Table 1. Rate Constants for the Reconstituted BR-DPPC Vesicular Catalyzed Hydrolysis of PNPP at 35 °C, pH 11.75[a]

Condition	k1(min^{-1})	k2(min^{-1})	k1/k2	R°(fast)	R°(slow)
light on	0.242	0.00701	34.6	0.0715	0.179
light off	0.172	0.0114	15.1	0.0715	0.192
none BR	0.0845	0.00772	10.9	0.0707	0.236

[a] R° is the absorbance of the chemical species at $t=0$. $[BR]=3\times10^{-7}M$, $[DPPC]=2\times10^{-3}M$, $[PNPP]=2\times10^{-4}M$, $[borate]=0.01M$.

became decreased. By contrast, at extinction of light, proton was back diffused, and the reaction rate of PNPP at the inside of vesicle became decreased. The change of k1/k2 at the light illuminated condition suggested that the H$^+$ pumped by light affected the hydrolysis. The difference between the light off condition and none BR[1] condition might be understood as the integral protain's general effect on the fluidity of the bilayer; those effects usually increase the overall reaction rate of the hydrolysis[9], as in our case. The results of Table 1 suggested that fast reaction and slow reaction occured inside and outside of the vesicle, respectively. The present work might support biphasic kinetics of vesicular reaction, and demonstrate how the vesicle can be chemically differentiated at inside and outside of vesicle site.

Acknowledgement. This work was supported by the Ministry of Education (1988-1989). We also thank proffesor Y. S. Lee for the helpful discussion.

References

1. R. A. Moss and R. P. Schreck, *J. Am. Chem. Soc.*, **105**, 6767-6768 (1983)
2. R. A. Moss, T. F. Hendrickson and G. O. Bizzigotti, *J. Am. Chem. Soc.*, **108**, 5520-5527 (1986)
3. R. R. Birge, L. A. Finsen and B. M. Pier, *J. Am. Chem. Soc.*, **109**, 5041-5043 (1987)
4. E. Racker, *Methods in Enzymology*, **55**, 699-711 (1979)
5. T. Kunitake and T. Samamoto, *J. Am. Chem. Soc.*, **100**(14), 4615-4617 (1979)
6. M. Iolanda and M. V. Regina, *Tetrahedron Letters*, **33**, 3065-3068 (1979)
7. The light was illuminated for 1 hour before hydrolysis
8. J. Peters, R. Peters and W. Stokenius, *FEBS Letters*, **61**(2), 128-134 (1976)
9. T. Kunitake, H. Ihara and Y. Okahata, *J. Am. Chem. Soc.*, **105**, 6070 (1983)

Influence of Dealumination and Nonframework Aluminum on the Catalytic Activity of Y Type Zeolite

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Received March 13, 1989

The removal of aluminum from the framework of Y type zeolites strongly influences the catalytic activity[1-3]. For Y zeolite prepared by dealumination, interpretation of catalytic data is complicated by the presence of nonframework aluminum species. We have examined the influence of dealumination and nonframework aluminum species on catalytic cracking activity.

Dealuminations were carried out by three preparation methods. A series of dealuminated Y type zeolites without nonframework aluminum was prepared by reaction of NaY with EDTA, according to the procedure described by Kerr[4]. These samples are denoted by a symbol of EDY (Si/Al), where the framework silicon to aluminum ratio is given in parenthesis. A steam-dealuminated Y zeolites (designated SDY) with nonframework aluminum were prepared according to the method of Ward[5]. A $SiCl_4$-dealuminated Y zeolites (designated DY) with nonframework aluminum were prepared according to the procedure described by Beyer *et al.*[6]. The all zeolites thus dealuminated were ion-exchanged three times, 12 hr each, in 1M NH_4NO_3 at 70 °C to remove any remaining Na$^+$ ions.

The zeolites were tested as catalysts for cumene cracking at 350 °C after pretreatment at 400 °C for 2 hr. Catalyst samples were prepared by mixing the zeolite with silica (Davison 952 grade SiO_2) in order to keep conversions low. Catalytic activities were measured in a pulse microreactor constructed of 1/4 in stainless-steel. The products were analyzed with a Shimadzu 3 BT gas chromatograph using a 3 m Bentone 34 on chromosorb W column at 130 °C.

The initial activity was given in terms of μmole cumene converted perg zeolite during the first pulse reaction. As shown in Figure 1, there is a correlation between cumene cracking activity and the number of framework aluminum ions per unit cell. With EDY samples, the activity increases with the dealumination to a maximum and then decreases. Namely, activity increases progressively according as the number of framework aluminum ions per unit cell changes from 56 to 28. This is related to the increase of acid strength after aluminum removal and the extraction of weak acid site. It has been known that in Y zeolites the location of all the framework aluminum atoms is crystallographically identical, but 35% of these atoms are chemically different[7,8]. Upon fur-

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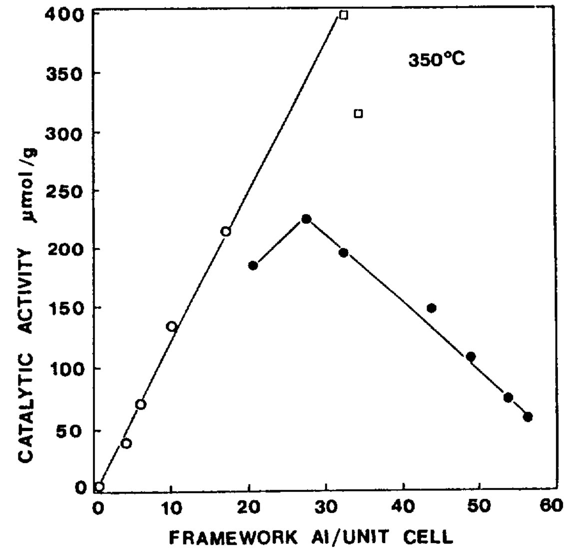

Figure 1. Dependence of cumene cracking activity on framework aluminum content: (○) EDY series, (●) DY series, (□) SDY series.

Table 1. Analysis and Catalytic Activity of Dealuminated Zeolites

Zeolite	Unit Cell Constant(Å)	Al per Unit Cell Framework[a]	Nonframework	Total[b]	Catalytic Activity μmol/g (350°C)
SDY(4.6)	24.556	34.1	20.0	54.1	316
SDY(5.0)	24.536	31.9	22.7	54.6	397
EDY(4.9)	24.540	32.4	0	32.4	197

[a] Determined according to the equation, $N_{Al} = 107.1\ (a_o - 24.238)$ in reference 11, where a_o is unit cell constant. [b] Based on atomic absorption data.

ther removal of framework aluminum, the catalytic activity decreased as shown in Figure 1. The drop in cumene conversion from EDY (5.9) to EDY (8.3) may be accounted for by the decrease in the number of strong acid sites and a partial loss of crystallinity. A partial loss of crystallinity was confirmed by the X-ray diffraction pattern. It has been reported earlier that about 50% of framework aluminum atoms can be removed by EDTA treatment without the loss of crystallinity[4].

There is a linear relationship between cumene cracking activity and the number of framework aluminum atoms per unit cell, over the range of 0.75-32 Al/unit cell. The correlation includes zeolites dealuminated with $SiCl_4$ and by steaming. This linear relationship implies that the turnover frequency based on framework aluminum is constant. It is further implied that the acid strength of the zeolite does not vary over this same range, at least to the extent that cumene cracking can probe the acid strength.

Hydrothermal treatment of zeolites results in the expulsion of tetrahedral aluminum from the framework into nonframework positions, but the aluminum remains in the zeolite cages or channels as given in Table 1. In order to investigate the effects of nonframework aluminum, cumene cracking was carried out on two SDY catalysts. A marked enhancement in catalytic activity is exhibited by each of these materials. SDY (5.0), which is estimated to have 32 framework aluminum atoms per unit cell (Table 1), shows higher catalytic activity by two times than EDY (4.9) having nearly the same framework aluminum content. The increasing activity exhibited by SDY samples means that nonframework aluminum species entrained in the lattice during hydrothermal treatment are playing a positive role in the enhanced perfomance. In addition to the earlier X-ray diffraction data there is a support from recent NMR, IR and ion exchange studies that part of the nonframework aluminum resides inside the small cavities, presumably in a cationic form[9,10]. Nonframework species such as Al^{3+}, AlO_2^+, $Al(OH)^{2+}$, $Al(OH)_2^+$, $AlO(OH)$, and $Al(OH)_3$ *etc.* have been suggested[9]. The strength of Brönsted acid is probably increased through the electron attraction of acidic hydroxyl group by nonframework aluminum species. Maher *et al.*[9] found that nonframework aluminum species occupied SI′ sites in ultrastable zeolite. These aluminum species inside the sodalite unit may enhance the acidity of protons attached to structural oxygens through inductive effects.

Acknowledgement. This work was supported by the Korean Science and Engineering Foundation (1986–1987).

References

1. R. Beaumont and D. Barthomeuf, *J. Catal.*, **26**, 218 (1972).
2. R. Beaumont and D. Barthomeuf, *J. Catal.*, **27**, 45 (1972).
3. A. Yoshida, H. Nakamoto, K. Okanishi, T. Tsuru, and H. Takahashi, *Bull. Chem. Soc., Jpn.*, **55**, 581 (1982).
4. G. T. Kerr, *J. Phys. Chem.*, **72**, 2594 (1968).
5. J. W. Ward, *U. S. Patent*, **3**, 929672 (1975).
6. H. K. Beyer and I. Belenykaya, "Catalysis by Zeolites" ed. B. Imelik *et al.*, Elsevier, Amsterdam, (1980) p. 203.
7. D. Barthomeuf, *ACS Symposium Series*, **40**, 453 (1977).
8. D. Barthomeuf and R. Beaumont, *J. Catal.*, **30**, 288 (1973).
9. P. K. Maher, F. D. Hunter, and J. Scherzer, *Adv. Chem. Ser.* **101**, 266 (1979).
10. V. Bosacek, D. Freude, T. Fröhlich, H. Pfeifer, and H. Schmiedel, *J. Colloid Interface Sci.*, **85**, 502 (1982).
11. J. R. Sohn, S. J. Decanio, J. H. Lunsford, and D. J. O'Donnell, *Zeolites*, **6**, 225 (1986).