RESEARCH NOTE

Quantification of Acid Sites in H-ZSM-5, H-β, and H-Y Zeolites

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The effect of sodium poisoning on the activity for *n*-hexane cracking over H-ZSM-5, H-β, and dealuminated H-Y zeolites was compared with spectroscopic changes in the region of the stretching vibration of the surface hydroxyls. For all zeolites, there was a high correlation between the *n*-hexane cracking activity and the intensity of the IR bands assigned to strongly acidic hydroxyl bands. The lethal sodium doses for H-β and H-ZSM-5 indicate that about 80% of the framework aluminum of these zeolites gives rise to catalytically active sites. For the dealuminated H-Y sample, only 15% of the framework aluminum results in catalytically active sites. © 1999 **Academic Press**

The determination of Brønsted acid site density is an important aspect of the characterization of protonated zeolites. Although numerous techniques have been employed for this purpose, determination of the framework aluminum (FAL) concentration is a particularly useful approach because it links the acidic property of the zeolite to its structural origin. In the absence of other cations, charge balance requires an equal number of aluminum ions and Brønsted acid sites. However, this method introduces some ambiguity to the interpretation of results based solely on the concentration of the framework aluminum. First, if extraframework aluminum is present, cationic aluminum can partially compensate the charge of the zeolitic lattice and would consequently lead to a systematic overestimate of the proton concentration in the zeolite (1). Second, within the same sample there may be present a variety of Brønsted acid sites with different acid strength and catalytic capabilities. Starting from the framework aluminum concentration, a better understanding of the nature and quantity of acid sites can be achieved by partially ion exchanging the zeolitic material with monovalent cations and monitoring the resulting catalytic and spectroscopic changes (2) The aim of this work was to study the effect of sodium ions on the catalytic and spectroscopic properties of acidic dealuminated Y, β, and ZSM-5 zeolites and to determine the acid site density by the amount of sodium that is needed to completely poison the catalytic activity for *n*-hexane cracking. Finally, the results were used to determine intrinsic catalytic cracking activities

for *n*-hexane over dealuminated H-Y, H-β, and H-ZSM-5, which are reported in a separate publication (3).

H-β (PQ-Corp., VALFOR CP-811Al-25), H-ZSM-5 (PQ-Corp., CBV 5020E) and dealuminated H-Y (Linde, Y-84 C1523732) zeolites were transformed into their ammonium forms by ion exchange, and the framework aluminum concentration was determined via ^{29}Si- and ^{27}Al-NMR and X-ray diffraction (XRD). Details of the experimental procedures are reported elsewhere (3). The framework Si/Al ratios were 16.6, 35.0, and 4.7 for the H-β, H-ZSM-5, and dealuminated H-Y zeolites, respectively. To reintroduce controlled amounts of sodium ions, the zeolites were ion exchanged in an aqueous solution containing appropriate amounts of NaCl at 80°C for 6 h. The sodium contents of the partially poisoned zeolite samples were then determined by atomic absorption spectroscopy (AAS) using the flame technique. *n*-Hexane cracking reactions were carried out in a conventional plug flow reactor consisting of a fused-quartz tube with an internal diameter of 4 mm. The amounts of catalyst were 30–140 mg for H-β, 60–270 mg for H-ZSM-5, and 100–300 mg for dealuminated H-Y. The flow rate was 65 ml/min for all experiments. The initial rate constants for *n*-hexane cracking were determined at 623 K and an *n*-hexane pressure of 5.3 kPa. The initial conversion was obtained by extrapolating the results to zero time on stream. For infrared measurements, a thin self-supporting wafer (10–15 mg/cm^2) of a sample was degassed *in vacuo* in a FT-IR cell by heating the catalyst stepwise to 373, 473, 573, and 673 K for 1 h at each temperature. The sample was subsequently cooled to room temperature and the FT-IR spectrum was recorded, using a Perkin–Elmer Spectrum 2000 spectrometer in the range 3000 to 4000 cm^{-1}. Spectra were collected for 20 scans with a resolution of 4 cm^{-1}. The resulting spectra, obtained in the absorbance mode, were then normalized to a standard density of $\delta = 10$ mg/cm^{-2}. For each individual zeolite sample, an averaged spectrum was obtained from three experiments.

The effect of the sodium poisoning on the catalytic activities of dealuminated H-Y, H-β, and H-ZSM-5 zeolites is shown in Fig. 1. In all cases the cracking activity and, hence, the acidity declined proportionally with increasing
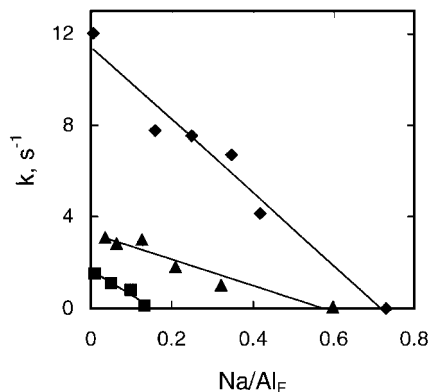
FIG. 1. Effect of sodium addition on the apparent catalytic activity for *n*-hexane cracking at $p_{Hex} = 5.3$ kPa and 623 K over (■) dealuminated H-Y, (◆) H-β, and (▲) H-ZSM-5.

H-ZSM-5, the position of the acidic (Si–OH–Al) hydroxyl groups did not change with increasing amounts of sodium, whereas the acidic (Si–OH–Al) hydroxyl groups of the H-β samples experienced a considerable blue shift. As shown in Fig. 3a, the IR band of the acidic (Si–OH–Al) groups can be decomposed into two bands at 3608 and 3623 cm^{-1}. The former was affected preferentially by sodium poisoning, whereas the latter was affected only after the sodium content reached 50% of the FAL concentration. In contrast to the H-β zeolite, only one band is needed to describe the Brønsted OH stretching mode of the H-ZSM-5 zeolite (Fig. 3b).

The IR spectrum of the dealuminated H-Y sample consists of six bands in the OH stretching region (Fig. 2c). Similar to H-β and H-ZSM-5, the bands at 3745 and 3670 cm^{-1} are associated with silanol groups and extraframework
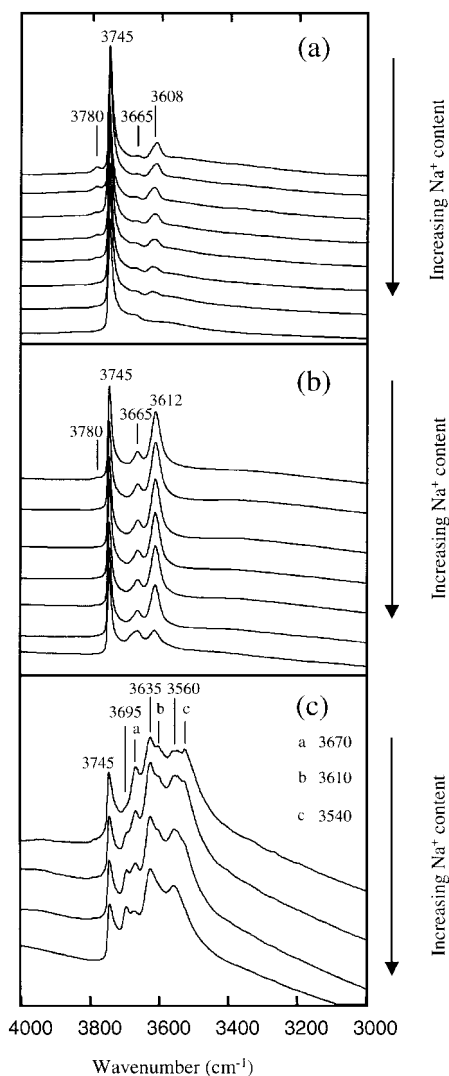
sodium content. Although the apparent rate constants for the unpoisoned ZSM-5 and β samples are considerably different, the lethal doses (i.e., amount of sodium required to completely inhibit the activity) of both samples indicate that a similarly large fraction of the framework aluminum gives rise to catalytically active Brønsted sites. On the other hand, an amount of sodium corresponding to less than 20% of the framework aluminum of the dealuminated Y sample was sufficient to cause complete deactivation. This result is consistent with earlier observations (4, 5) and implies that a large percentage of the Brønsted acid sites is not active for *n*-hexane cracking in this material.

The introduction of sodium poisoning also shows a strong effect on the intensities of OH stretching bands of the three zeolite samples. Changes that occurred in the spectral range from 3000 to 4000 cm^{-1} on adding sodium to dealuminated H-Y, H-β, and H-ZSM-5 zeolites are shown in Fig. 2. The OH stretching bands of H-β and H-ZSM-5 reveal similar characteristics. In both cases, four types of OH groups, at about 3610, 3740, 3780, and 3680 cm^{-1}, can be distinguished. These bands are assigned to acidic (Si–OH–Al) hydroxyl groups, silanol groups, and two different kinds of Al–OH groups, respectively (5, 6). Additionally, there is a broad background signal with a maximum at about 3500 cm^{-1}, which is associated with hydrogen-bonded species, such as silanol and acidic (Si–OH–Al) hydroxyl groups (7, 8). The IR bands of silanol and AlOH species remain largely unaffected by sodium poisoning. A small addition of sodium results in the disappearance of the weak band at 3780 cm^{-1} for H-β and H-ZSM-5. The IR band of the acidic (Si–OH–Al) stretching mode at 3610 cm^{-1} shows the most pronounced loss of intensity with increasing sodium content, suggesting that protons of this type of OH group are those replaced primarily by the sodium cations. Despite the similar spectroscopic characteristics for the OH groups of H-β and H-ZSM-5, changes are apparent in the position and shape of the bands associated with Brønsted acid sites. In the case of

FIG. 2. Hydroxyl IR bands of (a) β, (b) ZSM-5, and (c) dealuminated Y with increasing sodium content.

the cause of the catalytic activity of this material. In conclusion, an amount of sodium equal to about 80% of the framework aluminum is sufficient to completely suppress the catalytic activity as well as the hydroxyl stretching bands of the strongly acidic species in the H-β zeolite. For dealuminated H-Y, the lethal dose was found to be about 15% of the framework aluminum, and correspondingly, only a small fraction of the hydroxyl groups was affected (Fig. 2).

Baba *et al.* (11) have recently reviewed the literature on the poisoning of acid sites by NH_4^+, Na^+, and K^+ ions, and they presented evidence in favor of a long-range effect that these cations have on acidic OH groups. According to their results for *n*-hexane cracking over H-ZSM-5, the conversion of *n*-hexane approached zero when the M^+/Al_F ratio was ca. 0.25 and 0.35 for K^+ and Na^+, respectively. The poisoning effect was linear with respect to Na^+ and nonlinear
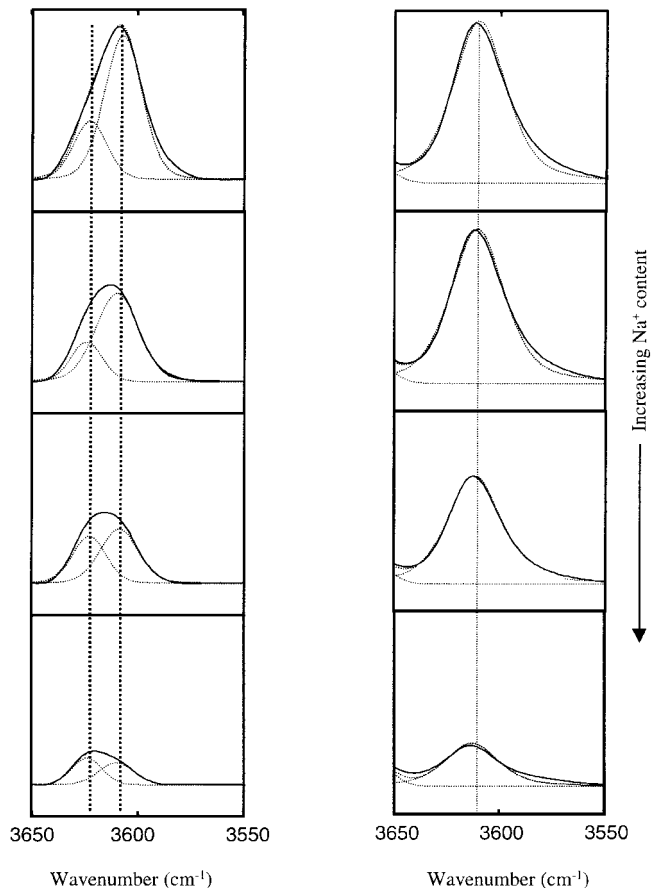
FIG. 3. Deconvolution of the IR band of the acidic (SiOHAl) groups for (a) β and (b) ZSM-5 with increasing sodium content.

Al–OH groups, respectively (9). The bands at 3635 and 3560 cm^{-1} are assigned to the original Brønsted acid site of normal H-Y. The bands at 3610 and 3540 cm^{-1} result from the dealumination of this material and are believed to be associated with strong acidic hydroxyl species (4). As the sodium content increased, the intensities of the bands at 3610 and 3540 cm^{-1} decreased, and a new IR band at 3695 cm^{-1} intensified. This new band was attributed to the interaction of the sodium cation with residual water molecules (4, 10). It is significant that at the maximum level of the Na$^+$ ion exchange used in these experiments, only the pair of bands at 3610 and 3540 cm^{-1} significantly decreased in intensity.

The decline of the most affected OH stretching bands is compared in Fig. 4 with the loss of catalytic cracking activity on sodium poisoning. For the three zeolites, there is a high correlation between the loss of activity and the weakening of these bands for all three zeolites. In case of H-β, one has to distinguish between the OH species absorbing at 3623 and 3608 cm^{-1}. Only the latter is highly correlated with the cracking activity of this material. This suggests that the OH species associated with the IR band at 3608 cm^{-1} is primarily
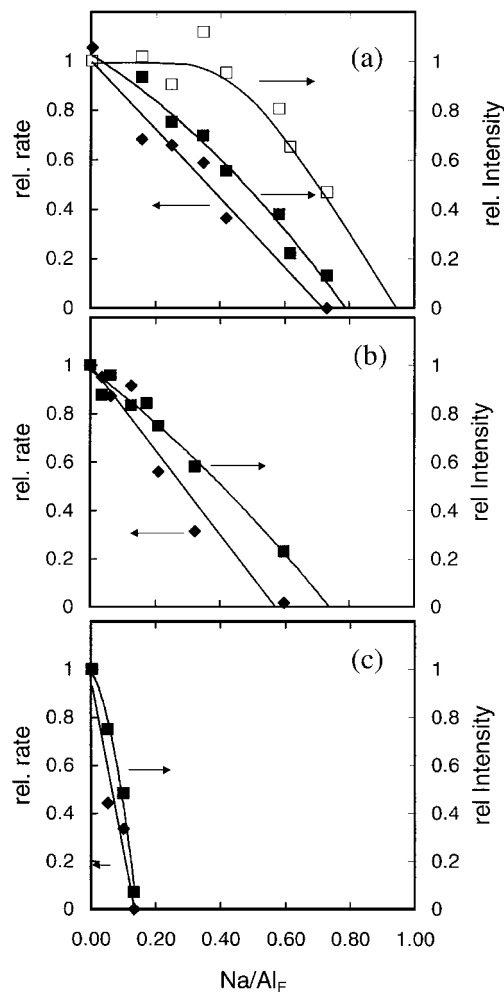
FIG. 4. Comparison of the effect of increasing sodium levels on the (◆) catalytic activity for *n*-hexane cracking at $p_{Hex} = 5.3$ kPa and 623 K over (a) β, (b) ZSM-5, and (c) dealuminated Y and the relative intensity of the IR bands at (■) 3608 cm^{-1} and (□) 3623 cm^{-1} for (a) β, (■) 3610 cm^{-1} for (b) ZSM-5, and (■) 3610 cm^{-1} for (c) dealuminated Y.

TABLE 1

Intrinsic Rate Constants for H-ZSM-5, H-β, and Dealuminated H-Y Zeolites at 623 K and $p_{Hex} = 5.3$ kPa, Based on Either the Total Amount of Framework Al or the Fraction of Framework Al Associated with Strongly Acidic Sites

Catalyst	Active site/FAL	k_{int} (1/s $\times$ 100)	
		Based on FAL	Based on active sites
H-ZSM-5	0.75	111	148
H-β	0.8	51	64
Dealuminated H-Y	0.15	6	40

with respect to K^+. These lethal amounts are substantially less than the value of ca. 0.6 reported here. The origin of the differences in poisoning effects is not clear; however, it should be noted that the results of Baba *et al.* were apparently obtained at larger hydrocarbon pressures, and the conversion data were not extrapolated to zero time on stream. Thus, the zeolite could have been partially poisoned by coke. Beyerlein *et al.* (12) studied the effect of monovalent ions on the activity of dealuminated H-Y zeolites for the cracking of isobutane. They also found that K^+ ions were more effective than Na^+ ions, but, curiously, the poisoning by K^+ ions in their study was comparable to the poisoning by Na^+ ions in our study.

In view of the large lethal Na/Al_F ratios required with H-ZSM-5 and H-β zeolites, as well as the nearly linear relationship with the acidic OH bands (Fig. 4), we believe that the effect of Na^+ ion poisoning is largely a local phenomenon and occurs via ion exchange mainly with the most acidic protons in the zeolite. This is consistent with the conclusion reached earlier by Lunsford and co-workers (4, 13). Gorte and co-workers (14) likewise suggested that alkali ions affect only a single site and that the framework Al content is not a good measure of the absolute site concentration in dealuminated Y.

The intrinsic rate constants of the three catalysts based on the total amount of FAL and the fraction of FAL associated with strongly acidic sites are compared in Table 1. The value of k_{int} was determined after considering the amount of n-hexane in the zeolite (3). The considerably lower active site/FAL ratio for the dealuminated Y zeolite sample leads to an estimate for the intrinsic activity for dealuminated H-Y that is much closer to the intrinsic activity of H-β.

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