Journal of Zhejiang University SCIENCE
ISSN 1009-3095
http://www.zju.edu.cn/jzus
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Rapid synthesis of ZSM-5 zeolite catalyst for amination of ethanolamine*

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Received July 7, 2003; revision accepted Nov. 7, 2003

Abstract: ZSM-5 zeolite was rapidly synthesized in system containing ethylenediamine from the initial gel: (5−8) Na_2O: 44 EDA:Al_2O_3:100 SiO_2:4000 H_2O. The crystals were lath-shaped. The effect of pretreatment and alkalinity on crystallinity was investigated. The pretreatment of silicate source can cut down the crystallization time. Tuning the system alkalinity and controlling crystallization time can ensure forming of pure crystal.

Key words: ZSM-5 zeolite, Synthesis, Pretreatment, Alkalinity
Document code: A **CLC number:** TP2032.4

INTRODUCTION

ZSM-5 zeolite is a typical high silica zeolite with MFI-type structure which makes ZSM-5 zeolite widely useful as catalysts in petroleum and petrochemical industry. In recent years, the application of ZSM-5 is expanding into the synthesis fields of specialty and fine chemicals (Davis, 1998), such as the preparation of ethylene amines. The excellent catalytic performance of ZSM-5 was noted (Hua and Hu, 2001).

In most cases, the synthesis of ZSM-5 is achieved by hydrothermal synthesis. The crystallization process and final product are sensitively dependent on the composition of source materials, temperature, time, template agents and other initial conditions of the reaction system. As the crystallization time is relatively long, usually over 3 days, the rapid synthesis of ZSM-5 zeolite in system containing simple amines holds researchers' interests (Hu *et al.*, 2001; Liu and Xiang, 2001). In order to prepare ZSM-5 for amination of ethanolamine, we investigated the effect of pretreatment of silicate source and alkalinity on synthesis of ZSM-5 zeolite, and found a new method with which the crystallization time in ethylenediamine-containing system was shortened greatly.

EXPERIMENTAL

Synthesis of ZSM-5 zeolite

The reactants used were: water glass (Na_2O% = 23%, SiO_2=77%), $Al_2(SO_4)_3 \cdot 18H_2O$(AR), H_2SO_4 (AR), ethylenediamine (AR) and deionized water.

For the pretreatments, the water glass was first aged at 160 °C with stirring for 8 hours (All of the following ZSM-5 zeolite were synthesized with pretreatment unless indicated). Then appropriate amount of so-treated water glass and ethylenediamine (EDA) were added to the deionized water to

* Project (No. 29976036) supported by the National Natural Science Foundation of China

yield solution A, which was rapidly added with rigorous stirring to solution B prepared by resolving $Al_2(SO_4)_3 \cdot 18H_2O$ and H_2SO_4 in deionized water; after which the mixed solution was stirred for about 15 minutes to get a homogeneous gel-mixture which was then transferred to several stainless-steel autoclaves (internal capacity 100 ml) lined with PTFE. The sealed autoclaves were placed in an air oven already maintained at the desired temperature.

At the end of crystallization, the autoclaves were cooled to room temperature. The crystalline product was separated by filtration and washed with deionized water. The product was then dried at 110 °C for 12 hours and calcined at 500 °C for 8 hours.

Some selected experiment data on the composition of source materials and crystallization conditions are listed in Table 1.

Characterization

The crystalline phase synthesized was characterized by using Ni-filtered CuKa-radiation (λ= 0.15405 nm) originating from a Rigaku D/max-2000/PC X-ray generator with a rotating Cu-anode operating at 40 kv and 300 mA at 25 °C. Diffraction was measured with a monochromator from 5° to 50° with a 2θ step interval of 0.02°. The scanning electron microscopy (SEM) analysis of the synthesized materials was made on JEM-200CX transmission electron microscope.

The mole ratio of SiO_2/Al_2O_3 was obtained by conventional chemical analysis. These data also are given in Table 1.

RESULTS AND DISCUSSION

Crystalline phase and morphology

The XRD pattern of sample (Fig.1) indicated that highly crystallized ZSM-5 zeolite formed with- out impurities. The characteristic peaks showed typical MFI-type structure. The morphology of the crystals is lath-shaped (Fig.2).

Influence of pretreatment of water glass

It is well known that aging of gel mixture can affect the nucleation, crystallization, and distribution of crystal size (Zhang *et al*., 1995). But little research has been done to investigate the effect of

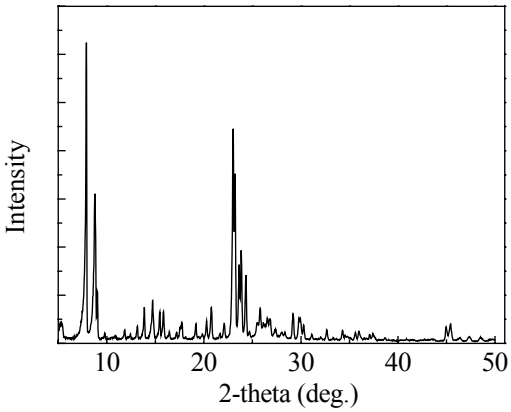

Fig.1 X-ray diffraction patterns of ZSM-5 at 180 ºC, 33 h

Fig.2 Scanning electron micrograph of ZSM-5 at 180 ºC, 33 h

Table 1 Experiment data

NO	Reactant, mole ratio					Crystallization conditions		Product determination	
	Al_2O_3	SiO_2	Na_2O	EDA	H_2O	Temperature (K)	Time (h)	X-ray	SiO_2/Al_2O_3
1	1.0	100	8.0	44	4000	455	33	ZSM-5	68.4
2	1.0	100	5.0	44	4000	455	54	ZSM-5	69.2
3	1.0	100	5.0	44	4000	435	74	ZSM-5	65.2
4	1.0	100	5.0	44	4000	425	85	ZSM-5	66.3

treatment of water glass before the formation of gel. We pretreated the water glass at 160 °C for 8 hours, and compared the crystallization kinetics of systems using pretreated and unpretreated water glass. Fig.3 indicates that under the same temperature and alkalinity, with pretreatment of water glass it only takes 33 hours to obtain fully crystallized zeolite, while 75 hours are needed to obtain fully crystallized zeolite without pretreatment of the water glass. It indicates that pretreatment of water glass can cut down the induction period greatly. Plenty of secondary building units can form during the ageing of water glass at high temperature. And this probably accounts for the shortening of induction period.

Influence of alkalinity

Alkalinity is an important variable during the hydrothermal synthesis of zeolite and can affect the crystallization greatly. Fig.4 show the crystallization curves with different alkalinity at 180 °C. It indicates that high alkalinity can shorten the induction period and accelerate crystallization. When the alkalinity is 8 Na_2O/4000 H_2O, fully crystallized ZSM-5 zeolite was obtained in only 33 hours. The decrease in induction period is attributed to the much greater concentration of reactants dissolved by the alkali. The nuclei will grow quickly because there are more numerous encounters between the precursor species in the solution phase. The enhanced rate of growth after nucleation can be explained by the fact that a greater concentration of dissolved reactant in high alkalinity system allows faster transport to the surface of the growing crystals, higher concentration at the surface, and faster surface reaction to extend to the crystal lattice.

Besides the effect of alkalinity on crystallization, we also found that by tuning the system alkalinity, the formation of other crystals can be controlled efficiently. In a high alkalinity system, the crystallinity will decline after peaking with the extension of time (Curve a in Fig.4). ZSM-5 zeolite is a metastable phase in hydrothermal system, especially when alkalinity is high. It will be re-resolved by hydroxy and be translated to a more stable phase, such as alpha-quartz (α-SiO_2). Fig.5 indicates that with the extension of time, more and more α-SiO_2 formed in high alkalinity system. In the synthesis of ZSM-5 zeolite, α-SiO_2 is always accompanied by ZSM-5 zeolite. The higher the SiO_2/Al_2O_3 of source materials is, the more difficult it is to avoid the formation of α-SiO_2. The conventional method to avoid the formation of α-SiO_2 is to nucleate and crystallize in separate system (Li *et al.*, 1983). We found that formation of α-SiO_2 could be prevented by moderating the alkalinity or controlling crystallization time. When the alkalinity was 5.0 Na_2O/4000 H_2O, no α-SiO_2 formed even if the crystallization time extended to 56 hours.

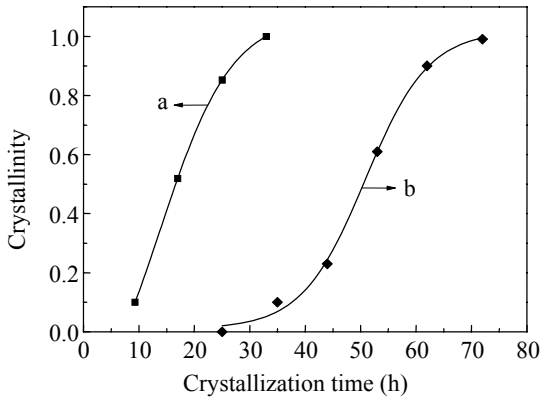

Fig.3 Crystallization kinetics of system at 180 ºC, alkalinity=8.0 Na_2O/4000 H_2O
(a) with pretreatment of water glass; (b) without pretreatment of water glass

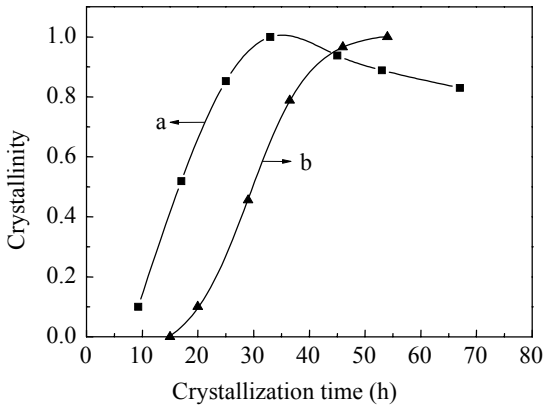

Fig.4 Crystallization kinetics at 180 ºC with pretreatment of water glass but different alkalinity
(a) 8.0 Na_2O; (b) 5.0 Na_2O

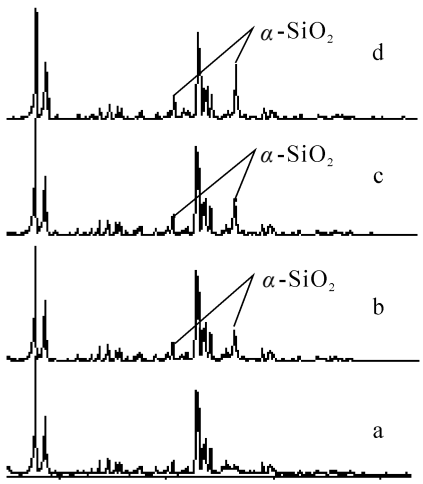

Fig.5 XRD patterns of samples with different crystallization time: (a) 33 h; (b) 45 h; (c) 53 h; (d) 69 h

CONCLUSIONS

1. Pretreatment of water glass at high temperature (e.g. 160 °C) will shorten the induction period greatly in system containing simple amine. As a result the total crystallization time is cut down. For example, at 180 °C, with the pretreatment of water glass at 160 °C for 8 hours, about 33 hours was enough to obtain the fully crystallized ZSM-5 zeolite.

2. Alkalinity can affect the crystallization greatly. Less time is needed for crystallization in higher caustic system, but alpha-quartz will still probably form. By adjusting alkalinity or controlling crystallization time, the formation of α-SiO_2 can be prevented.

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