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DEALUMINATION OF ZSM-5 ZEOLITE. SELECTIVE REMOVAL OF ALUMINUM ON EXTERNAL SURFACE OF ZEOLITE CRYSTALLITES

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Upon the $SiCl_4$ treatment at 723 - 923 K the dealumination of NaZSM-5 zeolite took place without destruction of zeolite structure. At the higher temperature the more selective removal of framework aluminum on the external surface of zeolite crystallites was performed.

ZSM-5 zeolite exhibits beautiful shape-selectivities for many acid-catalyzed reactions.[1)] The shape-selectivity of ZSM-5 zeolite is caused by its unique pore structure. Therefore, the acid sites, associated with the framework aluminum, not in the pores but on the external surface of ZSM-5 zeolite crystallites do not essentially contribute to the shape-selectivity. If aluminum atoms on the external surface can be selectively removed, the shape-selectivity of ZSM-5 zeolite will be essentially improved.

The dealumination of a zeolite by the treatment with $SiCl_4$ was first reported by Beyer and Belenykaja.[2)] Namely, by treating NaY zeolite with $SiCl_4$ vapor at 730 - 830 K, the Si/Al atomic ratio of NaY was increased from 2.5 to 50 without destruction of zeolite structure. They claimed that the aluminum atoms in the framework of NaY zeolite were substituted by silicon atoms as follows.

$$Na_x[(AlO_2)_x(SiO_2)_y] + SiCl_4 \longrightarrow Na_{x-1}[(AlO_2)_{x-1}(SiO_2)_{y+1}] + AlCl_3 + NaCl$$

In this study, we will examine the dealumination of ZSM-5 zeolite by treating NaZSM-5 with $SiCl_4$ vapor.

HZSM-5 used was prepared in a similar manner described previously.[3)] Its external surface area determined by the pore filled method[4)] was 37 $m^2 \cdot g^{-1}$ and was about 8 % of the total surface area (445 $m^2 \cdot g^{-1}$). The HZSM-5 was transformed into NaZSM-5 by ion exchange. The NaZSM-5 was placed in powder form in a quartz tube reactor and dehydrated for 1 h at 823 K and then for 1/2 h at dealumination temperature (723 - 923 K) in dry helium stream through the 13X zeolite bed. After dehydration the helium sream was saturated at 273 K with $SiCl_4$. The $SiCl_4$ treatment was carried out for 1/6 - 4 h. Then the product was purged with dry helium, washed and transformed into H-form by ion exchange. The bulk Si/Al ratio of HZSM-5 was determined by analyzing the hydrofluoric acid solution of HZSM-5 using an atomic adsorption photometer. The surface Si/Al ratio was determined in a similar manner reported by Finster et al.[5] using a XPS spectrometer (Hewlett Packard 5950A ESCA Spectrometer).

By the $SiCl_4$ treatment the dealumination of NaZSM-5 took place and a white deposite was observed on the interior wall of the reactor outlet. About 70 % of framework aluminum atoms was removed by the treatment with $SiCl_4$ at 923 K for 1 h. If the overall dealumination rate is proportional to both $SiCl_4$ pressure and concentration of framework aluminum (C), it can be expressed as follows.

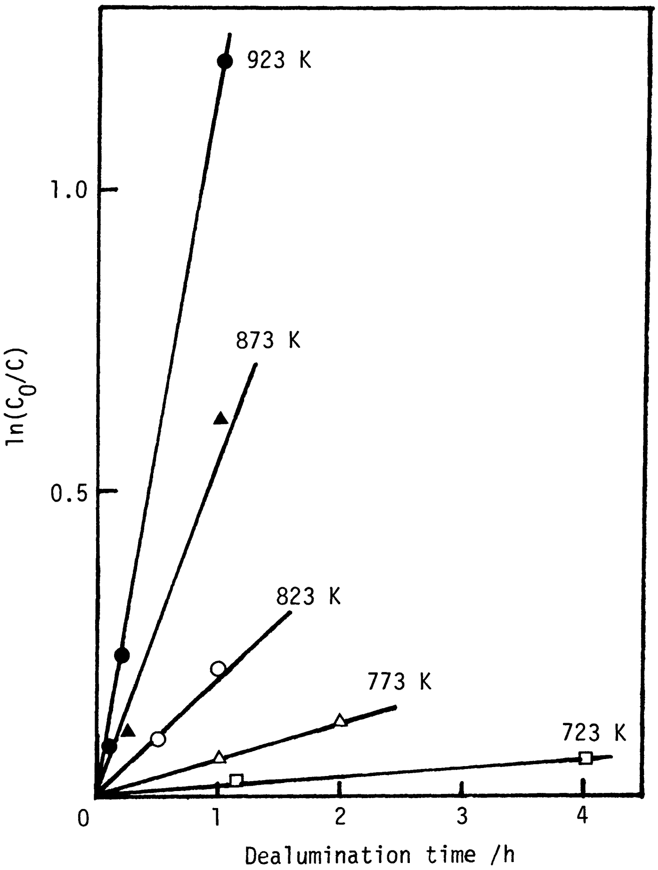
$$-\frac{dC}{dt} = kPC \qquad \text{k; rate constant} \qquad \text{t; dealumination time}$$

P can be regarded as a constant, because the consumption of $SiCl_4$ by the dealumination is very small. Then the following equation is given.

$$kPt = \ln \frac{C_0}{C} \qquad C_0\text{; C at t =0}$$

Fig. 1 shows the relation between $\ln(C_0/C)$ and t at various temperatures. The overall dealumination obeyed the first order kinetics and the rate constant were calculated from the slopes of the straight lines in Fig. 1 and were 0.14, 0.56, 2.0, 6.2, and 11.7 $atm^{-1} \cdot h^{-1}$ for 723, 773, 823, 873, and 923 K, respectively. The apparent activation energy obtained from these values was 134 $kJ \cdot mol^{-1}$.

The HZSM-5 zeolites, which were dealuminated at various temperatures and whose bulk Si/Al ratios were adjusted to 20 - 24 by controlling the dealumination time, were prepared. The surface areas determined by N_2 adsorption at 77 K and the bulk and surface (determined by XPS) Si/Al ratios of these zeolites are summerized in Table 1. The zeolite structure is not destroyed by the $SiCl_4$ treatment, because the surface areas of these zeolites were almost the same as that of the parent HZSM-5. The surface Si/Al ratio increased with increasing



Reaction conditions:
Dehydrated at 823 K for 1 h and at dealumination temperature for 1/2 h.
The initial pressure of $SiCl_4$; 10.5 kPa.
Carrier gas; He, 50 $cm^3 \cdot min^{-1}$.

Fig. 1. Pseudo first oder plots.

Table 1. Properties of dealuminated HZSM-5

Dealumination temperature /K	Dealumination time /h	Si/Al ratio Bulk	Si/Al ratio Surface	Surface area $/m^2 \cdot g^{-1}$
none		19	18	445
723	4	20	20	427
773	2	21	24	439
823	1/2	21	25	422
823	1	24	32	458
873	1/4	21	35	446
923	1/6	24	39	432

dealumination temperatures. Therefore, at the higher temperature the more highly selective removal of framework aluminum atoms on the external surface of zeolite crystallites takes place. This tendency may be explained by assuming that the diffusion of $SiCl_4$ molecules into zeolite pores is very slow and the activation energy for the dealumination without influence of the diffusion is higher than that for the diffusion of $SiCl_4$ molecules into the zeolite pores.

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