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# Development of Long-life Dealuminated Mordenite for Methanol Conversion to Hydrocarbons

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A long-life catalyst for the methanol conversion was obtained by the dealumination where the temperature and concentration of HCl solution were precisely controlled.

Zeolite ZSM-5 is known for a catalyst to convert methanol into hydrocarbons, and its long life is believed to be caused by the shape-selectivity owing to the structure. The durable activity for this reaction has not been obtained on any other zeolites than ZSM-5 and related pentasil metallo-silicates.1) However, attentions should be paid to the acidity profile of ZSM-5 also in order to understand the durable activity,2) and a new long-life catalyst could be obtained by controlling the acidity of other kinds of zeolites. Some efforts have already been performed for the purpose, e.g., doubly dealumination of mordenites.3) Then, we focused our attention to the modification of acidity of mordenites to gain a new long-life catalyst. We will report in this communication that a dealuminated mordenite has a long life for this reaction. It will be emphasized that a novel and careful method for the dealumination, i.e., precise control of temperature and concentration of HCl solution, is required for obtaining the long-life catalyst.

H-mordenite (Norton 100-H; apparent silica to alumina ratio,4) 13.6) was dealuminated in a hydrochloric acid solution. Silicon oil bath equipped with stirrers and heaters was used to heat up the vessel homogeneously. A thermocouple sealed in a 6-mm o.d. glass tube was dipped into the solution; the temperature of solution was monitored with a recorder. Throughout dealumination, the temperature of the solution was controlled precisely in an accuracy of ± 1 K. At the top of the vessel, a water condenser was attached to circulate the vaporized hydrogen chloride. Five grams of zeolite were dealuminated in 113 ml of a hydrochloric acid solution for 24 h. After dealumination, zeolites were filtered and washed with deionized water until no $Cl^-$ was detected with a $AgNO_3$ solution, followed by drying at 393 K.

Conversion of methanol was carried out in a continuous flow reactor. The zeolite (200 mg) was dried at 773 K in a flow of helium, and the experimental run was carried out at 623 K. Flow rate of helium was 40 ml $min^{-1}$ and partial pressure of methanol was 29 Torr (1 Torr = 133.3 Pa). Every one hour, products were collected and flown into gas chromatography; a silicon OV 101 glass capillary column and a squalane on alumina column were used for separation of liquid and gaseous products, respectively.

Acidity of zeolites was measured by temperature programmed desorption (TPD) of ammonia.[5,6]

The activity of methanol conversion on inherent H-mordenite (HM) was diminished rapidly, as shown in Fig. 1. Also on dealuminated mordenite (DM) obtained under usual refluxing conditions, i.e., at boiling point, rapid decline of activity was observed. In the latter case, the initial concentration of hydrochloric acid was 8 mol dm$^{-3}$, and the temperature of the solution attained 380 K. In former papers,[7-12] dealuminations by acid leaching were carried out with 0.1 to 12 mol dm$^{-3}$ of hydrochloric acid at room temperature to boiling point. In particular, refluxing conditions were used usually in order to remove aluminum atoms effectively. However, very little was known about the dependence of the dealumination degree upon experimental conditions. Then, we studied an influence of the temperature of a HCl solution on the degree of removal of aluminum atoms where HCl concentration was kept a constant (8 mol dm$^{-3}$).

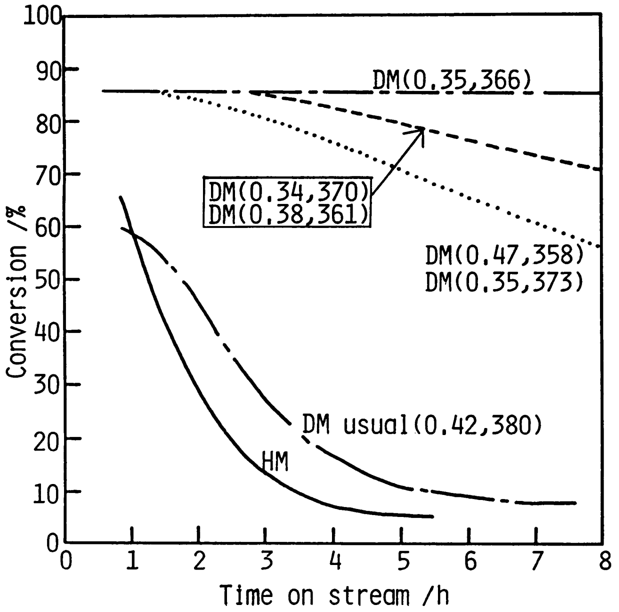

Fig. 1. Decline of activity with time-on-stream: numerical values in parentheses denote Al concentration in mmol g-cat$^{-1}$ and dealumination temperature (K); DM usual, obtained under usual refluxing conditions.

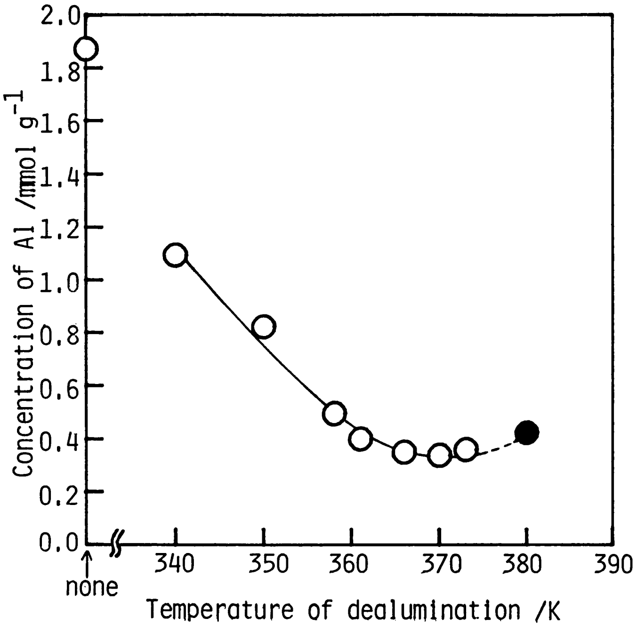

Fig. 2. Dependence of the concentration of Al in the zeolite upon the temperature of dealumination; ●, under usual refluxing conditions; none, inherent HM.

A hydrochloric acid and water system has an azeotropic mixture in the 20.2 wt % of HCl (6.9 mol $dm^{-3}$) where the boiling point 381 K is the maximum temperature of this system. Hydrochloric acid below and above the azeotropic concentration boils at temperatures lower than 381 K, and the boiling point of 8 mol $dm^{-3}$ hydrochloric acid is 375 K. However, under the refluxing conditions described above, the temperature of the solution attained 380 K. This was because hydrochloric acid vapor was lost from the vessel during the dealumination. In fact, the concentration of HCl decreased to 6.1 mol $dm^{-3}$ after the dealumination; loss of HCl was much greater than that required for the dealumination of 5 g of mordenite.[13)] Therefore, in order to maintain the hydrochloric acid concentration, the solution temperature was adjusted below 375 K.

Dealuminated mordenites were thus obtained at 340 to 373 K, and their aluminum concentrations were plotted against the temperature in Fig. 2. The Al concentrations at 361 to 373 K were lower than that obtained under the refluxing conditions. In other words, aluminum atoms were removed effectively under these lower temperatures. Moreover, dealuminated mordenites obtained at 358 to 373 K possessed longer lives for the methanol conversion than that of DM obtained under the refluxing conditions, as was shown in Fig. 1. Especially, the DM (Al conc., 0.35 mmol $g^{-1}$ and obtained at 366 K) had an extremely improved life for the reaction.

The catalyst life was not simply related with the aluminum concentration, since the longest life was not found on the DM with the least Al concentration. Although the acidic profiles were characterized by TPD of ammonia, a simple relationship between the acidity and the catalyst activity was not observed. However, from TPD profiles, relatively strong acidity of the DM obtained under the refluxing conditions was remarkable (temperature maximum of the desorption peak, 677 K on HM; 638 K on DM usual (0.42, 380); 628 K on DM (0.35, 366)).

On the other hand, the distribution of products on these zeolites showed that heavier products such as $A_{10}^{+}$ (aromatics with more than 10 carbons) were enhanced on the long-life catalyst (Fig. 3). Therefore, the durable activity was caused by retardation of formation of coke residue due to the complementary formation of heavy aromatics. Because the coke formation from the heavy aromatics was reported to occur on strong acid sites,[2)] it was suggested that strong acid sites were removed upon dealumination to improve the catalyst life.

In conclusion, lowering the dealumination temperature is effective in maintaining hydrochloric acid in the vessel, thus increasing the degree of dealumination. Besides, the condition of low temperature such as 366 K is important in weakening the acidity of mordenite; it seems that, due to the slow dealumination, aluminum atoms are removed homogeneously from the whole body of zeolite crystal, and homogeneous distribution of aluminum atoms is obtained. When the temperature is lowered further, it will take a longer time to remove aluminum atoms. Therefore, in this communication, it is emphasized that the mordenite activity is improved by the dealumination in the precisely-controlled temperature and acid concentration; as far as the concentration of the HCl solution is 8 mol $dm^{-3}$, the temperature of HCl solution has to be controlled at

366 K.

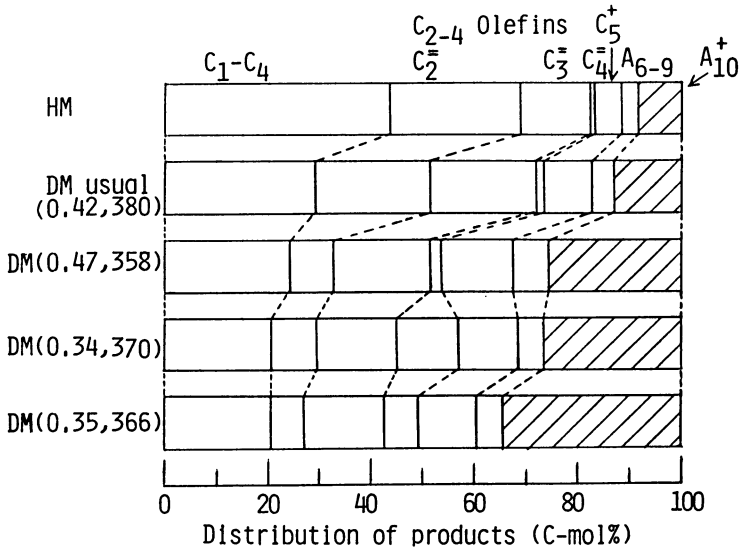

Fig. 3. Distribution of products in the conversion of methanol; C, hydrocarbons with corresponding number of carbons; A, aromatics.

References

1) T.Inui, O.Yamase, K.Fukuda, A.Itoh, J.Tarumoto, M.Morinaga, T.Hagiwara, and T.Takegami, "8th Int. Congr. Catal. Proceedings," Vol. III, Verlag Chemie, Weinheim (1984), p.569.

2) H.Itoh, C.V.Hidalgo, T.Hattori, M.Niwa, and Y.Murakami, J. Catal., 85, 521 (1984).

3) J.Bandiera, C.Hamon, and C. Naccache, " Proceedings of The Sixth International Zeolite Conference," Butterworths, Surrey (1984), p.337.

4) Mordenite Norton 100-H includes 42% of extraframework aluminum atom other than in the tetrahedral sites, as observed by $^{27}$Al MAS NMR.

5) C.V.Hidalgo, H.Itoh, T.Hattori, M.Niwa, and Y.Murakami, J. Catal., 85, 362 (1984).

6) M.Niwa, M.Iwamoto, and K.Segawa, Bull. Chem. Soc. Jpn., 59, 3735 (1986).

7) P.E.Eberly, Jr., and C.N.Kimberlin, Jr., Ind. Eng. Chem., Prod. Res. Dev., 9, 335 (1970).

8) D.K.Thakur and S.W.Weller, J. Catal., 24, 543 (1972).

9) N.Y.Chen and F.A.Smith, Inorg. Chem., 15, 295 (1976).

10) R.W.Olsoon and L.D. Rollman, Inorg. Chem., 16, 651 (1977)

11) A.K.Ghosh and G.Gurthoys, J. Chem. Soc., Faraday Trans., 1, 79, 147 (1983).

12) P.Bodart, J.B.Nagy, G.Debras, Z.Gabelica, and P.A.Jacobs, J. Phys. Chem., 90, 5183 (1986).

13) 0.25 mol dm$^{-3}$ of HCl is required to remove aluminum atoms in the zeolite.

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