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Long-Range Interaction of Alkali Cations with the Acidic OH Groups in H-ZSM-5

Toshihide Baba, Yoshihiro Inoue, and Yoshio Ono

Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

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The effect of alkali cations on the properties of the acidic OH groups of H-ZSM-5 was studied by different methods. The temperature dependence of the line-width of the ^{1}H MAS NMR signal attributed to acidic protons is greatly affected by substituting only 1% of Na^+ or NH_4^+ ions for protons. The line-width broadens significantly upon raising the temperature of measurement from room temperature to 373 K. The line-broadening was almost completely suppressed when only 1% of protons was replaced by Na^+ or NH_4^+ ions. The rate of H–D exchange between acidic OH groups and D_2 molecules in the gas phase is also greatly suppressed by a small introduction of Na^+ ions by ion exchange, though the whole of the protons behave homogeneously for the exchange. These results indicate the presence of a long-range interaction between alkali metal cations and the remaining acidic OH groups. The catalytic activities for the acid-catalyzed reactions of cyclopropane isomerization and hexane cracking are reduced greatly when a small percentage of protons is replaced by alkali cations. K^+ ions are a more effective poison than Na^+ ions. These results further support the view that alkali cations in H-ZSM-5 exert a long-range inductive effect on the activity of the acidic OH groups.

INTRODUCTION

The catalytic activity of sodium-free H-ZSM-5 for hexane cracking was reported to be proportional to the number of framework aluminum atoms or the number of acidic OH groups (1–3). A linear correlation between activity and concentration of acidic OH groups was also found for several other reactions (3). This has been interpreted to mean that acidic OH groups in H-ZSM-5 are remote from each other, with the result that they are all essentially identical. The homogeneity of the acid sites was supported by the progressive Cs poisoning observed in hexane cracking. The catalytic activity was proportional to the concentration of the remaining unpoisoned protonic sites (4). Guisnet *et al.* (5) found that the catalytic activities of H-ZSM-5 for o-xylene isomerization and for dimethyl ether conversion to hydrocarbons were proportional to the OH-group concentration, which was controlled by the amount of Na^+ cations.

Recently, Hall and co-workers (6, 7) have reported on the poisoning effect of ammonia on neopentane cracking over high-silica zeolites, i.e., H-ZSM-5, H-mordenite, and H–Y at 673 K. They found that poisoning no more than 10% of the sites was sufficient to eliminate the activity. A similar salient feature of the poisoning has been observed also by introduction of a small amount of Na^+ cations by ion-exchange. For example, Fritz and Lunsford (8) reported that the introduction of one Na^+ ion was equivalent to removal of about five aluminum ions from the framework in hexane cracking over dealuminated Y-type zeolites at 623 K. A similar effect of Na^+ poisoning was reported also for heptane cracking over ZSM-20 at 623 K (9).

The possible reasons for the effectiveness of Na^+ and NH_4^+ poisoning on high-silica zeolites may be conceived as follows:

(a) the concentration of strong acid sites active for the cracking of the alkanes is actually only a small fraction of the total Brønsted acid sites;

(b) the NH_4^+ or Na^+ ions induce long-range interactions depressing the activity of all the remaining sites.

The concept of zeolites having acid sites with differing strength (hypothesis a) has already been suggested by Barthomeuf and Beaumont (10). Evidence for hypothesis b is provided by Dyer and Singh (11), who examined the initial catalytic activities of Na^+ and K^+ ion-exchanged H-mordenites for butane cracking and found that K^+ ions had a much large detrimental effect than Na^+ ions. Kumar *et al.* (12) suggested that the major effect of alkali cations on heptane cracking over USY is to reduce the intrinsic activity per acidic site by an order of magnitude or more. However, hypotheses a and b cannot be distinguished by simply comparing the catalytic activities. A scarce amount of work has examined how alkali cations have an effect on the phenomena more directly related to the properties of the acidic OH groups.

The aim of this work is to study the effect of Na^+ ions on the properties of the OH groups in ZSM-5 zeolites. The salient feature of this work is to examine the nature of the OH groups directly, by observing the ^{1}H-NMR spectra of the OH groups and by measuring the rate of H–D exchange of the OH groups and D_2. The change in the catalytic activities with Na^+ introduction has also been studied.

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EXPERIMENTAL

Materials

ZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 42 was obtained from Toso Co. Ltd. The bulk of the occluded organic material was removed by heating at 723 K for 40 h, exchanging this material in a NaCl solution and then removing the final trace of organic material at 793 K in air. The zeolite was then converted to the ammonium form by cation exchange in a NH_4Cl solution. A part of the NH_4^+ in the NH_4-ZSM-5 was then exchanged with Na^+ in a NaCl solution. The Na^+ contents in the NH_4-ZSM-5 were determined by inductively coupled plasma atomic emission spectroscopy.

When the extent of Na^+ ion exchange in H-ZSM-5 is 1%, the zeolite is denoted as Na(1%)-H-ZSM-5. Similarly, when the adsorbed amount of NH_3 is equal to 1% of the amount of protons in H-ZSM-5, the zeolite is denoted as NH_4(1%)-H-ZSM-5. NH_3 was adsorbed on H-ZSM-5 at 423 K.

In no case were extralattice aluminum species detected by ^{27}Al MAS NMR.

^{1}H MAS NMR Measurements

The NH_4 form of ZSM-5 was converted into the H-form in a glass tube with side arms which was connected to glass capsules used for ^{1}H MAS NMR measurements. NH_4-ZSM-5 (0.70 g) was calcined at 673 K for 10 h and heated under vacuum at the same temperature for 3 h. The sample was transferred into a glass capsule under vacuum to fill it completely and evenly. The neck of the capsule was then sealed, while the sample itself was maintained at 77 K.

^{1}H MAS NMR spectra were recorded on a Bruker AM 400 spectrometer with 6 μs of 90° pulse. The acquisition time and the repetition time were 0.2 and 20 s, respectively. The rotation frequency of the glass capsule was 4.0 kHz. The spectra were recorded by raising the sample temperature stepwise. The chemical shifts were expressed relative to tetramethylsilane (TMS) with the usual conventions.

H–D Exchange of the OH Groups and D_2

The H–D exchange of the OH groups on H-ZSM-5 and the gaseous D_2 molecules was carried out in an infrared cell which was connected to a conventional vacuum system. The NH_4-ZSM-5 was pressed into a wafer and placed in the cell. The sample was then heated in a dry air stream at 773 K for 1.5 h, evacuated at the same temperature for 2 h, cooled to the reaction temperature (423 K) and exposed to D_2 (2.7 kPa). The exchange reaction was followed by monitoring the intensities of the OH stretching band at 3608 cm^{-1} and of the OD stretching band at 2658 cm^{-1} with time. Infrared spectra were recorded on a Shimadzu IR-460 spectrometer.

Catalytic Reactions

a. Cyclopropane isomerization. The isomerization reaction was carried out in a conventional gas-recirculation system. The NH_4-ZSM-5 was heated under dry air at 673 K for 10 h, evacuated at 673 K for 3 h, and then cooled to the reaction temperature (373 K). Cyclopropane (40 kPa) was then introduced. A part of the gas in the reactor was withdrawn at intervals and analyzed by a gas chromatograph.

b. Hexane cracking. The cracking reaction was carried out in a fixed-bed flow reactor (10 mm i.d.) at atmospheric pressure. The NH_4-ZSM-5 catalyst was heated in the reactor in a dry air stream at 773 K for 1.5 h prior to the reaction. Hexane was fed by a motor-driven syringe to the preheating zone of the catalyst bed. The product was withdrawn periodically and analyzed by gas chromatography. Contact time was defined by W/F, where W and F are the weight of the catalyst and the total flow rate of hexane plus nitrogen.

RESULTS AND DISCUSSION

Temperature Variant Study of ^{1}H MAS NMR

Figure 1 shows the temperature dependence of ^{1}H MAS NMR spectra of H-ZSM-5. Two signals were observed at

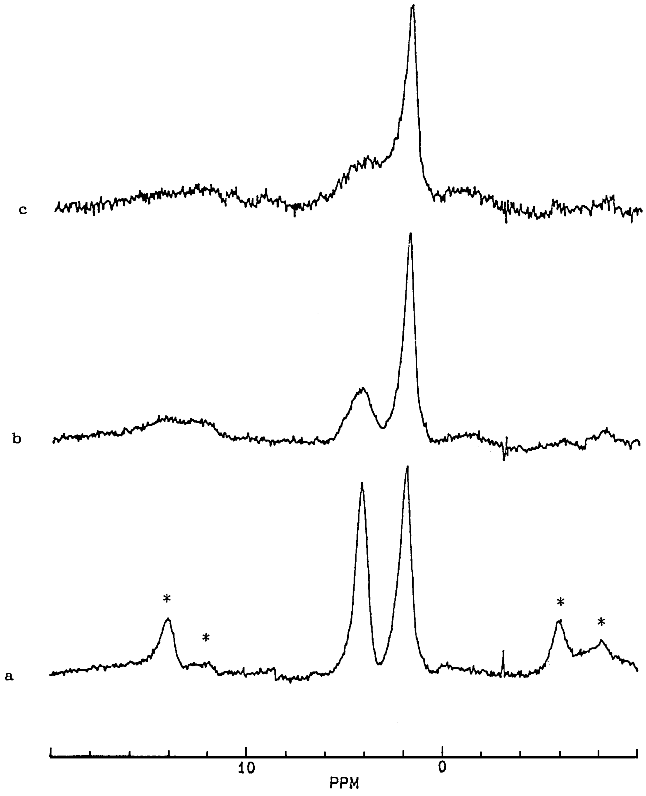

FIG. 1. Change in the ^{1}H MAS NMR spectrum of H-ZSM-5 with temperature. The asterisks denote spinning sidebands. Temperature: (a) 298, (b) 333, and (c) 373 K.

1.9 and 4.3 ppm and they are attributed to protons of the silanol groups and the acidic OH groups, respectively (12).

Upon raising the temperature of the measurement, the peak at 4.3 ppm was broadened significantly. The line-width of the peak increased from $(3.4 \pm 0.2) \times 10^2$ Hz at 298 K to $(6.1 \pm 0.3) \times 10^2$ Hz at 353 K (Figs. 1a and 1b). By further raising the sample temperature up to 373 K, the peak was further broadened (Fig. 1c). The change in the line shape was completely reversible. Upon decreasing the sample temperature to 298 K, the original spectrum was completely restored. In contrast to the peak at 4.3 ppm, the line-width of the peak at 1.9 ppm did not change with temperature.

We have attributed the line-broadening to the mobility of the protons of the OH groups (13). The results indicate that the protons attributed to bridging OH groups (acidic protons) are much more mobile than those of silanol groups. The chemical shifts of both signals did not change in the temperature range of 298 to 373 K. Thus, since the chemical shift did not change with temperature, the line-broadening is a more sensitive measure of the acidic property of the OH groups than the chemical shift values.

Figure 2 shows the temperature dependence of the ^{1}H MAS NMR spectrum of Na(1%)-H-ZSM-5. At 298 K, the spectrum of Na(1%)-ZSM-5 was almost same as that of H-ZSM-5. The line-width of the peak at 4.3 ppm was $(3.2 \pm 0.2) \times 10^2$ Hz, which was slightly narrower than that of H-ZSM-5 at 298 K. No change in the chemical shift values was observed between the two samples.

The line-broadening of the peak due to acidic protons was drastically suppressed by exchanging only 1% of protons in H-ZSM-5 with Na^+ ions. The influence of the temperature on the line-width of Na(1%)-H-ZSM-5 was much smaller compared with that of H-ZSM-5. Thus, the line-width values of the peak increased from $(3.2 \pm 0.2) \times 10^2$ Hz to $(3.5 \pm 0.2) \times 10^2$ Hz and $(4.1 \pm 0.3) \times 10^2$ Hz at 298, 353, and 373 K, respectively.

The temperature dependence of the ^{1}H MAS NMR spectrum of NH_4(1%)-H-ZSM-5 was also examined in the range of 298 to 373 K (Fig. 3). In this temperature range, the chemical shifts of both the acidic (4.3 ppm) and nonacidic (1.9 ppm) protons did not change by adsorbing NH_3. The signal due to NH_4^+ was not clear because of a too-small dose of NH_3. The line-width of the peak at 4.3 ppm was (3.4 ± 0.2) Hz at 298 K (Fig. 3a). Upon raising the sample temperature to 373 K, the line-width increased slightly to $(4.5 \pm 0.3) \times 10^2$ Hz. In contrast to the peak at 4.3 ppm, the line-width of the peak at 1.9 ppm did not change with temperature as in the case of H-ZSM-5.

The temperature dependence of the line-width of the acidic OH groups on the three zeolites, H-ZSM-5, Na(1%)-H-ZSM-5, and NH_4(1%)-H-ZSM-5, are illustrated in Fig. 4. The results indicate that a very minute amount of NH_4^+ or Na^+ ions effectively suppresses the thermal motion of the whole of the remaining protons in H-ZSM-5. This means that NH_4^+ and Na^+ ions have an influence on active sites by a long-range interaction.

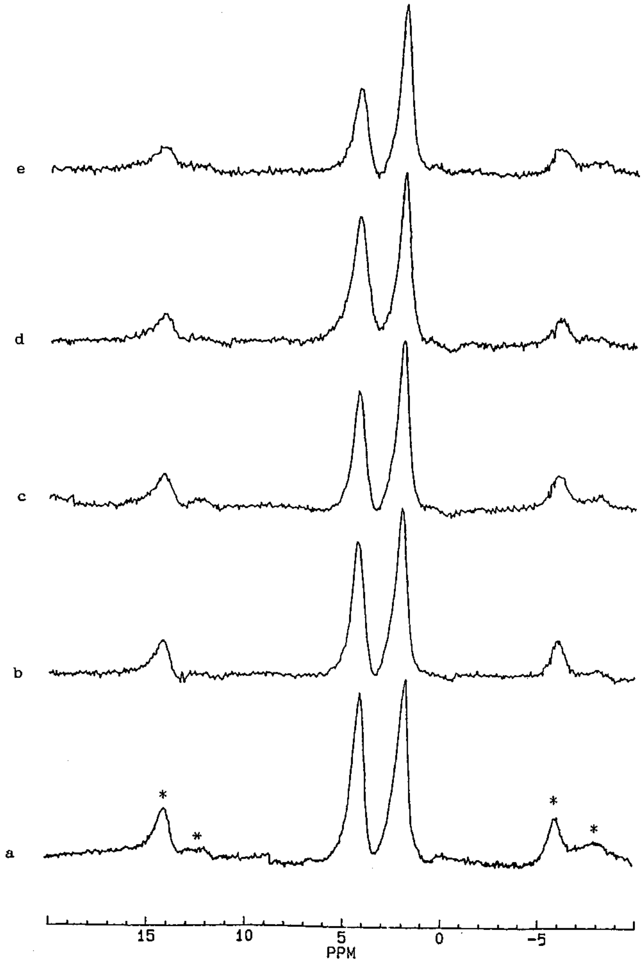

FIG. 2. Change in the ^{1}H MAS NMR spectrum of Na(1%)-ZSM-5 with temperature. The asterisks denote spinning sidebands. Temperature: (a) 298, (b) 313, (c) 333, (d) 353, and (e) 373 K.

H–D Exchange between Surface OH Groups and D_2

To further investigate the direct evidence for modification of the activity of protons by introducing Na^+ ions, the H–D exchange between OH groups and D_2 was investigated. The wafer of the catalyst sample was placed in the cell for infrared spectroscopy and exposed to D_2 at 2.7 kPa pressure at 423 K. The rate of the exchange was monitored by the bands due to OH and OD groups, which appeared at 3608 and 2658 cm^{-1}, respectively. The samples studied were H-ZSM-5, Na(1%)-H-ZSM-5, and Na(20%)-H-ZSM-5. The change in the percent exchange of the acidic OH groups with reaction time is shown in Fig. 5. Over H-ZSM-5, the extent of the exchange increased with reaction time and reached 100% in 55 h. By substituting only 1% of Na^+ for H^+, the rate of exchange decreased significantly.

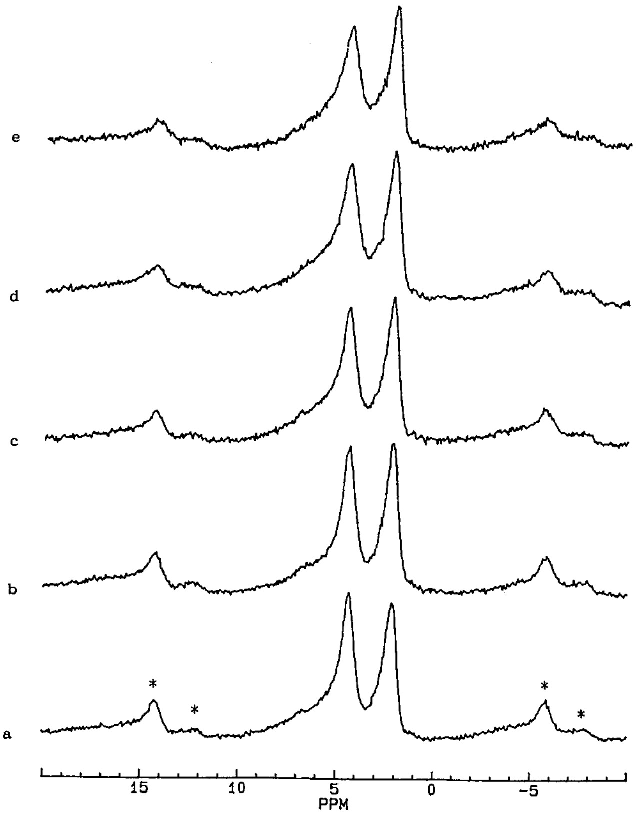

FIG. 3. Change in the ^{1}H MAS NMR spectrum of NH_4(1%)-H-ZSM-5 with temperature. The asterisks denote spinning sidebands. Temperature: (a) 298, (b) 313, (c) 333, (d) 353, and (e) 373 K.

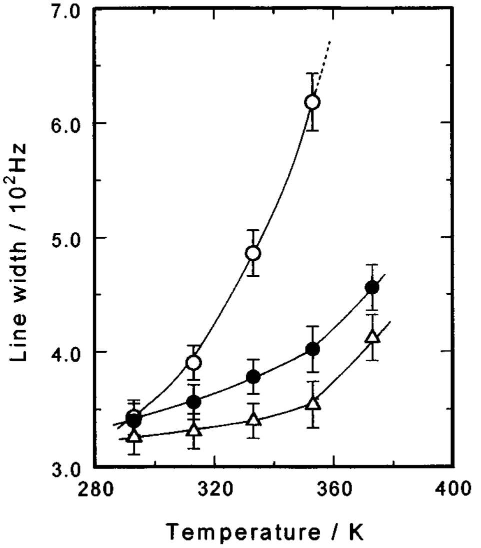

FIG. 4. Change in the line-width of the NMR signal of acidic OH groups of H-ZSM-5 (○), Na(1%)-H-ZSM-5 (△), and NH_4(1%)-H-ZSM-5 (●) with temperature.

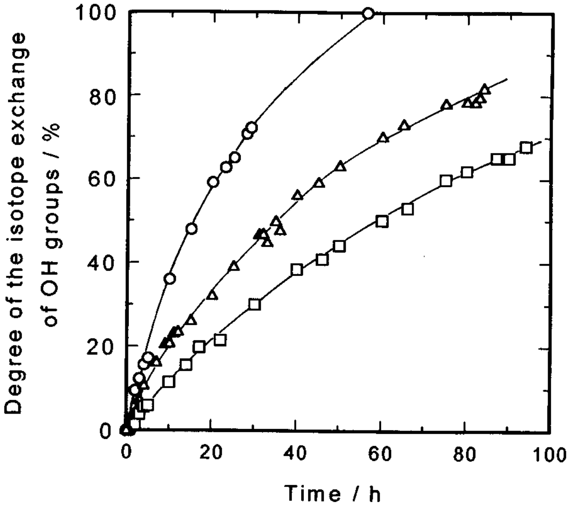

FIG. 5. Change in percent exchange of OH groups in H-ZSM-5 (○), Na(1%)-H-ZSM-5 (△), and Na(20%)-H-ZSM-5 (□) with D_2. Reaction conditions: temperature = 423 K, D_2 = 2.7 kPa.

Further increase of Na^+ ion exchange to 20% resulted in a further decrease in the rate of the reaction of OH and D_2.

As shown in Fig. 6, the rate of the exchange is first order with respect to the surface concentration of the acidic OH groups in every case. This indicates that all the OH groups in each sample behave equivalently and that there are no extremely reactive sites among them. The values of the first-order rate constants are 4.5×10^{-2} h^{-1}, 2.0×10^{-2} h^{-1}, and 1.2×10^{-2} h^{-1} for H-ZSM-5, Na(1%)-H-ZSM-5, and Na(20%)-H-ZSM-5, respectively. It follows that only 1% substitution of Na^+ for H^+ leads to 56% decrease in the

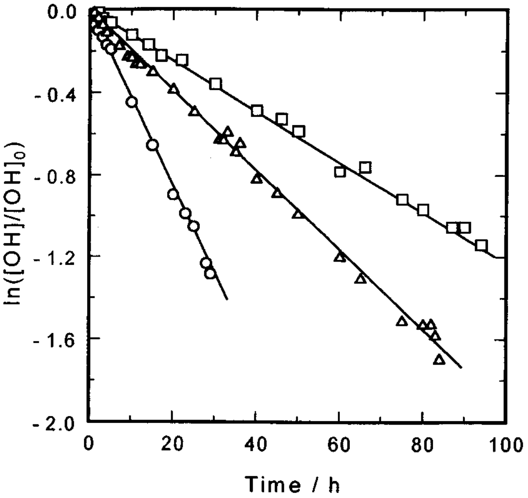

FIG. 6. The first-order plot of the time course of the exchange of OH with D_2 over H-ZSM-5 (○), Na(1%)-H-ZSM-5 (△), and Na(20%)-H-ZSM-5 (□). Reaction conditions: see Fig. 5.

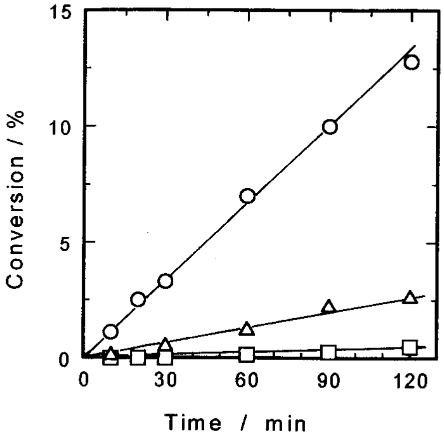

FIG. 7. The percent conversion of cyclopropane isomerization into propene over H-ZSM-5 (○), Na(1%)-H-ZSM-5 (△), and Na(20%)-H-ZSM-5 (□). Reaction conditions: temperature = 373 K, cyclopropane pressure = 40 kPa.

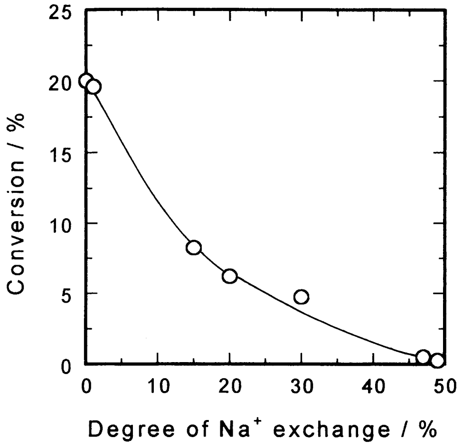

FIG. 8. Change in the catalytic activity of H-ZSM-5 with the degree of Na$^+$ exchange in hexane cracking at 811 K. Reaction conditions: hexane pressure = 8 kPa, $W/F = 0.10$ g h mol^{-1}.

reactivity of the remaining protons. This result is in conformity with the temperature dependence of the line-width in ^{1}H MAS NMR.

Catalytic Activity for Cyclopropane Isomerization

The effect of Na$^+$ ions on the catalytic activity was examined for isomerization of cyclopropane to propene at 373 K. The reaction was carried out over H-ZSM-5, Na(1%)-H-ZSM-5, and Na(20%)-H-ZSM-5 under an initial cyclopropane pressure of 3.9 kPa in a conventional gas-circulation system. Figure 7 shows that, in every case, the cyclopropane conversion linearly increased with reaction time in the low conversion range. The initial rates over H-ZSM-5 and Na(1%)-H-ZSM-5 were calculated to be 1.22×10^{-4} mol h^{-1} g^{-1} and 0.25×10^{-4} mol h^{-1} g^{-1}, respectively. Only 1% of Na$^+$ substitution for H$^+$ reduced the activity of H-ZSM-5 to about 20% of the original H-ZSM-5. By increasing the degree of Na$^+$ ion exchange, most of the activity at this temperature was quenched. These results confirm that a minute amount of alkali cations in H-ZSM-5 is very effective in reducing the catalytic activity.

The drastic suppression of catalytic activity of H-ZSM-5 was also observed by substituting 1% of H$^+$ by NH$_4^+$. The isomerization rate was 0.28×10^{-4} mol h^{-1}. The NH$_4^+$ ions are almost equally effective as Na$^+$ ions in poisoning acid catalysis at 373 K.

Catalytic Activity for Cracking of Hexane

As described above, it has been reported that the activity for hexane cracking is proportional to the number of acidic OH groups (1–4). This was supposed to be a strong evidence for homogeneity of acid sites for high-silica zeolites. We reproduced the proportionality between the activity and the acid-site concentration (the number of aluminium ions in the framework), when hexane cracking was carried out at 811 K using H-ZSM-5 of varying SiO_2/Al_2O_3 ratio. However, the proportionality between the activity and the OH group concentration did not hold when the number of acid sites was changed by changing the degree of ion-exchange of H-ZSM-5 ($SiO_2/Al_2O_3 = 42$) with Na$^+$ ions, as shown in Fig. 8. This was also true for hexane cracking at 623 K (Fig. 9). At both temperatures, the catalytic activity dropped almost linearly with degree of Na$^+$ exchange and the activity disappeared when about a half of protons was replaced with Na$^+$. The effect of ion exchange with K$^+$ on hexane cracking at 623 K was also examined. The result is also shown in Fig. 9. In this case, the catalytic activity was lost at 25% exchange with K$^+$ ions. The K$^+$ions are more effective than the Na$^+$ ions in poisoning acid catalysis.

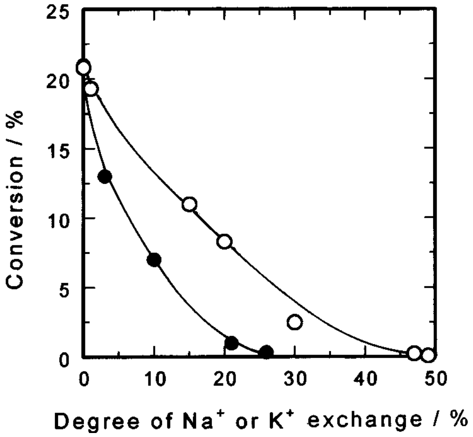

FIG. 9. Change in the catalytic activity of H-ZSM-5 with the degree of cation exchange with Na$^+$ (○) or K$^+$ (●) cations at 623 K. Reaction conditions: hexane pressure = 8 kPa, $W/F = 1.3$ g h mol^{-1}.

The results shown in Figs. 8 and 9 are essentially in conformity with those of the cracking reactions of neopentane over high-silica zeolites (6, 7), hexane over dealuminated Y-zeolites (8), and heptane over ZSM-20 (9). The effect of alkali-cation poisoning on the catalytic activities was more intense for cyclopropane isomerization at 373 K than for alkane cracking at higher temperatures. This difference of the alkali-cation effect could be caused by the different reaction conditions, especially the different reaction temperature and reactants; the details, however, are not yet clear.

CONCLUSIONS

(1) The temperature dependence of the linewidth of the ^{1}H MAS NMR signal due to acidic protons is greatly affected by substituting only 1% of Na^+ or NH_4^+ ions for protons. This gives strong evidence that a minute amount of Na^+ ions exerts a long-range interaction on the remaining acidic protons.

(2) The rate of H–D exchange between acidic OH groups and D_2 molecules in the gas phase is greatly suppressed by Na^+ exchange, although the whole of the protons behave homogeneously for the exchange. This also supports the presence of a long-range interaction between alkali metal cations and the remaining acidic OH groups.

(3) The catalytic activities for the acid-catalyzed reactions of cyclopropane isomerization and hexane cracking are reduced greatly when a small percentage of protons is replaced by alkali cations. Potassium ions are a more effective poison than Na^+ ions. These results also show that alkali cations in H-ZSM-5 exert a long-range inductive effect on the activity of the acidic OH groups.

(4) The nature of the long-range interaction is not clear at this moment. Further detailed studies on the zeolite structures may be important for finally solving this problem.

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