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CRYSTALLIZATION OF ZEOLITE ZSM-5 FROM SINGLE CATION SYSTEM

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Crystallization rates of ZSM-5 from the reaction mixture of TPA single cation system was measured in relation with the composition of the reactants. The crystallization rate strongly depended on concentration ratios of the components such as $(TPA)_2O/SiO_2$, SiO_2/Al_2O_3 and H_2O/SiO_2, i.e., it increased along with increasing $(TPA)_2O/SiO_2$ and SiO_2/Al_2O_3 and decreased with increasing H_2O/SiO_2. Na cation did not seem to play a major role in the crystallization from the Na-TPA cation system with SiO_2/Al_2O_3 ratio above ca. 100.

A new kind of high siliceous zeolite, ZSM-5, has been recently announced by Mobil Oil Corporation, which shows outstanding properties as catalysts for a number of industrial processes dealing with hydrocarbons.[1] This ZSM-5 is hydrothermally synthesized in the presence of binary cations containing both of an alkali metal, e.g., Na, and tetrapropylammonium(TPA) in the conventional method.[2] Erdem and Sand[3] have commented that ZSM-5 could not be synthesized in the TPA monocation system. Bibby and coworkers[4] reported the synthesis of Na-free ZSM-5 from the binary cation system including NH_4 and TPA but free from Na. They have also commented that crystalline silicate silicalite-1,[5] the aluminium-free-analogue of ZSM-5, could be prepared from monocation system containing only TPA, although the reaction proceeded very slowly. However, they did not succeeded in preparing aluminosilicate zeolites in the presence of only TPA.

In our recent study, we have found that in the reaction mixture with the specifically defined concentration ratios of the reactants and only one kind of cation of TPA, ZSM-5 has been synthesized whose crystallinity is dependent on the ratios of $(TPA)_2O/SiO_2$, SiO_2/Al_2O_3 and H_2O/SiO_2 in the reaction mixture.

This report described the effect of the composition of the reaction mixture on the crystallization of ZSM-5 in the monocation system containing TPA but free from Na.

The reactant materials used for this preparation were colloidal silica with Na at very low concentration about 300 ppm by weight (Cataloid S-20L from Catalysts & Chemicals Ind. Co., Ltd.), TPA hydroxide (T964 from Tokyo Chemical Ind. Co., Ltd.), aluminum sulfate (1-213 from Wako Pure Chemical Ind. Co., Ltd.) and distilled water with and without sodium hydroxide (S228-01 from Junsei Chemical Co., Ltd.). A reaction mixture was prepared with the technic directed by Argauer and Landolt.[2] The resultant mixture was placed in a Teflon jar and then put in a Teflon lined stainless-steel autoclave and maintained at 150 °C under stirring for crystallization. The crystal structures of the synthesized specimens were identified from their X-ray powder diffraction profiles and their morphology observed with a scanning electronmicroscopy.

The reaction mixture with the composition in the mole ratios of Na/SiO_2: 3.8×10^{-3}, SiO_2/Al_2O_3: 100 and H_2O/SiO_2: 81 was adopted for further studies of the crystallization of ZSM-5. Fig. 1 shows the crystallization curves of ZSM-5 from the reaction mixture with different $(TPA)_2O/SiO_2$ ratio. It can be seen that the crystallization rate strongly depends on $(TPA)_2O/SiO_2$ ratio. That is, ZSM-5 is formed early in the reaction period up to 1 day from the reaction mixture with the higher ratio of $(TPA)_2O/SiO_2$ than 0.2, whereas no crystalline phase is formed even after 5 days from those with the lower ratio than 0.1. This indicates clearly that a higher ratio of $(TPA)_2O/SiO_2$ than about 0.2 is necessary for the formation of ZSM-5 in this system. Assuming that $(TPA)_2O/SiO_2$ ratio in the reaction mixture at constant ratio of H_2O/SiO_2 indicates the alkalinity of the mixture, the higher $(TPA)_2O/SiO_2$ ratio corresponds to the higher alkalinity. The increase of alkalinity effectively induces the dissolution of the amorphous solid in the solution to form soluble active species, and therefore, the crystallization rate would increase with increasing $(TPA)_2O/SiO_2$ ratio. The crystallization occurs rapidly after the induction period for the dissolution, from which the formation of nuclei is suggested as the rate-determining step in the overall process.

In Fig. 2, the crystallinity of ZSM-5 prepared in the reaction mixture with a fixed $(TPA)_2O/SiO_2$ ratio of 0.2 after 3 days of synthesis time was plotted in relation with the SiO_2/Al_2O_3 ratio. The crystallinity of ZSM-5 prepared in the conventional method[6] was also shown for comparison. The increase in the SiO_2/Al_2O_3 ratio seemed to favor the crystallization of ZSM-5 and that this trend is

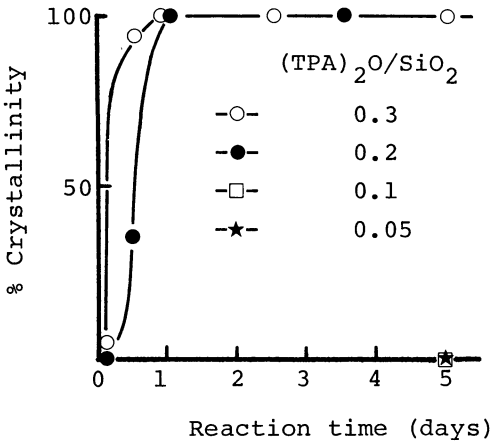

Fig. 1. Crystallization curves of ZSM-5 as a function of $(TPA)_2O/SiO_2$ ratio.

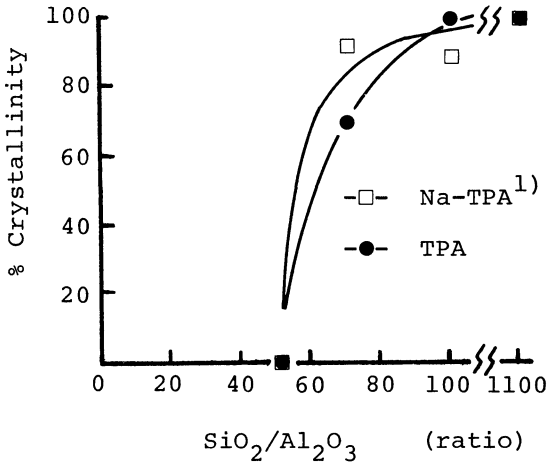

Fig. 2. Effect of SiO_2/Al_2O_3 ratio on ZSM-5 crystallization.
1), Reaction mixture; $(TPA)_2O/SiO_2$=0.2, Na/SiO_2=0.9, H_2O/SiO_2=81.

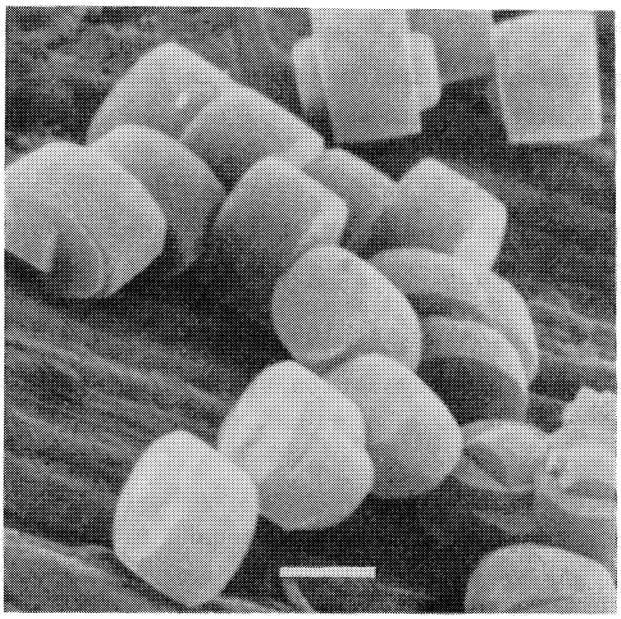

Fig. 3. Scanning electronmicrograph of ZSM-5.
The white horizontal mark corresponds to 2μm.

independent of the cation system whether single TPA or binary Na-TPA. However, at the lower SiO_2/Al_2O_3 ratio than 100, Na-TPA binary cation system bring about the better crystallization than TPA monocation system.

In view of these results, it is concluded that the crystallization rate is strongly dependent on $(TPA)_2O/SiO_2$ and SiO_2/Al_2O_3 ratios and that the higher the ratios are, the faster the crystallization of ZSM-5 proceeds. Besides, it is suggested that Na cation does not play an important role in the Na-TPA binary cation system with SiO_2/Al_2O_3 ratio above 100. We also found that H_2O/SiO_2 ratio also had influence on the crystallization rate. For example, only trace amount of ZSM-5 was formed from the reaction mixture with $(TPA)_2O/SiO_2$ of 0.6, SiO_2/Al_2O_3 of 100 and H_2O/SiO_2 of 140.

Our results are significantly different on some points from those reported by Erdem and Sand[3] and Bibby and coworkers[4] as already mentioned. Such difference would be probably resulted from the difference in the nature of the employed reaction mixtures, that is, the reaction mixtures adopted by them had compositions with lower ratios of $(TPA)_2O/SiO_2$ and/or SiO_2/Al_2O_3 and/or higher ratio of H_2O/SiO_2. In such systems, they observed no formation of crystalline phase and/or the very slow crystallization.

$(TPA)_2O/SiO_2$ and/or SiO_2/Al_2O_3 ratios also have influence on the morphology of ZSM-5. As the ratios increased, the larger, well-defined crystals were formed. Fig. 3 shows the morphology of ZSM-5 prepared in the Na-free-TPA monocation system with $(TPA)_2O/SiO_2$ at 0.3 and SiO_2/Al_2O_3 at 100, which shows different appearance from that prepared in the Na-TPA binary cation system as previously reported.[7]

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