The Migration of Barium into Zeolite Channels from the Outer Surfaces of Zeolite Crystals

Tsuneji Sano,* Hideo Okado,† Hiroshi Shoji,† Shigeru Ikai,†† and Haruo Takaya
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305
†Maruzen Petrochemical Co., Ltd., Hatchobori, Chuo-ku, Tokyo 104
††Ube Industries Co., Ltd., Kasumigaseki, Chiyoda-ku, Tokyo 100

(Received November 30, 1989)

Synopsis. For the ZSM-5 zeolite mechanically mixed with barium carbonate, the migration of barium into the zeolite channels from the outer surfaces of zeolite crystals occurs at 600 °C in both the absence of and the presence of steam, resulting in a modification of the strong acid sites.

There are many patents and articles concerning selective catalysts for the production of light olefins, such as ethylene and propylene, from methanol.[1—5] Recently, we have found that the zeolites containing alkaline earth metals show high selectivities to light olefins at temperatures above 500 °C[6,7] and that, among them, the zeolite containing calcium (AEZ-Ca) shows the best catalyst performance. We have concluded that a part of the calcium changes the strong acid sites of the zeolite to weak ones. It was also found that, when a moisture-rich atmosphere is encountered in methanol conversion, calcium is released from the weak acid sites and migrates to the outer surfaces of zeolite crystals.[8] The release of calcium from the weak acid sites brings about the regeneration of the strong acid sites. The strong acid sites tend to promote the formation of coke deposits, which are responsible for the deactivation of the catalysts. Therefore, the release of calcium is undesirable for controlling catalyst activity in order to extend catalyst life.

From the fact that calcium in the zeolite crystals migrates through channels to their outer surfaces, it is assumed that, in the presence of large amounts of an alkaline earth metal salt on the outer surfaces, a part of the alkaline earth metal migrates into the zeolite channels and modifies the strong acid sites. Hence, it is expected that the regeneration of the strong acid sites due to the release of calcium from the weak ones is apparently depressed when AEZ-Ca is mixed with alkaline earth metal salt. From this standpoint, in this paper the migration of barium into zeolite channels has been investigated for zeolites mechanically mixed with, in particular, a powder of barium carbonate.

Experimental

ZSM-5 with SiO_2/Al_2O_3 ratio of 200 was synthesized as follows. Aluminium nitrate and colloidal silica (Cataloid SI-30 from Shokubai Kasei; 30—31 wt% SiO_2, 0.36—0.47 wt% Na_2O) were stirred into a solution containing tetrapropylammonium bromide and sodium hydroxide. The resultant hydrogel, with the composition of $0.05\,R_2O\cdot 0.052\,Na_2O\cdot 0.005\,Al_2O_3\cdot SiO_2\cdot 40\,H_2O$ (R=tetrapropylammonium), was then transferred into a 300-ml stainless steel autoclave and stirred at 160 °C under an autogeneous pressure for 18 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 18 h in order to remove the organic base occluded in the zeolite framework. The zeolite thus obtained was protonated in a 0.6 mol dm^{-3} hydrochloric acid solution at room temperature for 18 h and then calcined at 500 °C for 6 h. Silicalite was similarly synthesized without aluminium in hydrogel. The analytical data of the zeolites are summarized in Table 1.

$BaCO_3$ was prepared by the calcination of barium acetate at 500 °C for 18 h. The mechanical mixing of ZSM-5 or silicalite with $BaCO_3$ was performed in a weight ratio of 2:1. The steaming[3] of the catalyst was carried out at 600 °C for 7—40 h in an argon stream of 60 vol% to H_2O. The catalysts were calcined in air at 600 °C for 7—96 h, while the HCl treatment was done with a 0.6 mol dm^{-1} hydrochloric acid solution at room temperature for 18 h.

The elemental compositions of the zeolites were determined by the use of an X-ray fluorescence spectrometer (Rigaku 3080E). The samples for the measurement were prepared as glass beads by mixing 0.3 g of the zeolites with 3 g of lithium borate. The BET surface areas of the zeolites were measured by a method of single-point N_2 adsorption at −196 °C (Shimadzu Micromeritics 2200). The morphology of the zeolites was observed by means of a scanning electron microscope (Shimadzu ASM-X). The diffuse reflectance infrared spectra of the zeolites were measured at room temperature using a Digilab FTS-60 spectrometer equipped with an evacuable, heatable chamber. The powdered zeolites were placed in thin-walled ampules with a diameter of 8 mm and then evacuated to about 10^{-6} Torr at 500 °C for 2 h. The spectra were taken at a 2-cm^{-1} resolution for 1000 scans.

Results and Discussion

Migration of Barium in Calcining at 600 °C in the Absence of Steam; The calcination of mechanical mixtures of ZSM-5 and silicalite with $BaCO_3$ was carried out at 600 °C. The calcined zeolite mixtures were treated with a 0.6 mol dm^{-3} HCl solution in order to remove the free $BaCO_3$ from the mixtures with the zeolite crystals. Table 2 shows the chemical composi-

Table 1. Characteristics of Zeolites

Zeolite	SiO_2/Al_2O_3 ratio[a)]	BET surface area/m^2 g^{-1}	Particle size/μm
ZSM-5	196	360	2—4
Silicalite	3300	390	1—9

a) After acidification by 0.6 mol dm^{-3} HCl.

Table 2. Characteristics of Various $BaCO_3$-Mixed Zeolites

$BaCO_3$-mixed zeolite[a)]	Time of treatment/h		Molar or atomic ratio after HCl treatment[d)]		
	Calcining[b)]	Steaming[c)]	SiO_2/Al_2O_3	Ba/Si	Ba/Al_2
$BaCO_3$/ZSM-5	7		202	0.0008	0.16
	18		203	0.0015	0.31
	40		204	0.0016	0.33
		7	212	0.0013	0.27
$BaCO_3$/Silicalite	18		3300	0.0000	
	96		3400	0.0000	
		7	3300	0.0000	
		40	3500	0.0008	

a) 1 g of the zeolite (ZSM-5 or Silicalite) was mechanically mixed with 0.5 g of $BaCO_3$. b) Temp=600 °C in air. c) Temp=600 °C, LHSV of $H_2O=1.2\ h^{-1}$, $H_2O/Ar=0.67$. d) The treatment of HCl was performed with a 0.6 mol dm^{-3} HCl solution at R. T. for 8 h.

tions of the zeolites after the treatment of HCl. The Ba/Si (Ba/Al_2) ratios of $BaCO_3$-mixed ZSM-5 increased with the time of calcination until 18 h, becoming nearly constant after that. On the other hand, the Ba/Si ratio of $BaCO_3$-mixed silicalite was zero, even after 96 h. These results suggest that barium is occluded in the zeolites, presumably through the interaction of the metal with the strong acid sites, since strong acid sites are present on ZSM-5, but not on silicalite.

The IR spectra of hydroxyl groups of ZSM-5 and $BaCO_3$-mixed ZSM-5 before and after calcining were also measured. The spectrum of ZSM-5 was characterized by a well-defined peak at 3605 cm^{-1} assigned to an acidic bridged OH of Si(OH)Al, which is supposed to be an essential chemical formula of strong acid sites.[9)] Curves (1) and (1′) in Fig. 1 indicate that, for ZSM-5, simple calcining does not affect the peak intensity at 3605 cm^{-1}. For the $BaCO_3$-mixed ZSM-5, however, the same peak was decreased to some extent by calcination, as is shown by Curves (2) and (2′). This decrease in the peak intensity supports the earlier indication that barium interacts with the strong acid sites.

On the assumption of a homogeneous distribution[10)] of aluminium in a zeolite crystal of 1-μm size, aluminium above 99% is present inside the crystal. Hence, the Ba/Al_2 ratios of about 0.3, shown in Table 2, indicate that most of the barium is also present inside the zeolite crystals, provided that the barium interacts with the strong acid sites containing aluminium. Therefore, it seems quite reasonable to consider that barium migrates from the outer surfaces of zeolite crystals into their channels during calcination.

This is also supported by the report of Kucherov et al.[11)] that the calcination of mechanical mixtures of copper compounds with the H forms of the high-silica zeolites in air at 520—800 °C is accompanied by a migration of a part of the Cu^{2+} ions into zeolite channels. The location of the Cu^{2+} ions at the cationic sites was determined by means of ESR.

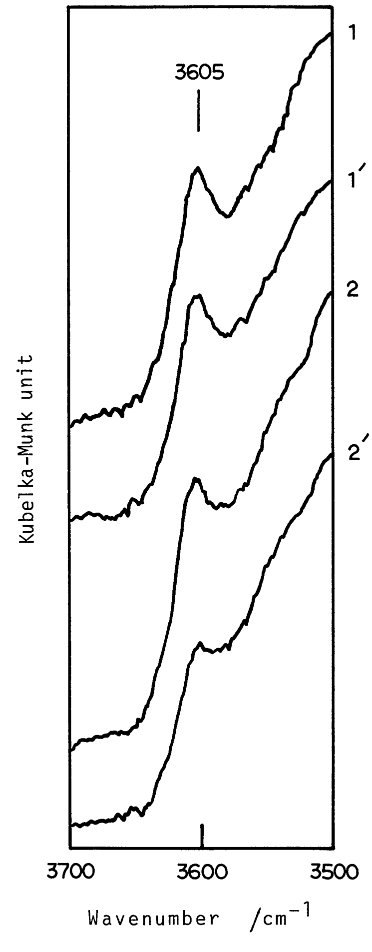

Fig. 1. FT-IR spectra of various zeolite catalysts before and after calcining. 1: ZSM-5 before calcining. 1′: ZSM-5 after calcining. 2: $BaCO_3$-mixed ZSM-5 before calcining. 2′: $BaCO_3$-mixed ZSM-5 after calcining. Calcining conditions: Temp=600 °C in air, Time=18 h.

Migration of Barium by Steaming at 600 °C: The migration of barium under steaming at 600 °C was investigated in order to compare this with the case of calcination. The chemical compositions of both $BaCO_3$-mixed ZSM-5 and $BaCO_3$-mixed silicalite after steaming and HCl treatment are shown in Table 2. It was found that, for ZSM-5, the Ba/Si ratio after steaming is higher than that after calcining. This table also shows that dealumination from the ZSM-5 zeolite framework occurs upon steaming. The SiO_2/Al_2O_3 ratio of the steamed zeolite increased a little. In addition, it is understood that barium is introduced into ZSM-5 by steaming in a way similar to the case of calcining. The Ba/Si ratio of $BaCO_3$-mixed silicalite steamed for 40 h is 0.0008, indicating the introduction of barium into silicalite. In the presence of steam, it is probable that many silanol groups are formed in the channel of zeolites and that $BaCO_3$ is transformed into $Ba(OH)_2$. The formation of silanol groups and $Ba(OH)_2$ by steaming would promote the introduction of barium even into silicalite. By the same reaction, the introduction and the migration of barium for ZSM-5 may be much enhanced by steaming.

From the above results, it was concluded that, in the presence of large amounts of an alkaline earth metal salt on the outer surfaces of zeolite crystals, a part of the alkaline earth metal migrates into the zeolite channels and modifies the strong acid sites. Although we have already reported that the catalyst life of AEZ-Ca is much expanded by mixing with alkaline earth metal carbonate,[12,13] now it has become evident that the stabilization of weak acid sites by the use of alkaline earth metal carbonate contributes greatly to the elongation of the catalyst life of AEZ-Ca.

This work is a part of the "C_1 Chemistry Project," a 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) C. D. Chang, C. T-W. Chu, and R. F. Socha, *J. Catal.,* **86**, 289 (1984).
2) W. W. Kaeding and S. A. Butter, *J. Catal.,* **61**, 155 (1980).
3) C. D. Chang, W. H. Lang, and A. J. Silvestri, U. S. Patent 4062905 (1977).
4) C. D. Chang, *Catal. Rev.-Sci. Eng.,* **26**, 323 (1984).
5) W. Hoeldrich, H. Eichhorn, R. Lehnert, L. Marosi, W. Mross, R. Reinke, W. Ruppel, and H. Schlimper, Proc. 6th Intern. Zeolite Conf., ed by D. Olson and A. Bision, Butterworths, London (1984), p. 545.
6) H. Okado, T. Sano, K. Matsuzaki, K. Kawamura, K. Hashimoto, H. Watanabe, and H. Takaya, *Nippon Kagaku Kaishi,* **1987**, 791.
7) H. Okado, H. Shoji, K. Kawamura, Y. Shiomi, K. Fujisawa, H. Hagiwara, and H. Takaya, *Nippon Kagaku Kaishi,* **1987**, 962.
8) H. Okado, H. Shoji, T. Sano, K. Suzuki, Y. Kiyozumi, H. Hagiwara, and H. Takaya, *Nippon Kagaku Kaishi,* **1987**, 1654.
9) P. A. Jacobs and H. K. Beyer, *J. Phys. Chem.,* **83**, 1174 (1979).
10) E. G. Derouane, J. P. Gilson, Z. Gabelica, C. M-Desbuquoit, and J. Verbist, *J. Catal.,* **71**, 447 (1981).
11) A. V. Kucherov and A. A. Slinkin, *Kinet. Katal.,* **27**, 671 (1986).
12) H. Okado, H. Shoji, T. Sano, K. Suzuki, Y. Kiyozumi, H. Hagiwara, and H. Takaya, *Nippon Kagaku Kaishi,* **1987**, 2255.
13) T. Sano, T. Murakami, K. Suzuki, S. Ikai, H. Okado, K. Kawamura, H. Hagiwara, and H. Takaya, *Appl. Catal.,* **33**, 209 (1987).