A novel method for the preparation of ferrierite zeolite

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A novel method to synthesize zeolites is described. Zeolite ZSM-35 is synthesized in an extremely dense system in which there is almost no mother-liquor separated before and after the crystallization due to the addition of very small amounts of amine and water. The used amounts of amine and water are much less than 1/6 and 1/15 in the usual hydrothermal method respectively. The products are characterised by powder X-ray diffraction and TG-DTA technology.

Keywords: Synthesis; extremely dense system; ZSM-35; method; zeolites

1. Introduction

Traditionally, zeolite is synthesized by the hydrothermal method. But there are many disadvantages in using this method. For example, a large amount of amine is employed as template and drained away after the crystallization, which results in much higher cost, more serious environmental pollution and a much lower productivity due to the large amount of mother-liquor in the reactant system.

Zeolite ZSM-35 is a novel high-silica zeolite which was first reported in 1977 [1]. It was synthesized using ethylenediamine or pyrrolidine as the templating agents in the hydrothermal system. Zeolite ZSM-35 has a good behaviour for xylene isomerization [2]. Recently, ZSM-5 [3], ZSM-35 [3], ZSM-48 [4] and Fu-9 [5] have been prepared from non-aqueous systems. This advanced method increases the molar ratio of solid to liquid phase and the yield per unit volume to a certain extent. But a large amount of organic compounds was still added to the reactant mixture.

A novel method for the preparation of zeolite ZSM-5, the vapour method, was reported [6]. But this method needs a special reactant autoclave in order to separate the reactant mixtures into the solid and liquid phase, and there are a lot of liquid compounds at the bottom of the autoclave. Here, we report a new method to synthesize zeolite, the kneading method. Zeolite ZSM-35 has been prepared by this method which used a paucity of ethylenediamine and H_2O. The molar ratios of H_2O/SiO_2 and R/SiO_2 are 0.47 and 0.1 respectively. So a paucity of liquid com-

pounds was adsorbed by the aluminosilicate gels at once and could not wet all of them when liquid compounds are added to the reactant system. Therefore, there are no mother-liquors separated before and after the crystallization. This method decreases the consumption of liquid compounds and increases the productivity by a great margin. It is a highly efficient and less consumable method.

2. Experimental

2.1. SYNTHESIS

A batch of aluminosilicate gels was prepared by mixing the solutions of aluminium sulphate, sodium silicate and sodium hydroxide [3]. This mixture is filtered washed and dehydrated overnight at 823 K. Then, the stoichiometric amounts of aluminosilicate gels, NaOH, ethylenediamine and H_2O were mixed and stirred. The weight ratio of solid to liquid compounds is 6.0 in the reactant mixtures. The mixtures were heated in a usual autoclave at 453–473 K for 20–45 h. The product is pure ZSM-35. The time of crystallization was measured after the reaction mixture had reached the required temperature. To stop the crystallization process, autoclaves were removed from the air oven and quenched in cold water.

2.2. CHARACTERIZATION

The powder X-ray diffraction data were recorded using Cu K_α radiation on a Rigaku 2304 diffractometer. The thermogravimetric analysis (t.g.) and the differential thermal analysis (d.t.a.) were both carried out at a heating rate of 20 K min^{-1} with a Rigaku PTC-10 thermobalance.

3. Results and discussion

Table 1 shows the compositions of synthesis media used for the preparation of ZSM-35 by the kneading method and the hydrothermal [7] method. It is clear that the molar ratio of SiO_2/H_2O in the reactant mixtures to the kneading method is 15 times higher than that to the general hydrothermal method and the molar ratio of R/SiO_2 to the kneading method is 1/6 less than that to the general hydrothermal method. The used amount of ethylenediamine is saved by a big margin.

Table 1
Synthesis of ZSM-35 by the different methods

Method	Synthesis mixture			
	SiO_2/H_2O	SiO_2/Al_2O_3	R/SiO_2	M/SiO_2
hydrothermal [7]	0.014–0.143	12–60	0.6–1.5	0.07–0.49
kneading	2.14	30.1	0.1	0.17

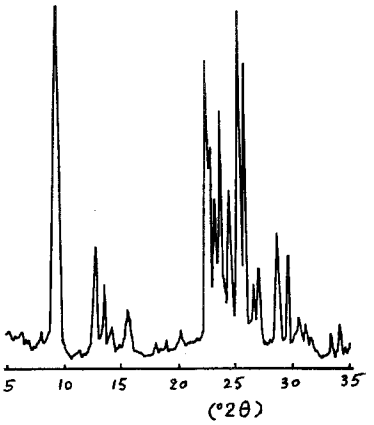

Fig. 1. XRD pattern of ZSM-35 sample synthesized by the kneading method.

Fig. 1 illustrates the XRD patterns of ZSM-35 samples synthesized by the kneading method. The XRD patterns indicate that ZSM-35 synthesized by this method is a product of high crystalline purity. The abovementioned results indicate that addition of a paucity of ethylenediamine as templating agent is enough to form ZSM-35 and a lot of amine and water added in the reactant mixtures, as in the hydrothermal method, is not necessary to synthesize zeolites.

The DTA curves of the two samples (sample A was formed by the kneading method and sample B by the hydrothermal method) are shown in fig. 2. In sample A, the endothermic procedures occur at 368 and 391 K. In sample B, they occur at 350 and 418 K. The weight losses between 298 and 438 K are 11.79 and 9.50% in samples A and B respectively. On the other hand, exothermic reactions are

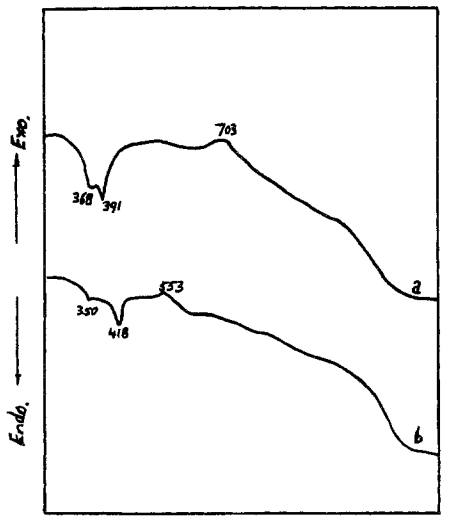

Fig. 2. DTA curves of (a) sample A, (b) sample B.

Table 2
The effect of the different seeds on the product

Sample No.	Seeds		Products	Crystallinity (%)
	type	content [a]		
LL-1	A	1	ZSM-5+SiO_2+trydynite	
LL-2	mordenite	1	ZSM-5+ZSM-35	
LL-3	ZSM-5	1	ZSM-5+ZSM-35	
LL-4 [b]		0	ZSM-35	80
LL-5	ZSM-35	0.5	ZSM-35	89
LL-6	ZSM-35	2	ZSM-35	100

[a] Content (wt%) = (the weight of seeds)/(the weight of aluminosilicate gels) × 100.
[b] No type of zeolite added.

observed at 703 K in sample A and 553 K in sample B. But the weight losses between 438 and 1273 K are similar: 11.53% in sample A and 11.55% in sample B respectively.

The effects of the different crystalline seeds on the products formed by the kneading method are illustrated in table 2. It can be seen that the pure ZSM-35 was not formed when the crystalline seeds of A, mordenite or ZSM-5 were added. These seeds promote formation of ZSM-5. However, the pure ZSM-35 did form whether ZSM-35 seeds were added or not. It also clear that the crystallinity increases with the increase of the amount of seeds.

4. Concluding remarks

A new technique for synthesizing zeolite, the kneading method, is reported, which shows many advantages over the hydrothermal method. We suggest the other framework zeolites could be synthesized by this method. This method probably has a bright future of application in the industry.

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