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A novel approach to synthesize ZSM-23 zeolite involving *N*,*N*-dimethylformamide

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ABSTRACT

A novel synthesis approach for ZSM-23 zeolite involving *N*,*N*-dimethylformamide (DMF) was reported. Multi-techniques, such as XRD, XRF, SEM, TG–DTA, FT-IR, and GC–MS, were employed to investigate the roles of DMF during the synthesis process. It was found that DMF served as template precursor and hydrolyzed to produce dimethylamine (DMA), which acted as the actual structure-directing agent in the crystallization period of ZSM-23 zeolite. At the same time, the complexes of DMF with aluminum ion were formed in the synthesis system. The complexation effect of DMF with aluminum ion promoted nucleation and crystallization of the zeolite. Due to the synergistic effects of the complexation effect between aluminum ion and DMF and the structure-directing effect of DMA in-situ generated by hydrolyzation of DMF, ZSM-23 zeolite could be synthesized in a broad SiO_2/Al_2O_3 range.

1. Introduction

Zeolites and molecular sieves have been of peculiar importance to academic researchers due to the diversity of structures and property. Particularly, aluminosilicate zeolites play an important role in the industrial applications, including catalysis, sorption-separation, and ion-exchange processes, for their uniform pore structure and acids sites [1–6]. ZSM-23 zeolite, an aluminosilicate zeolite with high SiO_2/Al_2O_3 ratio and MTT topology structure, possesses non-interconnected one-dimensional 10-member ring channels and tear-drop-shaped pores with diameter of 0.52×0.45 nm [7]. KZ-1, ISI-4, EU-13, and SSZ-32 zeolites are isostructural types of ZSM-23. ZSM-23 zeolite was first synthesized by Plank et al. using pyrrolidine as template in 1976 [8]. Due to the unique characteristic of the one-dimensional 10-membered channels and acidities, ZSM-23 exhibits excellent catalytic activity and shape selectivity for the hydroisomerization of the long-chain paraffin [9–11], isomerization of xylenes [12,13], and skeletal isomerization of *n*-butylene [14]. Recently, ZSM-23 has been reported as a catalyst to produce ethylene and propylene in catalytic cracking of mixed C4 alkene [15].

More and more interests have been focused on the synthesis strategy of ZSM-23 zeolite due to its potential application in industry [16–21]. A variety of organic amines and quaternary ammonium molecules were used as templates for the synthesis of ZSM-23 zeolite [22–28]. Nevertheless, it is repeatedly stated in some literatures that failure often occurred in the synthesis of pure ZSM-23, sometimes ZSM-5 was formed instead [29–31].

Generally, organic amines and quaternary ammonium molecules are used to synthesize zeolite and molecular sieves as: (i) "true" templates, (ii) structure-directing agents (SDA), and (iii) space-filling species [32]. In the synthesis process, organic compounds are directly introduced at the preparation stage of initial synthesis gels. The compounds play important roles of inducing nucleation, promoting crystallization, determining phase selectivity throughout the synthesis process, and finally occluding into the zeolite framework [33]. The organic molecules maintain their original forms in the whole synthesis process and even in zeolite framework.

In the present work, we described a novel approach for the synthesis of aluminosilicate zeolite involving alkylformamide compounds. Through the introduction of *N*,*N*-dimethylformamide (DMF), we successfully obtained the pure ZSM-23 zeolite in a wide SiO_2/Al_2O_3 range. In the synthesis process, DMF did not directly serve as SDA but hydrolyzed to generate dimethylamine (DMA). The in-situ-generated DMA was the actual SDA to induce the crystallization of ZSM-23 zeolite and finally occluded into the framework of ZSM-23 zeolite. The roles of DMF in the synthesis process were investigated.

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2. Experimental

2.1. Raw chemicals

Aluminum sulfate ($Al_2(SO4)_3.18H_2O$, AR, 99%, Tianjin Kermel Chemical Reagents Development Center), sodium metaaluminate ($NaAlO_2$, AR, 41%, Sinopharm Chemical Reagent Co., Ltd.), sodium hydroxide (NaOH, AR, 96%, Tianjin Kermel Chemical Reagents Development Center), *N*,*N*-dimethylformamide (DMF, AR, 99%, Tianjin Kermel Chemical Reagents Development Center), dimethylamine (DMA, AR, 99%, Tianjin Kermel Chemical Reagents Development Center), ethylenediaminetetraacetic acid tetrasodium salt tetrahydrate ($C_{10}H_{12}N_2Na_4O_8 \cdot 4H_2O$, AR, 99.0–100.5%, Sinopharm Chemical Reagent Co., Ltd.), silica sol (30% SiO_2 in water, Zhejiang Yuda Chemical Co., Ltd.) were used without further purification. The deionized water was made in our laboratory.

2.2. Synthesis of zeolites

The hydrothermal synthesis of ZSM-23 zeolite in the presence of DMF was carried out at 160–200 °C for 2–20 days with a molar ratio of starting gel of SiO_2:Al_2O_3:NaOH:DMF:H_2O = 100:x:y:z: 4500, where x varied from 0.66 to 3.33, y from 35 to 140, and z from 30 to 100, respectively. Silica sol was used as silicon source and aluminum sulfate as the aluminum source. A typical synthesis procedure was described as follows: a clear solution was prepared by mixing 0.55 g aluminum sulfate, 3.6 g water, and 4.1 g DMF under stirring, followed by reacting at room temperature for 6 h. The obtained clear solution was added to a mixture of 2.5 g NaOH, 37 g H_2O and 16.6 g silica sol, giving the gel with a ratio of SiO_2:Al_2O_3:NaOH:DMF:H_2O = 100:1.0:72:67:4500. After stirring for 3 h and ageing for 6 h, the gel was transferred into an autoclave and crystallized at 165 °C for 50 h. The product was collected by filtration, washed with deionized H_2O, and dried in air at 110 °C for 24 h.

2.3. Characterization

X-ray diffraction (XRD) patterns were recorded by Phillips X'Pert Pro X-ray diffractometer using nickel-filtered Cu Kα radiation (λ = 1.54 Å) at 40 kV and 40 mA. The 2θ angles were scanned from between 5° and 65° at a rate of 5° min^{-1}. Chemical composition of the zeolites was measured by X-ray fluorescence (XRF, Philips spectrometer Magix X). Scanning electron microscopy (SEM) images were recorded with a JEOL JSN-6460LV scanning electron microscope. Thermo-gravimetric and differential thermal analyses (TG–DTA) were performed with a Perkin–Elmer Diamond Analyzer. The Samples were stored in a closed vessel over saturated calcium nitrate solution. Ten milligrams of sample were quickly transferred and tested in the temperature range of 20–900 °C with an air flow of 20 ml/min with a heating rate of 10 °C/min. Infrared spectra were recorded with a Bruker EQUINOX55 FT-IR spectrometer. Powder samples were dispersed in KBr pellets for IR analysis. The spectra were recorded in the range between 400 and 4000 cm^{-1} at 4 cm^{-1} resolution and 32 scans. The analysis and determination of organic compounds were performed by a GC–MS system with HP GC6890-MS5973 N combined instruments.

3. Results and discussion

3.1. Synthesis of ZSM-23 zeolite with DMF

A series of synthesis experiments with DMF introduction in initial aluminosilicate gel were performed. Table 1 summarizes the experimental conditions and XRD characteristic results of the as-synthesized samples. The XRD patterns of some samples are shown in Fig. 1, and are in consistent with the reported patterns of MTT zeolite [8,24], indicating that ZSM-23 zeolite was synthesized successfully using DMF.

The results presented in Table 1 showed that through the introduction of DMF into the aluminosilicate gel, ZSM-23 zeolite could form in a broad range of SiO_2/Al_2O_3 molar ratio. Adjusting the SiO_2/Al_2O_3 ratio of the original mixture from 30 to 300, ZSM-23 zeolite could be obtained successfully by varing the crystallization conditions. In the case of SiO_2/Al_2O_3 = 100, ZSM-23 was synthesized with pure phase under crystallization conditions of 160 °C, 50 h. Trace cristobalite was then formed with increasing crystallization temperature to 165 °C, and most of ZSM-23 zeolite was converted to more stable cristobalite when crystallization conditions were changed to 175 °C, 65 h. Reducing the amount of DMF from DMF/SiO_2 = 0.67 to 0.45 had no effect on the synthesis of ZSM-23 zeolite.

3.2. The in-situ-generated template effect of DMF

It seemed that DMF acted as SDA in the synthesis process of ZSM-23 zeolite. In a previous study, by solvothermal synthesis in a quasi-non-aqueous system using DMF, a new microporous aluminophosphate whose structure was close to the sodalite type was obtained. A combined investigation using ^{13}C MAS NMR, ^{1}H MAS NMR, and TG–DTG–DSC confirmed that DMF acted as a true template by filling and stabilizing the sodalite cages [34,35].

IR spectra of as-synthesized samples were recorded to clarify the template occlusion in the zeolite channels. Carboxylic group

Table 1
XRD results of the products synthesized with DMF under different experimental conditions.

Entry	Initial gels		Temperature (°C)	Time (h)	Products	
	SiO_2/Al_2O_3	DMF/SiO_2			Phase	SiO_2/Al_2O_3
1	100	0.67	160	50	ZSM-23	93.8
2	100	0.67	165	50	ZSM-23 + cristobalite (trace)	–
3	100	0.67	175	65	Cristobalite + ZSM-23 (minor)	–
7	100	0.50	165	50	ZSM-23	94.2
8	100	0.45	170	50	ZSM-23	95.1
9	120	0.67	160	50	ZSM-23	112.2
10	150	0.67	160	50	ZSM-23	144.1
11	300	0.67	160	40	ZSM-23	291.7
12	40	0.67	185	65	Amorphous	–
13	40	0.67	185	96	ZSM-23	36.4
14	40	0.67	190	65	Amorphous	–
15	40	0.67	190	96	ZSM-23 + cristobalite (trace)	–
17	30	0.67	195	96	Amorphous	–
18	30	0.67	195	144	Amorphous + ZSM-23 (trace)	–
19	30	0.67	195	240	ZSM-23 (lower crystallinity)	28.2