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Modifications of H-ZSM-5 Catalysts by NaOH Treatment

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H-ZSM-5 samples were pretreated with dilute NaOH and then transformed into the acid state. The variation of framework Al was studied by ^{27}Al-MAS-NMR spectroscopy, the Al gradient by XPS and the OH groups by IR spectroscopy. The catalytic activity was studied in the conversion of propane and of methanol. The treatment of the parent zeolite (5.2 Al/u.c.) resulted in a slight decrease of the content of framework Al but in a strong enrichment of nonframework Al on the outer surface. The catalytic effect was an increased aromatization of propane and a prolonged lifetime in the methanol conversion. The treatment of a dealuminated sample, containing much nonframework Al, caused a partial reinsertion of Al into the framework. This modification leads to an enhanced aromatization of methanol. Thus treatment with NaOH can control the content of framework Al and the catalytic activity, selectivity, and stability. © 1994 Academic Press, Inc.

INTRODUCTION

H–ZSM-5, a zeolite of the pentasil type, is a well-known catalyst for the conversion of light alkanes and alcohols into the more valuable olefins and aromatics (1, 2). The outstanding activity is due to the strong acid sites, which are bound to the tetrahedral aluminum atoms in the framework (3). Therefore the acidity is directly connected with the content of framework Al and usually direct correlations between activity, acidity, and content of framework Al are observed (4–6). Hence the activity is governed by the content of framework Al. The latter is determined by the conditions of the synthesis. It is often useful or even necessary to vary this content by postsynthetic dealumination or realumination. Dealuminations by thermal or hydrothermal treatments are well-known and widely used. However, under certain conditions of mild hydrothermal treatment, the dealumination does not cause the expected deactivation but even produces an activation (4, 5, 7–9). A postsynthetic realumination is more difficult. Liu and Klinowski (10) observed a reinsertion of Al into the framework of a faujasite zeolite after treatment with a KOH solution. Applying NaOH in a similar way we could partially realuminate H–ZSM-5 and could observe distinct catalytic effects (11). Reschetilowski *et al.* (12) confirmed by NMR investigations that an NaOH treatment can lead to realumination.

In the present paper our continued studies on the structural and catalytic effects of a postsynthetic NaOH treatment are reported. The application of a strongly basic medium on the one hand represents the conditions of the zeolite synthesis, but on the other hand silicates can be dissolved by alkali. Thus controlled de- and realuminations were the aim to achieve a corresponding catalytic modification by a postsynthetic treatment. Therefore two samples with very different content of framework Al were treated; the structures were determined by NMR and IR spectroscopy, and by XPS. The catalytic effects were studied in the conversions of propane and methanol.

EXPERIMENTAL

The parent zeolite (P) with Al/u.c. = 5.2 and a crystallite size of about 7 μm, obtained from Chemie AG, Bitterfeld, was prepared without template. The as-synthesized Na-form was transformed into the acidic state by repeated refluxing with a solution of NH_4NO_3 and subsequent calcination for 2 h at 500°C.

A sample dealuminated by NaOH treatment (P + NaOH) was prepared from the as-synthesized parent sample by refluxing 50 g with 1500 ml NaOH solution (0.08 *M*) for 2 h at 100°C. After this treatment the acidic form was restored by repeated refluxing with a NH_4NO_3 solution and calcination at 500°C. A variation of the concentration of the NaOH between 0.04 and 0.15 *M* had only marginal effects.

A hydrothermally dealuminated sample (P + steam) with Al/u.c. = 0.8 was prepared by steaming the acidic parent sample for 6 h at 500°C (6).

A hydrothermally dealuminated and then NaOH-treated sample (P + steam + NaOH) with Al/u.c. = 1.8 was prepared in the following way. The sample (P + steam), being present in the acidic form, was firstly recationized. The sample (5 g) was refluxed for 1 h in 100 ml of a 0.5 *M* NaCl solution, then 2 ml of a 3.75 *M* NaOH

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solution was added and refluxing was continued for 1 h. Finally the sample was acidified by refluxing with 100 ml of a 0.2 *M* HCl solution for 1 h followed by a stepwise drying and calcination at 120 and 300°C and a calcination for 2 h at 500°C.

The chemical composition of the parent and the modified samples was studied by a conventional chemical analysis. The content of SiO_2 was determined after a dissolution with HF, and the content of Al_2O_3 after a dissolution with borax.

^{27}Al-MAS-NMR spectra were measured at 104.27 MHz on a Bruker MSL 400 spectrometer equipped with a 4-mm high speed MAS probe. The main experimental conditions were as follows: 10 kHz sample rotation frequency, 3600 scans/h and spectrum, single pulse excitation ($\pi/12$ pulse equivalent to 0.61 μs). The chemical shifts were recorded with respect to $[Al(H_2O)_6]^{3+}$ as an external reference ($\delta = 0$). For quantitative analysis of the spectra the samples were equilibrated in a desiccator for 24 h over water. Further for this purpose the spectra shown in Fig. 1 were treated in the absolute intensity mode.

The IR transmission spectra were recorded at room temperature by a grating-type spectrometer Specord M-80 (Carl Zeiss, Jena) using a vacuum cell with silicon windows. For the measurements self-supporting discs (6 mg/cm^2) were pressed and calcined at 427°C at a pressure of less than 10^{-1} Pa. The IR (DRIFT) measurements were performed with an IR reflectance Fourier transform spectrometer IRF-180 (Centre of Scientific Instrumentations, Berlin). A diffuse reflectance device was used for these measurements with a beam which could be focused downwards to a simple sample cup connected with a heater. The sample powders were measured undiluted at about 150°C in order to remove physically adsorbed water. The DRIFT spectra are given as $R' = R(\text{sample})/R(\text{standard})$, where R means reflectance of the sample or of the standard, respectively. KBr powder was used as the reference.

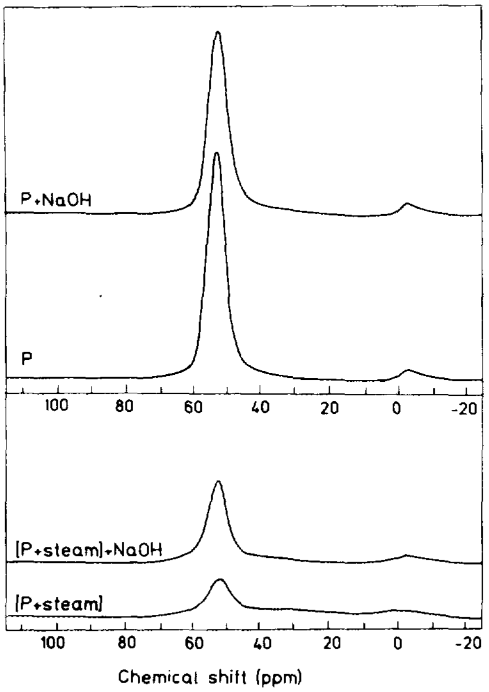

FIG. 1. ^{27}Al-MAS-NMR spectra of the parent sample (P) and the steamed sample (P + steam) before and after NaOH treatment.

The XP spectra were recorded employing an VG Escalab 200X with a hemispherical analyzer operated in the constant retarding ratio mode. Narrow scans were taken with MgKα excitation (20 mA, 15 kV) and a resolution giving an Al 2*p* FWHM of 2.1 eV measured with a NaY zeolite. With this resolution framework Al and nonframework Al cannot be resolved. The spectrometer was calibrated following the method used by Anthony and Seah (13). Photoelectron binding energies are referred to C 1*s* = 285.0 eV. The atomic ratios in the surface layer were calculated from the relative peak intensities by using *T*-corrected values for the photoelectric cross-sections (14–16).

The catalytic tests were carried out at normal pressure with integral reactors and on-line GC with FID. The amount of the zeolite catalyst was 1.00 g (diameter 0.3–0.8 mm). The feed for methanol conversion was a mixture with 90% N_2, and for propane conversion a mixture with 80% N_2. The space velocity for the methanol mixture was 2400 v/vh and for the propane mixture 2000 v/vh. The reaction temperatures were 380°C for methanol and 480°C for propane.

RESULTS

Characterization

The parent sample (P) and the hydrothermally dealuminated sample (P + steam) were treated with dilute NaOH and thereafter transformed into the protonic state. All the samples were characterized by chemical analysis, by NMR, XPS, and IR. Data of the varying Al content are summarized in Table 1. The chemical analysis exhibits a certain variation of the total Al content. The NaOH treatment of the parent sample (P) surprisingly causes a small increase of the total Al content from 5.2 to 5.7 Al/u.c. Simultaneously about 10% of the sample is dissolved. The dissolved proportion contains only 1 wt.% Al. This means that nearly only Si is dissolved and therefore the Al content in the solid is increased, as observed. The steaming of the parent sample has, as expected, no influence on the total Al content. The data show only marginal differences within the experimental error. However, the NaOH treatment of the steamed sample causes some decrease of the total Al content. This corresponds

TABLE 1

Al Content of the Untreated and NaOH-Treated H–ZSM-5

		Average Al content			Proportion of dissolved H–ZSM-5	
Pretreatments	Total Al (Al/u.c.)	Framework Al (Al/u.c.)	Nonframework Al (Al/u.c.)	Surface Al content (Al/u.c.)	Total amount (wt.%)	Al content (wt.%)
parent sample P	5.2	4.9	0.3	2.9	—	—
P + NaOH	5.7	4.0	1.7	6.4	~10	~1
P + steam	5.0	0.8	4.2	—	—	—
P + steam + NaOH	4.6	1.8	2.8	—	~5	~20

with the observed enrichment of Al in the dissolved proportion. The reason could be a selective dissolution of nonframework Al in the diluted HCl, which had been used in the reacidification procedure of this sample. The surface composition of the parent sample was studied by XPS. As can be seen in Table 1 the surface is strongly depleted of Al in comparison with the total Al content. This is a hint that the insertion of Al species is preferred during the initial period of the crystallization process. Remarkably the gradient of the Al distribution is reversed by the NaOH treatment. Now the surface displays a certain enrichment of Al.

The structure of the samples was studied by ^{27}Al-MAS-NMR spectroscopy. The spectra are shown in Fig. 1. The signal at +51 to +53 ppm indicates tetrahedrally coordinated, i.e., framework, Al: the signal at about −2 ppm indicates octrahedrally coordinated, i.e., nonframework, Al. The relative change of the signal intensity for the four-coordinated Al in comparison to sample P was used for the estimation of framework Al in the other investigated samples. The Si/Al ratio and therefore the content of Al/u.c. of the parent sample was estimated from their ^{29}Si mass spectra. The data are displayed in Table 1. It should be mentioned that in the case of dealuminated samples a very broad but low signal in the range between +70 and −15 ppm exists. A similar signal was observed by Klinowski *et al.* (17) with dealuminated Y zeolite. Their assignation to polymeric Al species may be valid in the present case, too. The approximate content of nonframework Al was calculated as the difference between the total Al content and the framework Al content. The treatment of the parent sample (P) with NaOH causes a distinct decrease of the framework content, i.e., the zeolite is dealuminated. The nonframework Al content increases. The NaOH treatment of the dealuminated sample (P + steam) remarkably causes a considerable increase of framework Al content from 0.8 to 1.8 Al/u.c.; i.e., this sample is realuminated. The nonframework Al content decreases. This nonframework Al only partially remains in the zeolite; another part is dissolved.

The de- and the realumination were monitored by the IR spectroscopy of the OH groups. Framework Al causes the formation of bridged OH groups. They have been indicated by absorption bands around 3605 cm^{-1} (18). Bands around 3660 and 3740 cm^{-1} have been assigned to nonframework Al (19) and to silanol groups (18), respectively. Figure 2 shows the spectra of the parent zeolite (1) and of the sample after the NaOH treatment (2). In this case the method of diffuse reflectance was used. The spectra display the bands of all three OH groups. The strongest influence of the NaOH treatment is exerted on the bridged OH group with the band at 3603 cm^{-1}. The intensity considerably decreases. On the other hand, a slight but distinct increase of those bands can be seen, indicating silanol groups (3736 cm^{-1}) and nonframework Al (3657 cm^{-1}). These differences confirm the dealumination process. Al is removed from the framework, perceptible by the diminishing band of the bridged OH groups, and nonframework Al is formed, the corresponding band increases, and more silanol groups are formed. This could be on sites, where Al is removed.

The influence of a NaOH treatment after a strong dealumination was studied using transmission spectroscopy. In this experiment a thermally heated sample (2 h, 800°C)

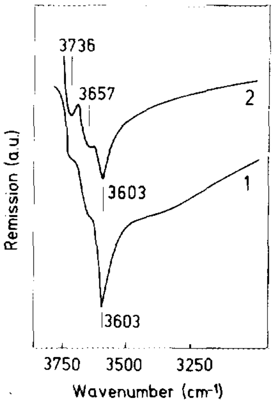

FIG. 2. IR reflectance (remission) spectra of H–ZSM-5: (1) parent sample; (2) after NaOH treatment.

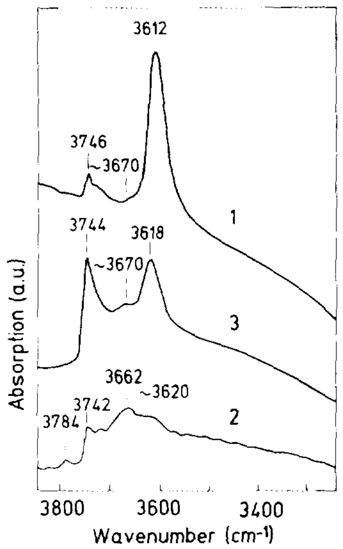

FIG. 3. IR absorption spectra of H-ZSM-5: (1) parent sample; (2) after thermal treatment; (3) NaOH-treated sample (2).

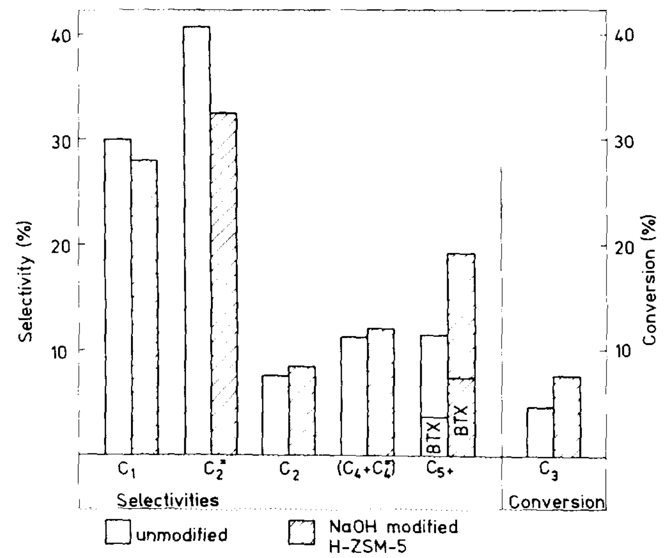

FIG. 4. Propane conversion and selectivity with unmodified (blank) and NaOH-modified (hatched) H-ZSM-5. Reaction temperature 480°C; time on stream 180 min; 2000 v/vh.

was used. Previously it could be shown that thermal treatment as well as hydrothermal steaming causes dealumination (6, 20). This is confirmed by the spectra of the parent sample (1) and the thermally treated sample (2), shown in Fig. 3. The band indicating the framework Al (3612 cm^{-1}) has nearly disappeared, whereas the band at 3670 cm^{-1} increases. This is in accordance with the reflectance spectrum, shown in Fig.2 . Morevoer, a band at 3784 cm^{-1} appears. This has been assigned to OH groups of bulk alumina (21). The effect of the NaOH treatment can be seen in the spectrum (3). Clearly, the band assigned to framework Al (3618 cm^{-1}) is considerably increased. This indicates the reinsertion of Al into the framework and confirms qualitatively the data of Table 1. Moreover, spectrum (3) reveals a slight decrease of the band indicating nonframework Al (3670 cm^{-1}) and a considerable increase of the band indicating silanol groups (3744 cm^{-1}). The latter could be seen in connection with an increase of the void volume, observed by Reschetilowski *et al.* (12).

Catalysis

The activity and the selectivity of the parent zeolite before and after the NaOH treatment were studied in the conversion of propane at 480°C. During a time on stream of 2 h no significant deactivation was observed. The spent samples were grey, not black, indicating only a moderate deposition of coke.

Kinetic data after 60 min on stream are shown in Fig. 4. The modified sample shows an increase of the conversion of about 65%. The selectivity is shifted, too. The cracking to C_1 and C_2 is decreased; the oligomerization and dehydrocyclization to C_{5+} is increased. Especially the aromatization to the C_6–C_8 aromatics (BTX) is increased by about 85%. Additional experiments indicated that a lowered space velocity (1000 v/vh) causes a typical shift in the composition of the C_{5+} products. The content of aromatics increases at the expense of intermediate olefinic and naphthenic products. This confirms the data and the mechanism published by Guisnet *et al.* (22).

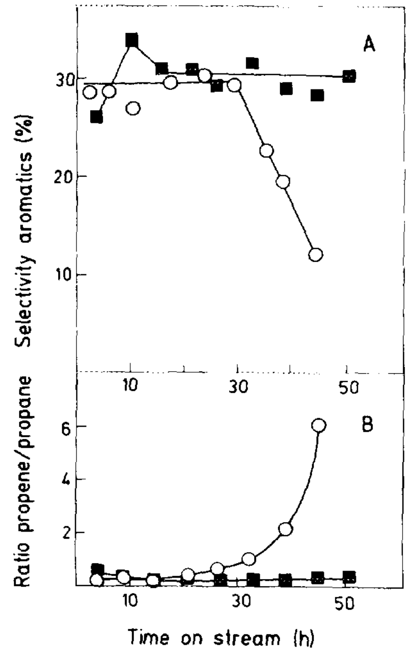

FIG. 5. Conversion of methanol on parent sample (○) and after NaOH treatment (■) as function of time on stream. (A) Selectivity for aromatics; (B) Ratio propene/propane. Reaction temperature 380°C; 2400 v/vh.

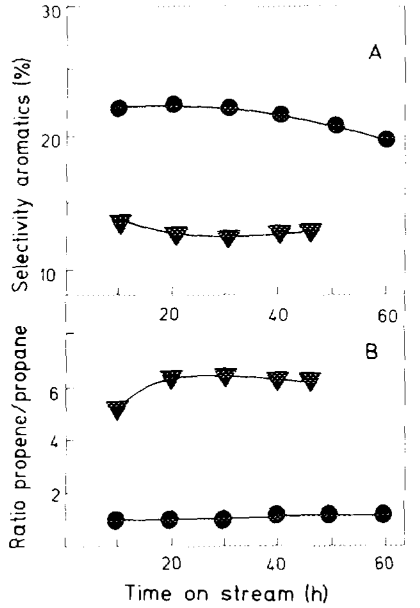

FIG. 6. Conversion of methanol on the dealuminated sample (▼) and after NaOH treatment (●) as function of time on stream. (A) Selectivity for aromatics; (B) Ratio of propene/propane. Reaction temperature 380°C; 2400 v/vh.

The conversion of methanol was used to study the effect of NaOH tratment on both the parent and the dealuminated sample. The reaction was performed at 380°C with 100% conversion. The spent catalysts were totally black from deposited coke. The results are shown in Figs. 5 and 6. The NaOH treatment of the parent zeolite causes the main effect on the stability. As shown in Fig. 5A, the parent sample exhibits a dramatic decay in selectivity for aromatics after 30 h on stream. However, the modified sample maintains its high and stable selectivity for more than 50 h. This stability can be seen in the formation of alkenes, too. The ratio of propene/propane remains low and constant, in contrast to the parent sample, where this ratio steeply increases with time on stream, as shown in Fig. 5B.

The behaviour of the hydrothermally treated samples is shown in Fig. 6. The selectivity for aromatics is very low and stable due to the dealumination, but after the alkali treatment the selectivity is distinctly higher (Fig. 6A). Corresponding variations are perceptible in the propene/propane ratio. This is high on the dealuminated sample. However, the consecutive NaOH treatment causes a specific inhibition of the alkene formation. Therefore the ratio propene/propane is lowered (Fig. 6B).

DISCUSSION

The characterization of the samples proves that a postsynthetic treatment with NaOH is a means for a controlled reconstruction of the zeolite lattice. Samples with a high content of framework Al can be dealuminated; those with a low content of framework Al and a high content of nonframework Al can be realuminated. Realuminations have been reported recently (11, 12). The observed dealumination sensitively depends on the reaction conditions, the amount and concentration of the NaOH, the reaction temperature, and the type of the H-ZSM-5 synthesis.

The dealumination is accompanied by a transport process, as shown by XPS. Framework Al is depleted in the bulk, and nonframework Al is considerably enriched in the outer surface. A similar transportation has been observed as a consequence of hydrothermal treatment of a NaY zeolite (23), but the temperatures for the steam treatment were at least 200°C higher than for the present NaOH treatment.

The XPS data do not enable one to decide whether the Al on the outer surface builds up a new lattice layer or whether it is deposited as nonframework Al. However, the IR and NMR data indicate a decrease of framework Al. This decrease is only consistent with the conclusion that the Al is deposited as nonframework Al.

The catalytic data display remarkable variations as a result of the NaOH treatments. The aromatization of propane is distinctly increased by the NaOH modification of the parent zeolite. This refers not only to the conversion but also to the selectivity. The same catalyst reveals in the aromatization of methanol a prolonged lifetime due to an inhibited deactivation by coking. This is important because deactivation is one of the main obstacles in the application of this zeolite in technical plants such as in the methanol-to-gasoline (MTG) process.

Altogether the results reveal that modification by NaOH is a new tool for the postsynthetic improvement of an as-synthesized zeolite. Moreover, this treatment can also improve a dealuminated zeolite. This is demonstrated by the increased selectivity for aromatics in the conversion of methanol. Dealumination can be the result of severe deactivation during a reaction or of steam treatment in order to improve the physical stability of the catalyst. These undesired side effects of dealumination can at least partially be reversed by the NaOH treatment.

The reason for the observed catalytic effects can be seen in the rearrangement of framework and nonframework Al. Framework Al causes the formation of bridged OH groups. They are the strong acid sites of the Brønsted type and in general the catalytic activity increases with the acidity (4–6). This relation is confirmed by the observed increase of aromatization of methanol with increased framework Al obtained by the reinsertion.

However, the reverse relation, an increased aromatization in spite of decreased framework Al, can be seen with the parent sample after the NaOH treatment. An increased activity in connection with some dealumination has been reported by several authors (4, 5, 7–9, 24), but the dealumination was obtained by a mild hydrothermal treatment at temperatures above 400°C. The present results reveal a new method for mild dealumination, namely NaOH treatment at 100°C. We conclude that this causes an analogous catalytic effect.

The reason for the enhanced activity is still a matter of debate. Lago *et al.* (5) developed a kinetic model on the basis of paired framework Al atoms creating stronger Brønsted sites. Sendoda and Ono (9) concluded that very strong centers are formed by the interaction of dislodged Al with Brønsted sites. Brunner *et al.* (24) could exclude the formation of stronger acid sites. They suggested an interaction of the hydrocarbon with a bridging OH group and a nonframework Al species. The present results confirm a decrease of the Brønsted acidity. In accordance with the model proposed by Brunner *et al.* (24), we assume that a synergistic cooperation of framework Al and nonframework sites, i.e., of Brønsted and Lewis sites, is the reason for the catalytic enhancement.

Corma (25) has reported that the activity of mordenite in the isomerization of light straight-run gasoline depends on the ratio framework Al/nonframework Al. The activity reaches a maximum when this ratio is about 3. The present results are in accordance with this observation. The increased activity of the modified parent sample (P) is accompanied by a decrease of the cited ratio from 16 to 2.3. The increased activity of the modified steamed sample (P + steam) is accompanied by an increasing ratio from 0.19 to 0.64.

In addition to this activating effect the NaOH treatment can cause an inhibition of the deactivation by coke, as shown by the prolonged lifetime of the modified parent sample in the conversion of methanol. This could be due to the observed rearrangement of the surface composition. The treatment causes a considerable enrichment of nonframework Al on the surface. This layer blocks the outer Brønsted sites. This transformation of the outer surface by nonframework Al together with the decrease of framework Al in the pores may cause an inhibition of the coke formation and therefore prolong the lifetime.

The shift of selectivities by deactivating coke on the one hand and by variation of the content of framework Al on the other hand displays an interesting correlation. Deactivating coke shifts the selectivities from aromatics to olefins (Fig. 5), whereas the reinsertion of Al into the framework causes the opposite shift (Fig. 6). This means that diminishing of the density of active Al sites either by coke or by dealumination causes the same shift of selectivities towards olefins. This could be at least partially due to a spatial or "ensemble" effect. The first step of the aromatization is the formation of olefins from methanol. This involves the interaction of smaller molecules than in the last step, the formation of aromatics from olefins. It could be that the aromatization requires larger ensembles with a high density of active sites. Such ensembles would be more easily disturbed by coke or by depletion of framework Al than the smaller ones.

CONCLUSIONS

The results reveal that NaOH treatment is a new method for a controlled variation of the zeolite structure and of the catalytic properties. The treatment of a zeolite with a high content of framework Al causes a mild dealumination connected with a considerable enrichment of nonframework Al on the outer surface. The catalytic consequence is an increased conversion and aromatization of propane. This enhancement is explained by a synergistic cooperation of framework and nonframework Al, similar to the explanation of the known effect observed after mild steaming (5). Moreover, this treatment causes an increased lifetime in the methanol conversion.

The treatment of a dealuminated sample, containing large amounts of nonframework Al, causes a reinsertion of Al into the lattice. The catalytic effect is an increased aromatization of methanol explained by the increased number of Brønsted sites.

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