ZSM-5 or Cs_xH_{1-x}-[Fe]-ZSM-5, where x denotes the Cs-exchange level (in molar fraction).

2.2. Methods

2.2.1. n-Hexane sorption

Adsorption measurements were made using a computer-controlled thermogravimetric balance consisting of a TA51 thermobalance and associated TA-2000/PC control system. The partial pressure of n-hexane was controlled by blending a dry N_2 flow and a flow of N_2 bubbling through n-hexane at ambient temperature and then passing through a condenser at 18 °C. The 1 atm, mixed flow through the electrobalance system was controlled via Macintosh-based LabView control software, Kinetic Systems Interface, mass flow controllers, and Eurotherm temperature controller.

2.2.2. TPAD

A combination of thermogravimetric analysis (TGA) and TPAD, based on a method described by Kerr and Chester [19], was used to determine the temperatures and quantities of ammonia desorption and weight loss in helium flowing at 100 cm^3/min with a heating rate of 10 °C/min. A Metrohm titration system (including a 614 Impulsomat, a 632 pH meter, and a 655 Dosimat) connected to a DuPont 951 TGA was used for this purpose. Heating and data recording (including time, temperature, weight, and titrant volume) are controlled by Macintosh-based LabView software.

Isopropylamine TPD-TGA measurements were performed as described elsewhere [12].

2.2.3. n-C6 cracking test

n-Hexane cracking tests were performed similar to the α test developed at Mobil [6,20]. In a typical test, a H-ZSM-5 sample (pressed and sieved to 14- to 30-mesh particles to improve diffusion) was activated in a tube reactor at 538 °C under dry N_2 and then exposed to a stream of N_2 carrying 10 Torr of n-hexane vapor. The partial pressure of n-hexane was controlled by blending a dry N_2 flow and a flow of N_2 bubbling through n-hexane in an ice bath with each flow rate set by a mass flow controller. The stream exiting the reactor was automatically sampled every 5 min by a GC, with a J & W Scientific DB-1 capillary column isothermal at 80 °C. Suitable sample amount and flow rate ($\sim$ 100 cm^3/min) were chosen so that the conversion was about 10% or less. Cracking activity was evaluated by determining the first-order rate constant of the reaction, k (s^{-1}),

$$k = f \times \ln(1-\varepsilon) \times \frac{d}{(m \times 60)}, \qquad (1)$$

where f is the flow rate (cm^3/min), ε is the conversion fraction, and d and m are the bulk density (0.55 g/cm^3) and the mass of catalyst particles, respectively [6,7].

For tests on Fe-containing ZSM-5, the n-hexane/N_2 flow was manually turned on shortly before each sampling and turned off immediately afterward so as to avoid unwanted aging during a GC run. Our experimental setup allows rapid data collection with intervals as short as 30 s and thus enabling the measurement of 30 s on stream time activities and also the recording of the aging process.

2.2.4. FTIR

Catalysts were tested in the mid-infrared range (MIR), using a Nicolet Magna 550 spectrometer equipped with a vacuum transmission (T) cell from CIC Photonics. Self-supporting sample wafers were fabricated and placed into a sample holder inside the water-cooled T cell. The sample holder has CaF_2 windows and is attached to an oil-free high vacuum pump working at $\sim 10^{-6}$ Pa. The samples were dehydrated at 400 °C under vacuum and IR measurements were done at room temperature. Further details are described elsewhere [21].

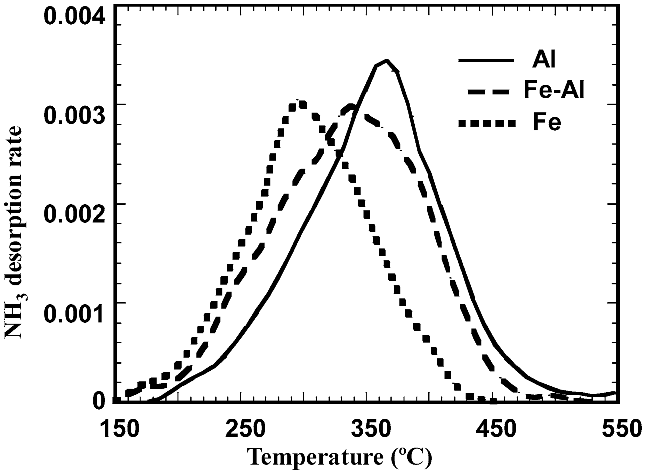

Fig. 1. The TPAD derivative plots of NH_3 desorption rate versus temperature for H-[Al]-, H-[Fe]-, and H-[Fe,Al]-ZSM-5.

3. Results and discussion

3.1. TPAD measurements

The typical TPAD curves, the derivative plots of NH_3 desorption rate as a function of temperature, for the three MFI zeolites are shown in Fig. 1. The desorption of NH_3 occurred at temperatures between 200 and 500 °C, which is characteristic for chemisorbed NH_3. The lack of any significant peak between 100 and 200 °C indicates that the samples are free of physisorbed NH_3. Therefore, the total amounts of desorbed NH_3 can be assigned to H–Al and H–Fe Brønsted acid sites. The concentrations of framework Al, Fe, and Fe plus Al-based acid sites are 0.45, 0.35, and 0.48 mmol/g for H-[Al], H-[Fe], and H-[Fe,Al]-ZSM-5, respectively (Table 1).

The peak temperature of a TPAD curve is qualitatively indicative of the acid strength. The values of 360 and 304 °C for H-[Al]- and H-[Fe]-ZSM-5, respectively, agree with earlier published data [9]. H-[Fe,Al]-ZSM-5 showed a broad

Table 1
Summary of the three H-ZSM-5 samples

	H-[Al]-ZSM-5 White	H-[Fe]-ZSM-5 Off white	H-[Fe,Al]-ZSM-5 Off white
n-Hexane sorption (mg/g)	104	95	102
Acid content (mmol/g)[a]	0.45[a] (0.43)[b]	0.35[a] (0.33)[b] ⟨0.003⟩[c]	0.48[a] (0.46)[b]
TPAD peak temperature (°C)	360	304	337
TPAD peakwidth (°C)	119	117	147
Si–OH–M-stretching frequency (cm^{-1})	3609	3630	3613
Si–OH–M bandwidth (cm^{-1})	30	30	40
k (s^{-1})	3.1	0.39 ⟨0.02⟩[d]	1.9
k^0 (g/(mmol s)) 538 °C	6.9	1.0[e]	4.0
Ea (kJ/mol)	121	108	110

[a] From TPAD measurements.
[b] From isopropylamine TPD TGA measurements.
[c] Al impurity level.
[d] The calculated cracking activity due to Al impurity.
[e] The contribution from Al impurity is excluded.

single peak at ~ 337 °C and spans the desorption range of the other two materials. This is consistent with coexistence of Al- and Fe-Brønsted acid sites that are unresolved by TPAD. Hence observation of one TPAD peak is not sufficient to assess the homogeneity of acid sites.

Sample preparations were carried out carefully so as to minimize formation of Lewis acid sites. Isopropylamine TPD-TGA, a technique developed by Gorte and co-workers [12], was employed to determine Brønsted acid site content via monitoring the decomposition of isopropylamine, adsorbed on Brønsted acid sites, into propene and ammonia. Values for the three H-form zeolites are very close to those from TPAD (Table 1).

3.2. *Cracking activity*

The hexane cracking activities of the three H-ZSM-5 materials at 538 °C are listed in Table 1. The k (first-order rate constant, s^{-1}) is related to the unit weight of catalyst and k^0 (normalized rate constant, g/(mmol s)) is the activity per Brønsted acid site obtained by normalizing k by the Brønsted acid site content. At 538 °C, the H–Fe cracking activity per site, k^0_{Fe} (1.0 g/(mmol s)) of H-[Fe]-ZSM-5, after excluding the contribution from Al impurity (~ 3 µmol/g), is 15% of the H–Al site activity, k^0_{Al} (6.9 g/(mmol s)). At 427 °C, k^0_{Fe} was found to be ~ 20% of k^0_{Al}. The hexane cracking activity of H–Al measured at 538 °C is consistent with that reported earlier [8]. However, the activity of H–Fe is significantly higher than previously published [12]. In that study, the activity of H-[Fe]-ZSM-5 at 427 °C, reported as turnover frequency (i.e., molecules reacted per Brønsted acid site per second), was merely 4% that of H-[Al]-ZSM-5 and was attributed to the 10 µmol/g Al impurity. These authors could not accurately determine the activity of H-[Fe]-ZSM-5 at 477 °C due to rapid aging. In this study the cracking activity of H-[Fe]-ZSM-5 was measured over a wide temperature range, as a function of Cs poisoning (addressed later), and furthermore as a function of aging time (addressed later), in an attempt to better quantify the cracking activity of H–Fe.

The activity of H-[Fe,Al]-ZSM-5 per Brønsted acid site, $k^0_{\mathrm{FeAl}} = 4.0$ g/(mmol s), is equal exactly to the average of k^0_{Fe} and k^0_{Al}. This agrees excellently with the 1:1 ratio of H–Fe and H–Al in this catalyst, assuming that the H–Fe and H–Al sites in H-[Fe,Al]-ZSM-5 have the same activity as the corresponding sites in H-[Fe]- and H-[Al]-ZSM-5, respectively.

3.3. *Activation energy*

Hexane cracking rate constants were measured over the temperature range 423–538 °C. For H-[Al]-ZSM-5 the rate constants at various temperatures were measured on one sample and were reproducible since there was no detectable aging, whereas for H-[Fe]- and H-[Fe,Al]-ZSM-5 each temperature point (rate constant) was measured on a fresh, activated sample to minimize aging effects. Aging is discussed in detail later. From Arrhenius plots, shown in Fig. 2, activation energies of 121, 108, and 110 kJ/mol were extracted for H-[Al]-, H-[Fe]-, and H-[Fe,Al]-ZSM-5, respectively. The activation energy for H-[Al]-ZSM-5 (~ 121 kJ/mol) is close to that previously measured for H-[Al]-ZSM-5 (~ 125 kJ/mol) [5], while those for H-[Fe] and H-[Fe,Al]-ZSM-5 are slightly lower. The obtained activation energies are essentially equal within the experimental error, although a higher activation energy might be expected for the weaker acid, H-[Fe]-ZSM-5. Note that a reduced activation energy for H-[Fe]-ZSM-5 may result from (i) a difference in heat of n-hexane adsorption and (ii) a larger reduction in the rate constants measured at higher temperatures due to faster aging. The true activation energies might reflect the differences in acid strength between H-[Al]- and H-[Fe]-ZSM-5. Such an issue would need further investigation and is beyond the scope of this study.

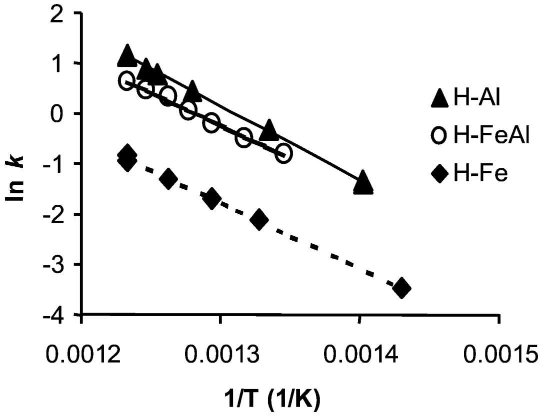

Fig. 2. The Arrhenius plots for H-[Al]-, H-[Fe]-, and H-[Fe,Al]-ZSM-5.

3.4. *Experiments with Cs-exchanged samples*

The measured Cs content of partially Cs-exchanged H-[Fe,Al]-ZSM-5 samples is shown in Fig. 3 as a plot ver-

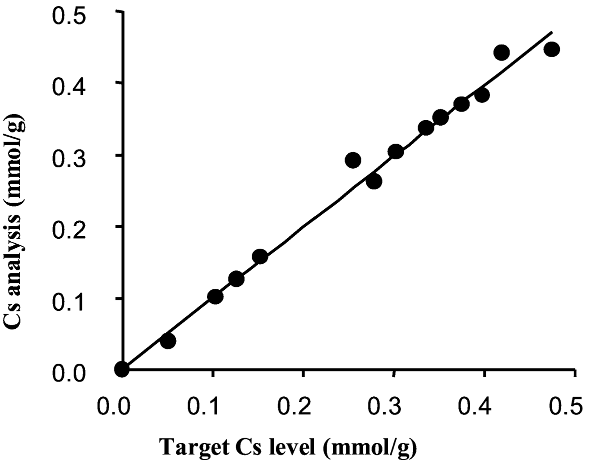

Fig. 3. Correlation of the measured and target Cs-exchange levels for a series of Cs_xH_{1-x}-[Fe,Al]-ZSM-5 materials.

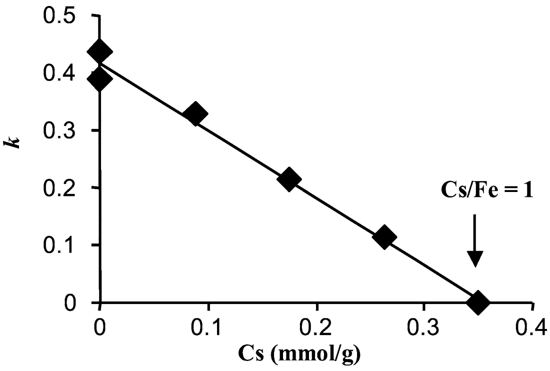

Fig. 4. The effect of Cs-exchange level on the n-hexane cracking activity of H-[Fe]-ZSM-5 at 538 °C.

sus the targeted Cs-exchange level. The excellent agreement between the measurements and the targets (slope = 0.99) confirmed the success of the quantitative exchange. Similar results were obtained for partially Cs-exchanged H-[Fe]-ZSM-5.

The hexane cracking activity of H-[Fe]-ZSM-5 at 538 °C, as a function of Cs-exchange level, noted as k-Cs plot hereafter, is displayed in Fig. 4. As anticipated, the linear decline in k occurs as H–Fe sites are progressively replaced (poisoned) by nonacidic Cs–Fe sites, similar to the case of H-[Al]-ZSM-5 [5]. Hence, these data indicate that the Brønsted acid sites in H-[Fe]-ZSM-5 are homogeneous, as they are in carefully prepared H-[Al]-ZSM-5.

In contrast to H-[Fe]- and H-[Al]-ZSM-5, the Cs-poisoning test at 538 °C on H-[Fe,Al]-ZSM-5 revealed a nonlinear decline in cracking activity with progressive Cs poisoning, as shown in Fig. 5. This resembles the findings of Mobil researchers for mildly steamed H-[Al]-ZSM-5 [5,8], and indicates that the Brønsted acid sites in H-[Fe,Al]-ZSM-5 are not homogeneous. In the case of mildly steamed H-[Al]-ZSM-5, a small amount (4%) of very strong, highly active acid sites (75 times compared to normal acid sites) was present that was selectively poisoned by addition of a small amount of Cs ions. Consequently a dramatic decrease in cracking activity occurs as the k-Cs plot in Fig. 6 demonstrates (adapted from Ref. [8]). In H-[Fe,Al]-ZSM-5, the coexistence of strong H–Al and weaker H–Fe sites gives rise to inhomogeneity.

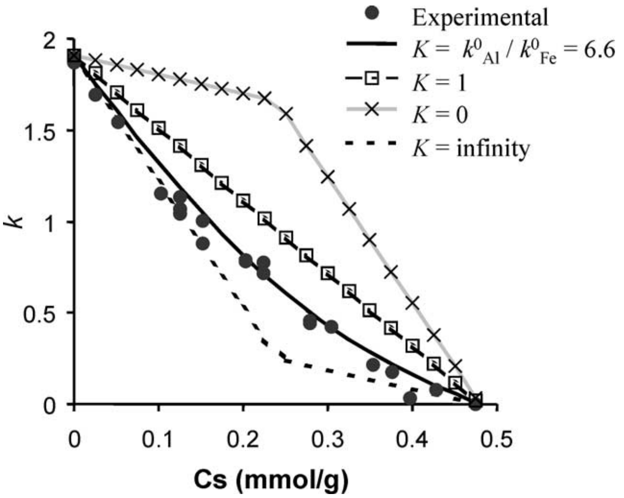

Fig. 5. The effect of Cs exchange on the n-hexane cracking activity of H-[Fe,Al]-ZSM-5: the experimental data (●), and the calculated k-Cs curves based on the proposed equilibrium (Eq. (3)) using equilibrium constant 6.6 (solid line), 0 (shaded line), 1 (dashed line), and ∞ (dotted line).

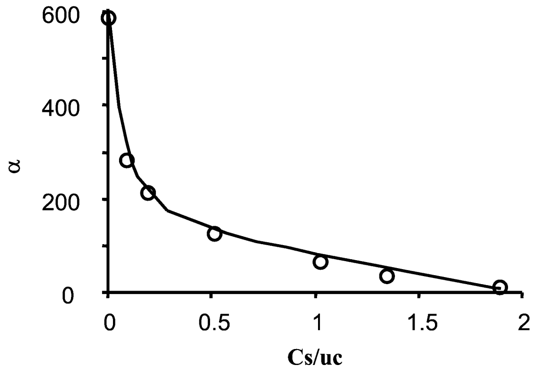

Fig. 6. The Cs-poisoning test on steamed H-[Al]-ZSM-5: the experimental data (circles) adapted from Refs. [5,8] and the calculated k-Cs curve (solid line) using an equilibrium constant of 75. k_e and k_n are the activity of an enhanced and a normal acid sites, respectively. Here the cracking activity is reported as the so-called α value, the rate constant relative to that of a standard SiO_2/Al_2O_3 cracking catalyst with $k = 0.016\ s^{-1}$.

We further examined the k-Cs plot of H-[Fe,Al]-ZSM-5 in effort to understand the nonlinearity. With the assumption that Cs poisoning does not affect the cracking activity per site of the remaining Brønsted acid sites, the calculated bulk activity, k^c, follows the expression,

$$k^c = [\text{H–Al}] \times k^0_{\text{Al}} + [\text{H–Fe}] \times k^0_{\text{Fe}}, \tag{2}$$

where [H–Fe] and [H–Al] are the concentrations of the corresponding Brønsted acid sites. In the first extreme case, if Cs ions poison H–Al and H–Fe sites nonselectively, a simple linear k-Cs curve whose slope equals $(k^0_{\text{Al}} + k^0_{\text{Fe}})/2$ would occur, as shown by the dashed straight line in Fig. 5. In a second extreme case, when Cs ions selectively poison H–Al first and do not poison H–Fe until after the exhaustion of H–Al, a k-Cs curve composed of two lines (dotted lines, Fig. 5) whose slopes are k^0_{Al} and k^0_{Fe}, respectively, would occur. In the third extreme case that is opposite to second, if Cs is totally selective for H–Fe, two lines in reverse order compared to the second case would form the shaded line k-Cs curve. None of those fit the experimental data points. Hence, an intermediate case must be considered where Cs^+ ions poison H–Fe and H–Al sites based on an equilibrium that involves two types of Cs sites, Cs–Fe and Cs–Al, and two corresponding types of Brønsted acid sites, H–Fe and H–Al:

$$\text{Cs–Fe} + \text{H–Al} \leftrightarrow \text{Cs–Al} + \text{H–Fe}. \tag{3}$$

The equilibrium constant, K, can then be defined as

$$K = [\text{Cs–Al}][\text{H–Fe}] \big/ [\text{Cs–Fe}][\text{H–Al}], \tag{4}$$

where [Cs–Al] and [Cs–Fe] are the concentrations of the corresponding Cs sites. The concentrations are correlated to each other as follows,

$$[\text{Cs–Al}] + [\text{Cs–Fe}] = [\text{Cs}], \tag{5}$$

$$[\text{Cs–Al}] + [\text{H–Al}] = [\text{H–Al}]_0, \tag{6}$$

$$[\text{Cs–Fe}] + [\text{H–Fe}] = [\text{H–Fe}]_0, \tag{7}$$

where [Cs] is the total Cs content, and $[\text{H–Al}]_0$ and $[\text{H–Fe}]_0$ are the known original concentrations of the corresponding acid sites. For a given Cs-poisoned sample, if K is known, the four unknown concentrations in Eq. (4) can be mathematically determined by combining Eqs. (4)–(7), and then the cracking activity can be calculated using Eq. (2).

This equilibrium includes the above-noted three extreme cases: if $K = 1$, Cs poisoning is nonselective; if $K = \infty$ or 0, Cs poisoning is totally selective for H–Al or H–Fe, respectively.

In the real H-[Fe,Al]-ZSM-5 system, however, $K > 1$, i.e., Cs poisoning favoring H–Al over H–Fe, agrees with the observed results. We found that when $K = k^0_{\text{Al}}/k^0_{\text{Fe}} = 6.6$, the calculated k-Cs plot (solid curve, Fig. 5) matched the experimental data points very well. This equilibrium constant is based on the relative cracking activity per Brønsted site and hence must also be related to the relative acid strength of these sites, and perhaps their ionic/covalent character. Such a relationship, involving the equilibrium constant, the relative acid strength, and the cracking activity, is in accord with chemical expectations.

To further test the validity of this model of equilibrated Cs poisoning based on the relative cracking activity, we took the same approach to simulate the k-Cs plot reported on mildly steamed H-[Al]-ZSM-5 (Fig. 6) [8]. This steamed catalyst contained ~ 2.0 acid sites per unit cell (i.e., 0.35 mmol/g) 4% of which has an enhanced activity 75 times that of a normal acid site. Again by using an equilibrium constant equal to the relative activity, i.e., 75, the calculated curve (solid line) fits well the experimental data points (circles) in Fig. 6, reproducing the dramatic nonlinear decline of cracking activity with progressive Cs exchange. This strongly supports our model and confirms that the distribution of Cs and H ions between two different types of Brønsted acid sites is governed by an equilibrium where the equilibrium constant is equal to the ratio of the two cracking rate constants.

3.5. FTIR measurements

IR spectroscopy was employed to characterize the Brønsted acid sites in H-[Al]-, H-[Fe]-, and H-[Fe,Al]-ZSM-5 as well as $\text{Cs}_{0.55}\text{H}_{0.45}$-[Fe,Al]-ZSM-5, a 55% Cs-exchanged H-[Fe,Al]-ZSM-5. Spectra are displayed in Fig. 7. The Si–OH–Al and Si–OH–Fe bands of H-[Al]- and H-[Fe]-ZSM-5 are at 3609 and 3630 cm^{-1}, respectively, consistent with reported values [9]. For H-[Fe,Al]-ZSM-5, the Si–OH–M band appears as a single peak at 3613 cm^{-1}, between those of H–Al and H–Fe, and is clearly broader than the latter two. This band is referred to as Si–OH–FeAl hereafter. The relative positions and linewidths of the IR bands of the three materials resemble those of the TPAD peaks. Hence, a similar conclusion can be drawn: The IR spectra are consistent with coexistence of Al- and Fe-Brønsted acid sites in H-[Fe,Al]-ZSM-5 that are unresolved by IR.

In the spectrum of $\text{Cs}_{0.55}\text{H}_{0.45}$-[Fe,Al]-ZSM-5, the Si–OH–M band shows up as a single peak at 3624 cm^{-1}. As the result of Cs exchange, this band shifted in position from the Si–OH–FeAl band toward Si–OH–Fe and is as broad as Si–OH–FeAl. That agrees qualitatively with our model of equilibrated Cs poisoning: At 55% Cs-exchange level, the remaining Brønsted acid sites consist of approximately $\frac{1}{4}$H–Al and $\frac{3}{4}$H–Fe, which give rise to an IR band close in position to Si–OH–Fe and similar in linewidth to Si–OH–FeAl. The IR spectroscopy in combination with Cs-poisoning method can thus be used to probe the acid homogeneity of H-ZSM-5. Work is underway to establish the quantitative correlation between the Cs-exchange level and the frequency peakwidth of Si–OH–M band.

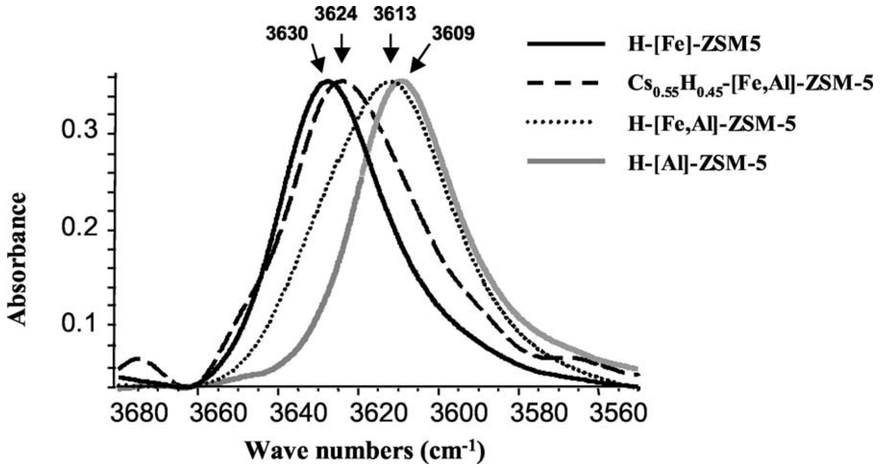

Fig. 7. The OH stretching bands in the FTIR spectra of H-[Al]-, H-[Fe]-, H-[Fe,Al]-, and $\text{Cs}_{0.55}\text{H}_{0.45}$-[Fe,Al]-ZSM-5. Peaks are maximized to aid visualization of their relative positions and should not be compared quantitatively.

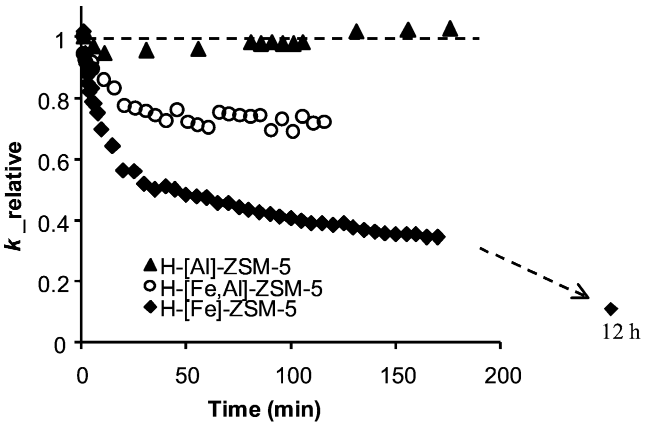

Fig. 8. The relative cracking activities of H-[Al]-, H-[Fe]-, and H-[Fe,Al]-ZSM-5 as a function of aging time during n-hexane cracking at 538 °C.

3.6. *Aging*

To examine the aging effect at 538 °C, we monitored the cracking on each of the three catalysts continuously with time intervals as short as 30 s. Fig. 8 shows the relative cracking activities (normalized to the corresponding initial activity) of H-[Al]-, H-[Fe]-, and H-[Fe,Al]-ZSM-5 as a function of aging time. Clearly, H-[Al]-ZSM-5 showed no sign of aging over the experimental period, while H-[Fe]-ZSM-5 aged rapidly, consistent with a previous report [12]. H-[Fe,Al]-ZSM-5 aged at a slower rate than H-[Fe]-ZSM-5, as expected. H-[Fe]-ZSM-5 apparently aged via two steps: a very rapid step in the first 30 min during which it lost half of its activity and a following slow step in which it continuously and steadily aged. After 12 h the activity dropped to 10% of its zero time activity. It seems that given longer aging time H-[Fe]-ZSM-5 would completely lose cracking activity. H-[Fe,Al]-ZSM-5, on the other hand, aged relatively quickly in the first 60 min and then maintained an activity level of $\sim$ 70%. The loss of 30% activity in H-[Fe,Al]-ZSM-5 is higher than anticipated, since the H–Fe sites accounts for only 13% of the total activity. Therefore, the aging of H–Fe appears to influence the aging of H–Al in H-[Fe,Al]-ZSM-5.

This work and the earlier Mobil studies [5,8] show that H–Al acid sites age very slowly during cracking reactions. If most of the activity of H-[Fe]-ZSM-5 were due to H–Al sites present as impurities, as suggested earlier [12], H-[Fe]-ZSM-5 would not have aged rapidly during cracking. Therefore, the rapid aging also indicates that the cracking activity of H-[Fe]-ZSM-5 arises mostly from H–Fe sites instead of H–Al.

The reason for aging of H–Fe is still unknown. During aging, essentially no change in cracking products (and their relative amounts) was detected by GC, and the cracking products from H-[Fe]-ZSM-5 are essentially the same as those from H-[Al]-ZSM-5. The aging in H-[Fe]-ZSM-5 must be due to blocking of the acid sites by large molecules that are trapped, e.g., in the channel intersections. These molecules appear to deactivate a portion of the Al-based acid sites also. A different distribution of Fe atoms than Al atoms in the T-sites could explain this observation but this point is speculative. The exact reason for aging of the Fe-containing ZSM-5 materials during hexane cracking requires further investigation.

4. Conclusions

In conclusion, H-[Fe]-ZSM-5 has weak but considerable n-hexane cracking activity that should not be ignored in its catalysis applications. The Brønsted acid sites in H-[Fe]-ZSM-5 have homogeneous acidity as do those in carefully prepared H-[Al]-ZSM-5, while [Fe,Al]-ZSM-5, with the copresence of two types of Brønsted acid sites, shows inhomogeneous acidity. The two types of copresent acid sites in H-[Fe,Al]-ZSM-5 are not yet directly distinguished by spectroscopic or temperature-programmed desorption methods. Thus observation of a single acidic feature on a zeolite by a spectroscopic or a desorption technique is not sufficient to conclude its homogeneity. The Cs-poisoning test, combined with n-hexane cracking or IR spectroscopy, seems to be a suitable method to probe the homogeneity of Brønsted acid sites in H-ZSM-5. In a partially Cs-exchanged H-ZSM-5 having acid site inhomogeneity, the distribution of Cs and H between different types of acid sites (in the dehydrated state) is found to be governed by an equilibrium wherein its constant is equal to the relative hexane cracking activities. Such an equilibrium relationship should be applicable to other acidic zeolites and/or other alkali cations. The reasons for rapid aging of H–Fe sites during hexane cracking at high temperature needs further investigation.

Acknowledgments

Mukesh Agarwal from PQ Corporation Research & Development Center is acknowledged for collection of the IR spectra. Oferi Kresnawahjuesa and Prof. Ray Gorte from University of Pennsylvania are acknowledged for providing isopropylamine-TPD TGA measurements. We also gratefully acknowledge Dr. Rudy Lago (Mobil R&D, retired) for informative discussions.

References

[1] D.W. Breck, in: Zeolite Molecular Sieves: Structure, Chemistry and Use, Wiley, New York, 1974, p. 677.
[2] N.Y. Chen, W.E. Garwood, F.G. Dwyer, in: Shape Selective Catalysis in Industrial Applications, Dekker, New York, 1989, p. 303.
[3] I.E. Maxwell, W.H.J. Stork, Stud. Surf. Sci. Catal. 58 (1991) 571.
[4] A. Corma, Chem. Rev. 95 (1995) 559.
[5] W.O. Haag, Stud. Surf. Sci. Catal. 84 (1994) 1375.
[6] D.H. Olson, W.O. Haag, R.M. Lago, J. Catal. 61 (1980) 390.
[7] W.O. Haag, R.M. Dessau, R.M. Lago, Stud. Surf. Sci. Catal. 60 (1991) 255.
[8] R.M. Lago, W.O. Haag, R.J. Mikovsky, D.H. Olson, S.D. Hellring, K.D. Schmitt, G.T. Kerr, in: Proceedings of the 7th International Zeolite Conference, Elsevier, Amsterdam, 1986, p. 677.

[9] C. Chu, C. Chang, J. Phys. Chem. 89 (1985) 1569.
[10] C.T.-W. Chu, G.H. Kuehl, R.M. Lago, C.D. Chang, J. Catal. 93 (1985) 451.
[11] W.E. Farneth, R.J. Gorte, Chem. Rev. 95 (1995) 615.
[12] D.J. Parrillo, C. Lee, R.J. Gorte, D. White, W.E. Farneth, J. Phys. Chem. 99 (1995) 8745.
[13] J. Kotrla, L. Kubelkova, C. Lee, R.J. Gorte, J. Phys. Chem. B 102 (1998) 1437.
[14] S.P. Yuan, J.G. Wang, Y.W. Li, H. Jiao, J. Phys. Chem. A 106 (2002) 8167.
[15] V.R. Choudhary, S.K. Jana, A.S. Mamman, Micropor. Mesopor. Mater. 56 (2002) 65.
[16] O. Kresnawahjuesa, G.H. Kuhl, R.J. Gorte, J. Catal. 210 (2002) 106.
[17] J. Perez-Ramirez, G. Mul, F. Kapteijn, A.R. Overweg, A. Domenech, A. Ribera, I. Arends, J. Catal. 207 (2002) 113.
[18] R.J. Argauer, G.R. Landolt, US Patent 3,702,886, 1972.
[19] G.T. Kerr, A.W. Chester, Thermochim. Acta 3 (1971) 113.
[20] J.N. Miale, N.Y. Chen, P.B. Weisz, J. Catal. 6 (1966) 278.
[21] I. Halasz, M. Agarwal, E. Senderov, B. Marcus, Appl. Catal. A: Gen. 241 (2003) 167.