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Seed-directed and organotemplate-free synthesis of TON zeolite

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ABSTRACT

The seed-directed synthesis of aluminosilicates TON zeolite (denoted as ZJM-4) in the absence of any organic templates under rotation conditions has been developed. Many factors such as the ratios of SiO_2/H_2O, SiO_2/K_2O together with SiO_2/Al_2O_3 in the starting aluminosilicate gel, crystallization temperature as well as crystallization time significantly influence the crystallization of ZJM-4 zeolite. The pure phase of TON zeolite could only be obtained in a narrow phase diagram of K_2O–Al_2O_3–SiO_2–H_2O by a comprehensive consideration of these factors.

1. Introduction

TON type zeolites including ZSM-22, Theta-1, Nu-10, KZ-2, and ISI-1, have a one-dimensional 10-membered ring pore system with medium-sized pores of *ca.* 0.47 nm × 0.55 nm [1,2]. The channels run along the longest dimension of the crystals (crystallographic *c* direction). The unique structure of TON zeolites offers superior catalytic performance in petrochemical processes such as isomerization [3–5], hydroisomerization dewaxing [6], and propylene oligomerization [7]. Generally, TON zeolite can be hydrothermally synthesized from aluminosilicate gels using a series of oxygen or nitrogen containing linear organics as structure-directing agents (SDAs) such as amines [8], α,ω-diamines [9], long-chain polyamines [10], and quaternary ammonium compounds [11]. Up to now, it is still necessary to use organic compounds as SDAs for preparation of TON zeolites, which normally involve in disadvantages in the following: (i) high-cost organic templates, (ii) toxicity of these nitrogen containing organics [12], (iii) production of environmentally undesirable gases by high temperature calcinations for removing these organic templates [13], and (iv) zeolite structure defects formed during high temperature calcinations [14–16]. These drawbacks of organic SDAs in the synthesis of TON zeolites strongly hinder their wide applications in industry. Therefore, it is still challengeable to hydrothermally synthesize pure phase of ZSM-22 zeolite in the absence of organic templates.

Recently, organotemplate-free syntheses of zeolites as green routes have become one of hot topics in the field of zeolite synthesis due to its economical and environmental benefits [17–43]. For examples, ECR-1 [22] zeolite can be prepared by carefully adjusting the molar ratio in the starting gels; ZSM-34 [23,24] can be prepared in the assistance of L zeolite seeds solution; FER [25,26], Beta [27–30,43], FAU [31], RTH [32,33], MTW [34–36], MEL [37], MFI [38–40], SUZ-4 [41] zeolites can be synthesized *via* seed-directed routes. Besides overcoming the use of organic structure directing agents, seed-synthesis of zeolite is able to extend zeolite composition beyond natural limits [28] and also allowed to control zeolite crystals sizes in fluoride media [42]. Notably, seed-directed routes have been proven to be a popular and powerful tool for the syntheses of zeolites in the absence of organic SDAs since it was first reported in 2008 [27]. In the present work, we reported a successful seed-directed and organotemplate-free synthesis of TON zeolites. Very interestingly, compared with seed-directed synthesis of Beta [43], the seed-directed synthesis of ZJM-4 exhibits very high silica utilization.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate (TEOS), aluminum sulfate [$Al_2(SO_4)_3{\cdot}18H_2O$], were purchased from Chinasun Speciality Products Co. Ltd. Potassium hydroxide (KOH) was purchased from Sinopharm Chemical Reagent Co. Ltd. 1,6-hexanediamine (HDA) was purchased from Shanghai Qiangshun Chemical Reagent Co.

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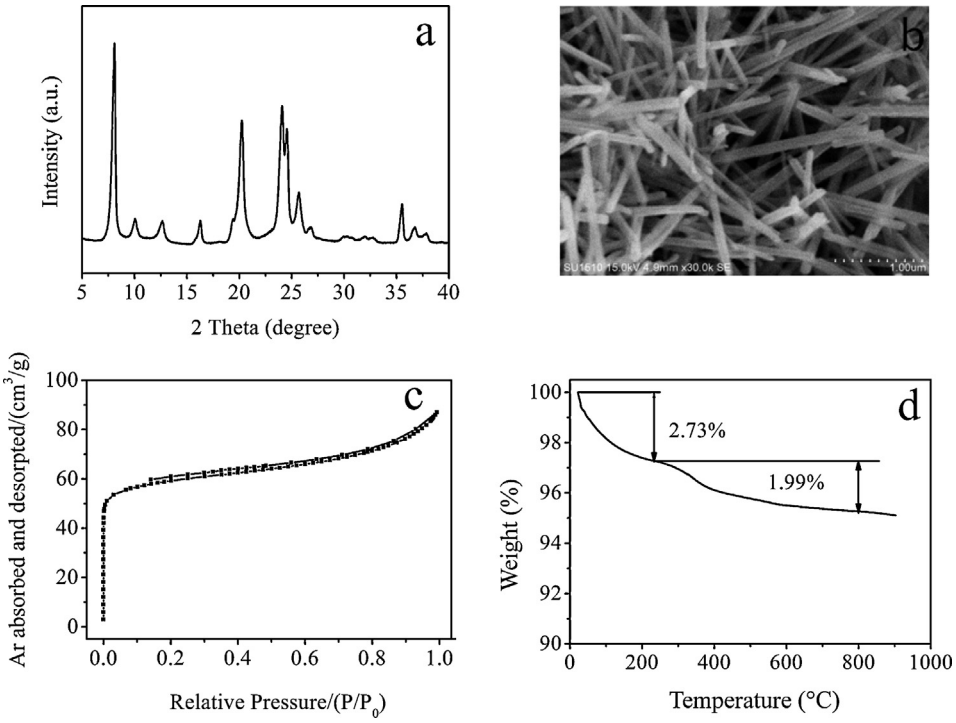

Fig. 1. (a) XRD patterns and (b) SEM image of the as-synthesized ZJM-4 sample, (c) Ar sorption isotherms of the H-form of the ZJM-4 sample, and (d) TG curve of the as-synthesized ZJM-4 sample.

Ltd. Ammonium nitrate was purchased from Chengdu Kelong Chemical Reagent Factory.

2.2. Synthesis

ZSM-22 seeds were prepared according to the literature [1]. As a typical run, 0.18 g of KOH was dissolved in 10.3 g of deionized water, followed by the addition of 0.43 g of 1,6-hexanediamine (HDA) and 0.094 g of $Al_2(SO_4)_3{\cdot}18H_2O$, resulting in a clear solution. Then, 3 g of TEOS were added into the mixture. After stirring for 1.5 h, the aluminosilicate gel (molar ratio at 0.0098 Al_2O_3:1.0 SiO_2:0.089 K_2O:0.257 HDA:40.2 H_2O) was transferred in a Teflon-lined autoclave oven and crystallized at 160 °C for 33 h under rotation conditions (40 rpm). Finally, the product was filtrated, washed with deionized water, dried at 100 °C for 4 h, and calcined at 550 °C.

As typical run for seed-directed synthesis of ZSM-22, 0.18 g of KOH was dissolved in 11.5 g of deionized water, followed by the addition of 0.096 g of $Al_2O_3{\cdot}18$ H_2O, resulting in a clear solution. Then, 3 g of TEOS were added into the mixture. After stirring for 3 h, 0.043 g of calcined ZSM-22 zeolite seeds were added into the mixture. After further stirring for 10 min, the aluminosilicate gel (molar ratio at 0.01 Al_2O_3:1.0 SiO_2:0.095 K_2O:45.0 H_2O) was transferred in a Teflon-lined autoclave oven and crystallized at 140 °C for 48 h under rotation conditions (45 rpm). Finally, the products was filtrated, washed with deionized water, and dried at 100 °C for 4 h. The sample was denoted as ZJM-4.

H-form of ZJM-4 was obtained by ion-exchange with 1 M NH_4NO_3 solution at 80 °C for 1 h (1 g of ZJM-4 zeolite in 50 mL of solution) for three times, followed by calcination at 550 °C for 5 h.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were measured with a Rigaku Ultimate VI X-ray diffractometer (40 kV, 40 mA) using CuKα (λ = 1.5406 Å) radiation. The nitrogen sorption isotherms at the temperature of liquid nitrogen were measured using Micromeritics ASAP 2010 M and Tristar system. The sample compositions were determined by inductively coupled plasma (ICP) with a Perkin-Elmer plasma 40 emission spectrometer. Scanning electron microscopy experiments were performed on Hitachi S-1510 electron microscopes. ^{29}Si and ^{27}Al NMR spectra were recorded on Varian Infinity plus 400 spectrometer fitting the samples in a 7 mm ZrO_2 rotor, spinning at 8 kHz, and chemical shifts were referenced to TMS and Al-$(H_2O)_6^{3+}$, respectively.

Temperature-programmed desorption of NH_3 (TPD-NH_3) curve was carried out with a TCD-detector. As a typical run, 200 mg of H-ZJM-4 was placed in a quartz tubular reactor and pretreated at 500 °C in a nitrogen stream. After cooling to 110 °C, gaseous NH_3 was passed through the sample for 30 min. After removal of physically adsorbed NH_3 by flowing nitrogen for 2 h at 110 °C, the TPD-NH_3 curve of the sample was recorded by programmed heating from 100 to 600 °C with a heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Seed-directed and organotemplate-free synthesis of ZJM-4 zeolites

Fig. 1a shows wide-angle XRD pattern of ZJM-4 sample synthesized in the presence of ZSM-22 seeds (Fig. S1) without using organic templates under rotation conditions. Furthermore, SEM image (Fig. 1b) shows that ZJM-4 has uniform rod-like crystals with length at 2–4 μm and width at 100–200 nm, in good agreement with the typical morphology of TON-type zeolites reported previously [9]. Fig. 1c shows an Ar sorption isotherms of as-synthesized ZJM-4, exhibiting a steep increasing in the curve at a relative pressure $10^{-6} < P/P_0 < 0.01$, which is characteristic of Langmuir adsorption due to the filling of micropores. Correspondingly, HK pore size distribution is estimated at 0.53 nm. The sample gives a BET surface area and microporous volume of 176 m^2/g and 0.06 cm^3/g, respectively. These results confirm the opened