The Steam Stability of H-ZSM-5-Type Zeolites Containing Alkaline Earth Metals

Kazuyoshi Fujisawa,[†] Tsuneji Sano,* Kunio Suzuki, Hideo Okado,[††] Kichinari Kawamura,[†††]
Yasuhiko Kohtoku,[††††] Shigemitsu Shin, Hiroyuki Hagiwara, and Haruo Takaya
National Chemical Laboratory for Industry, Yatabe, Ibaraki 305
[†]Nippon Petrochemical Co., Ltd., Uchisaiwai-cho, Chiyoda-ku, Tokyo 100
[††]Maruzen Petrochemical Co., Ltd., Hatchobori, Chuo-ku, Tokyo 104
[†††]Idemitsu Petrochemical Co., Ltd., Marunouchi, Chiyoda-ku, Tokyo 100
[††††]Ube Industries Co., Ltd., Kasumigaseki, Chiyoda-ku, Tokyo 100

(Received June 18, 1986)

Synopsis. The steam stability of H-ZSM-5-type zeolites containing alkaline earth metals was investigated by means of ^{27}Al MASNMR, the TPD of NH_3, and methanol conversion reactions. It was found that the steam stability of the H-ZSM-5-type zeolites is greatly improved by adding alkaline earth metals.

The production of light olefins, such as ethylene and propylene, from methanol with zeolites has been extensively studied. Several patents and articles have claimed that high selectivities to light olefins are attained at high temperatures over highly siliceous zeolites.[1—3] Recently, we have also found that methanol is converted to light olefins with a high selectivity over H-ZSM-5-type zeolites containing alkaline earth metals, especially calcium.[4,5]

It is well-known that many types of zeolites undergo structural degradation when subjected to water vapor at elevated temperatures. Therefore, if the zeolites are used in a moisture-rich atmosphere such as is encountered in the methanol-to-olefin (or gasoline) conversion, their resistance to steaming must be much improved.

From this standpoint, the steam stability of the H-ZSM-5-type zeolites containing alkaline earth metals has been investigated; the results will be described in this paper.

Experimental

The reagents used were aluminium nitrate (Kokusan, guaranteed reagent), colloidal silica (Cataloid SI-30 from Shokubai Kasei, 30—31 wt% SiO_2, 0.36—0.47 wt% Na_2O, 0.03 wt% Al_2O_3), sodium hydroxide (Nakarai, guaranteed reagent), tetrapropylammonium bromide (Tokyo Kasei, guaranteed reagent), and alkaline earth metal acetates (Nakarai, guaranteed reagent). The H-ZSM-5-type zeolites containing alkaline earth metals (M-H-ZSM-5, M=alkaline earth metals) were synthesized as follows. Certain amounts of aluminium nitrate, colloidal silica, and alkaline earth metal acetate were added to a stirred mixture of tetrapropylammonium bromide and sodium hydroxide in a solution. The resultant hydrogel, with the composition of $0.025\,M\cdot0.1\,R\cdot0.052\,Na_2O\cdot0.005\,Al_2O_3\cdot SiO_2\cdot40H_2O$ (M=alkaline earth metal acetates; R=tetrapropylammonium bromide), was then transferred into a 300-ml stainless steel autoclave and stirred at 150—160 °C under an autogeneous pressure for 15—24 h. After the crystallization of the zeolite, the autoclave was rapidly cooled; the precipitated crystals were then filtered off, washed thoroughly with deionized water, dried at 120 °C, and calcined at 500 °C for 16 h in order to remove the organic base occluded in the zeolite framework. The zeolite thus obtained was protonated in a 0.6-M (1M=1 mol dm^{-3}) hydrochloric acid solution and calcined in air at 500 °C for 6 h.

The steaming was carried out using an atmospheric-pressure flow system at 600 °C in 100% steam for 2.5-g of the charged zeolite (14—28 mesh pieces). The rate of the addition of water was 3 ml h^{-1}.

High-resolution ^{27}Al NMR was measured at 51.9 MHz on a JEOL FX-200 Spectrometer equipped with a probe for magic-angle spinning (MAS). The spectra of the various H-ZSM-5-type zeolites were obtained using 0.33-g samples in Delrin bullets spinning at about 3.5 kHz, using 4.6 μs pulses. The chemical shifts in ppm were measured with respect to $Al(OH)_6{}^{3+}$ as an external reference.

The temperature-programmed desorption (TPD) spectra of the NH_3 adsorbed on the zeolites were obtained using a conventional TPD apparatus. A thermal-conductivity detector was employed for the detection of desorbed NH_3 molecules. The measurement was performed from 100 to 600 °C at a heating rate of 10 °C min^{-1} in helium as the carrier gas (a flow rate, 20 ml min^{-1}) for 0.30-g of the charged zeolite.

Methanol conversion was carried out by the use of an atmospheric-pressure flow reactor at 600 °C and LHSV=4 h^{-1}. The reaction gas was fed in a composition of 50 mol% methanol and 50 mol% argon. The products thus obtained were analyzed by gas chromatography. The methanol conversions and carbon-based selectivities were calculated from the concentration of argon used as the internal standard.

Results and Discussion

The prepared H-ZSM-5-type zeolites containing

Table 1. Characteristics of H-ZSM-5-Type Zeolites Containing Alkaline Earth Metals

	Zeolite	Atomic ratios[a)] Si/Al	Atomic ratios[a)] Alkaline earth metal/Al	BET surface area (m^2g^{-1})
1.	H-ZSM-5	120		342
2.	Mg-H-ZSM-5	94	0.89	336
3.	Ca-H-ZSM-5	117	1.63	341
4.	Sr-H-ZSM-5	93	1.29	301
5.	Ba-H-ZSM-5	90	1.35	301

a) Determined by X-ray fluoresence spectrometry.

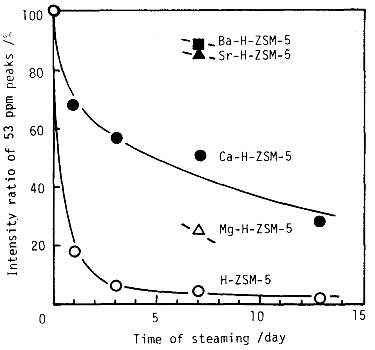

Fig. 1. Relationship between time of steaming and intensity ratio of 53 ppm peaks. Zeolite was subjected to water vapour at 600°C under atmospheric pressure.

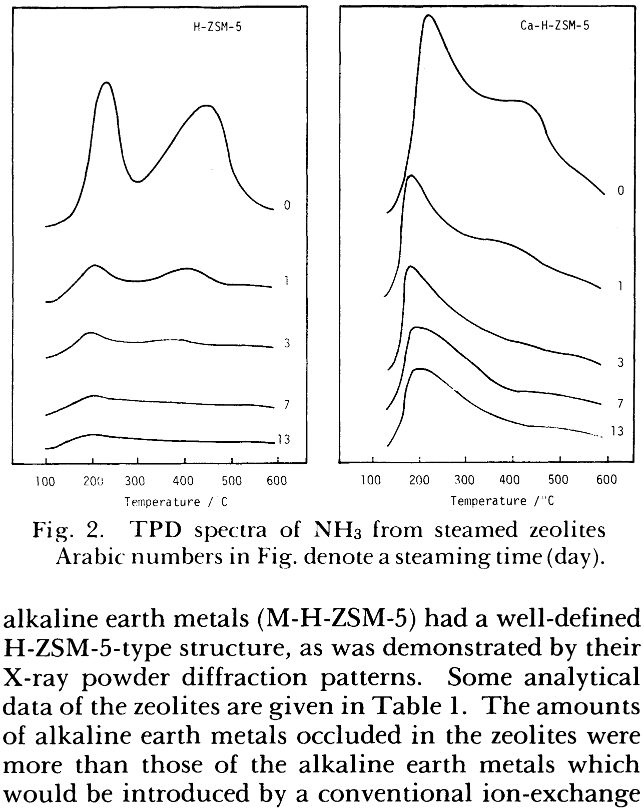

Fig. 2. TPD spectra of NH_3 from steamed zeolites Arabic numbers in Fig. denote a steaming time (day).

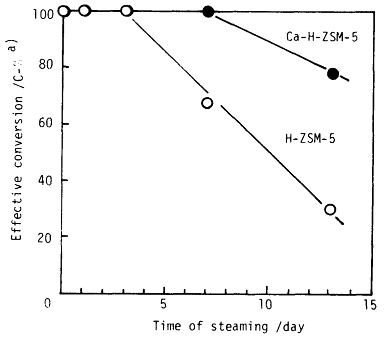

Fig. 3. Effect of steaming on catalytic activity. Reaction conditions: LHSV=4 h^{-1}, T=600°C. a) Effective conversion=100-(Methanol+Dimethyl Ether)-Yield

alkaline earth metals (M-H-ZSM-5) had a well-defined H-ZSM-5-type structure, as was demonstrated by their X-ray powder diffraction patterns. Some analytical data of the zeolites are given in Table 1. The amounts of alkaline earth metals occluded in the zeolites were more than those of the alkaline earth metals which would be introduced by a conventional ion-exchange method, in which the atomic ratio of alkaline earth metal to aluminium is, at most, 0.5. However, a full explanation of this rare phenomenon will be given in a future study.

As has already been reported, the ^{27}Al MASNMR spectrum of the conventional H-ZSM-5 has one peak, at about 53-ppm, assigned to the framework (tetrahedrally coordinated) aluminiums.[6] The ^{27}Al MASNMR spectra of various M-H-ZSM-5 have the same peak as that of H-ZSM-5. Figure 1 shows the relationship between the time of steaming and the intensity ratio, which means the percentage of a 53-ppm peak intensity of the steamed zeolites relative to that of the corresponding unsteamed zeolites. The rapid decay curve was obtained for H-ZSM-5, whereas the slow decay curves were obtained for M-H-ZSM-5. The intensity ratios of M-H-ZSM-5 decreased in the following order: Ba-H-ZSM-5 > Sr-H-ZSM-5 > Ca-H-ZSM-5 > Mg-H-ZSM-5 > H-ZSM-5, indicating a great stability of Ba- and Sr-H-ZSM-5 for steaming. These results suggest that the release of tetrahedrally coordinated aluminiums from a framework is depressed by the presence of alkaline earth metals to the different degree described above.

Some typical TPD spectra of NH_3 for H-ZSM-5 and Ca-H-ZSM-5 before and after the steaming are illustrated in Fig. 2. The TPD spectra from H-ZSM-5 exhibited two fairly sharp peaks at about 220 (l-peak) and 450 °C (h-peak). On the other hand, the two peaks of the TPD spectra from Ca-H-ZSM-5 are broad. The total amount of desorbed NH_3 decreased with an increase in the steaming time for both H-ZSM-5 and Ca-H-ZSM-5, but the amount of desorbed NH_3 of the former was less than that of the latter. As a part of the desorbed NH_3 might originate from physically adsorbed NH_3, the total amount of desorbed NH_3 is not necessarily proportional to the amount of acid sites which would originate from aluminiums in zeolites. Nevertheless, the result of the NH_3 TPD is in accordance with that of ^{27}Al NMR: less desorption for a lower intensity ratio.

Figures 3 and 4 show the results of methanol conversion over various zeolites before and after the steaming. The steaming affected both the catalytic activity and the product distribution. As is shown in Fig. 3, the catalytic activity of H-ZSM-5 decreased markedly with the increase in the steaming time, while that of Ca-H-ZSM-5 decreased slightly. For the steamed zeolites, a remarkable decrease in the selectivities to (C_2H_4+C_3H_6) and (benzen+toluene+xylene) was observed, while those to CH_4 and hydrocarbons with carbons more than six (C_6^+) were increased.

From all of these results, it is concluded that the steam stability of the H-ZSM-5-type zeolites is greatly improved by adding alkaline earth metals. The role of the alkaline earth metals in steam stability is considered to be similar to those of Co or Cu in the previously reported cobalt-ZSM-5 zeolites or cupper-Y-zeolites.[7,8] Although the essential role played by the alkaline earth metals is not very well understood in this work, in any event, the metals seem to prevent the release of aluminium species from the framework during the steaming.

This work is a part of the "C_1 Chemistry Project," a

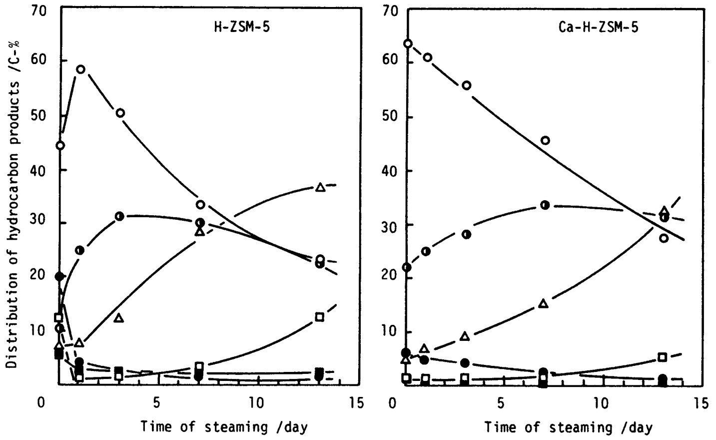

Fig. 4. Effect of steaming on distribution of hydrocarbon products.
○: $C_2H_4+C_3H_6$, ◑: $C_4H_8+C_5H_{10}$, □: CH_4, ■: (C_2-C_5) paraffins, ●: BTX, △: C_6^+.

National Research and Development Program of the Agency of Industrial Science and Technology, Ministry of International Trade and Industry (M.I.T.I.), Japan.

References

1) W. W. Kaeding, and S. A. Butter, *J. Catal.*, **61**, 155 (1980).

2) G. Chen, and J. Ling, China-Japan-U.S. Symposium on Heterogeneous Catalysis, Dalian, China, A010C (1982).

3) D. E. 3304479.

4) U. S. Pat. 4544793.

5) H. Okado, H. Shoji, K. Kawamura, K. Hashimoto, Y. Yamazaki, T. Sano, and H. Takaya, *Nippon Kagaku Kaishi*, **1987**, 25.

6) C. A. Fyfe, J. M. Thomas, J. Klinowski, and G. C. Gobbi, *Angew. Chem. Int. Ed. Engl.*, **22**, 259 (1983).

7) P. A. Jacobs, and H. K. Beyer, *J. Phys. Chem.*, **83**, 1174 (1979).

8) Eur. Pat. Appl. 18117.