Zeolite ZSM-35 Synthesized by the 'Kneading' Method in a Nonaqueous System

Li Jianquan,[a] Dong Jinxiang,[a] Liu Guanghuan,[a] Gong Shunquan[a] and Wu Feng[b]

[a] *Institute of Special Chemicals, Taiyuan University of Technology, Taiyuan 030024, PR China*
[b] *Department of Chemical Engineering, Beijing Institute of Technology, Beijing 100081, PR China*

The zeolite ZSM-35 has been synthesized from an extremely dense nonaqueous system in which the weight ratio of solid (aluminosilicate gels and NaOH) to liquid (ethylenediamine and triethylamine) mixtures is 2.9 : 1; the product has improved catalytic properties compared with samples prepared by previous methods.

The ZSM family of zeolites has been of interest for the past 20 years because of their useful properties. Improvements in synthetic methods and in the properties of the zeolites obtained continue to be sought. ZSM-35 is a novel high-silica zeolite which was first synthesised by a hydrothermal method using ethylenediamine as the templating agent in an aqueous system.[1] Recently, nonaqueous systems have been developed for zeolite synthesis,[2–10] and ZSM-35 has been prepared in the system ethylenediamine–Na_2O–SiO_2–Al_2O_3–Et_3N.[4–8] Detailed kinetic studies are available.[6] The effects of change of ions (K^+, Na^+) on the properties or ZSM-48 have been studied,[6,7] and Fu-9,[8] ZSM-39 and silicate-1[8] have also been prepared in a nonaqueous system. Nonaqueous systems have many advantages, and a new zeolite, CT-5, has been prepared.[10]

We now report a new method for synthesis of zeolites, which we have termed the 'kneading' method,[11] in which the amount of liquids used is not sufficient to wet all the solid particles so that the conglomerate reactant is actually a mixture of dry powder and small doughy lumps. A homogeneous zeolite product is nevertheless obtained after crystallization. This method has the great advantage that it

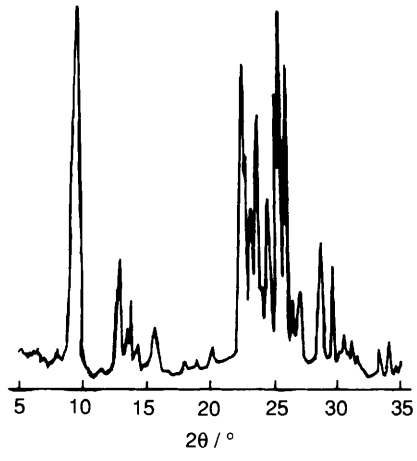

Fig. 1 The XRD pattern of ZSM-35 synthesized by the kneading method

uses a much smaller proportion of amines than the usual nonaqueous methods.[4] The reduction in the proportion of amines rquired leads to an increase in the weight ratio of solid (aluminosilicate gels and NaOH) to liquid ($NH_2CH_2CH_2NH_2$ + Et_3N) in the synthesis system to 2.9, and the molar ratios of SiO_2 to Et_3N and $NH_2CH_2CH_2NH_2$ are 8.7 and 3.9 respectively. The consumption of organic compounds could thus be reduced significantly, and the method does not involve the separation of liquid mixtures before and after crystallization. The ZSM-35 sample prepared by this method shows enhanced catalytic properties compared with the sample prepared by previous methods.

Aqueous aluminium sulfate, sodium silicate and sodium hydroxide were mixed and stirred for 15 min. The precipitate was filtered off, washed, and calcined at 823 K. The aluminosilicate gel thus produced, sodium hydroxide, ethylenediamine and triethylamine were mixed and stirred. An extremely dense mixture was obtained (solid : liquid 2.9 : 1), which was heated in an autoclave at 453–473 K for 60–95 h. The zeolite sample obtained was characterised by its X-ray powder diffraction (XRD) pattern (Fig. 1), which was similar to that reported for ZSM-35.[1] In the product, the molar ratio of SiO_2 to Al_2O_3 is 34.5 and the amine content is 10.41%.

The catalytic behaviour for the isomerization of *o*-xylene of this sample (*B*) and that synthesised by the method in ref. 4 (sample *A*) are compared in Fig. 2. The activity and selectivity for *p*-xylene formation of sample *B* are significantly better than for sample *A*. Both preparation methods involve the use of $NH_2CH_2CH_2NH_2$ and Et_3N but the weight ratio of solid to liquid in the preparation of sample *A* is 0.39, compared with the ratio of 2.9 for sample *B*.

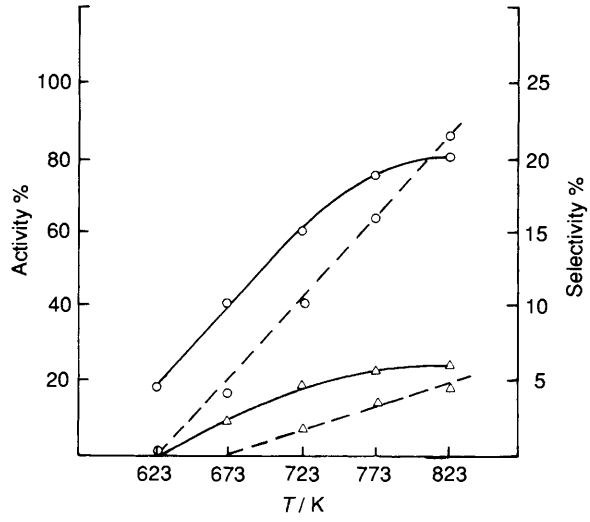

Fig. 2 *o*-Xylene isomerization properties for the two samples: △, sample *A*; ○, sample *B*; full lines, activity; broken lines, selectivity

The marked reduction in the amount of amines used in the 'kneading' method should lead to the lower costs and pollution, and increased productivity because the process is operationally simpler. The product obtained also has improved catalytic properties.

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