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Synthesis of mesoporous zeolite single crystals with cheap porogens

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ABSTRACT

Mesoporous zeolite (silicalite-1, ZSM-5, TS-1) single crystals have been successfully synthesized by adding soluble starch or sodium carboxymethyl cellulose (CMC) to a conventional zeolite synthesis system. The obtained samples were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), nitrogen sorption analysis, ^{27}Al magic angle spinning nuclear magnetic resonance (^{27}Al MAS NMR), temperature-programmed desorption of ammonia (NH_3-TPD) and ultraviolet–visible spectroscopy (UV–vis). The SEM images clearly show that all zeolite crystals possess the similar morphology with particle size of about 300 nm, the TEM images reveal that irregular intracrystal pores are randomly distributed in the whole crystal. ^{27}Al MAS NMR spectra indicate that nearly all of the Al atoms are in tetrahedral co-ordination in ZSM-5, UV–vis spectra confirm that nearly all of titanium atoms are incorporated into the framework of TS-1. The catalytic activity of meso-ZSM-5 in acetalization of cyclohexanone and meso-TS-1 in hydroxylation of phenol was also studied. The synthesis method reported in this paper is cost-effective and environmental friendly, can be easily expended to prepare other hierarchical structured zeolites.

1. Introduction

Mesoporous zeolite materials are hierarchical porous solids that combined the advantages of both zeolites and mesoporous materials. They can not only maintain the stability and strong acidity but also overcome the diffusion limitation of zeolites. They have been proven to be promising catalysts for the alkylation of benzene with ethane, the cracking of 1,3,5-triisopropylbenzene and cumene, the esterification reaction between benzyl alcohol and hexanoic acid, and so on [1–4]. Up to now, various attempts have been used to synthesize mesoporous zeolites [5,6]. Among all the synthetic methods, there are two basic routes: one is to generate mesopores by treating synthesized zeolites [7,8], such as steaming, acid or alkaline leaching. This method is very simple, but lack of control in generated mesopores. A recent report shows that partial detemplation and desilication can enhance the tailored degree of mesoporosity [9], which will promote the application of this method. The other is to synthesize by templating method. In a typical procedure, the mesopores are generated by the removal of auxiliary templates encapsulated in the zeolite during growth. Due to the special growth mechanism of zeolite materials, the conventional surfactants used in the synthesis of mesoporous materials are not valid in producing mesopores in zeolites. Therefore, selecting suitable template is crucial. Since Jacobsen et al. [10] first reported the preparation of mesoporous zeolite by using carbon particles as a template, many other hard templates, such as carbon nanotube [11], carbon nanofiber [12], carbon aerogels [13,14] and mesoporous carbon [15,16] have been used. Furthermore, some special polymers and supramolecular templates had strong interaction with silica were also used as templates to simplify the synthesis. For example, Wang and Pinnavaia [17] prepared MFI zeolite with small and uniform intracrystal mesopores by using silylated polyethylenimine as template. Xiao et al. [18] synthesized hierarchical mesoporous beta and ZSM-5 by using mesoscale cationic polymers as template. Ryoo et al. [19] obtained mesoporous zeolites with tunable pore size by using organosilane surfactants as supermolecular template. However, most of the templates are expensive and not easily available, result in hampering in their industrial applications. To the best of our knowledge, the synthesis of structure-controllable hierarchical zeolite with cheap and easily available templates was rarely reported. In recent years, several natural resources have been used to synthesize porous materials, for example, Mann et al. [20] fabricated zeolite materials with a hierarchical micro/meso/macrospore organization by using silicalite nanoparticles and starch gel as templates. Bao et al. [21] reported the synthesis of mesopore-modified ZSM-5 zeolites with hierarchical porous structure via adopting tetrapropylammonium hydroxide and starch as co-templates. Xiao et al. [22] obtained

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a hierarchical mesoporous ZSM-5 zeolite by using starch-derived bread as a meso-template.

Here, we also present a facile method by using cheap templates to synthesize mesoporous zeolite single crystal. Soluble starch is a nontoxic, harmless, biodegradable and environmental-friendly renewable natural resource. Sodium carboxymethyl cellulose (CMC) is a derivation of natural cellulose. Both of them are cheap, stable, and have been used in various fields. In this work, they are directly added to the synthesis system as meso-porogen and different type of mesoporous zeolite (silicalite-1, ZSM-5, TS-1) single crystals have been successfully synthesized.

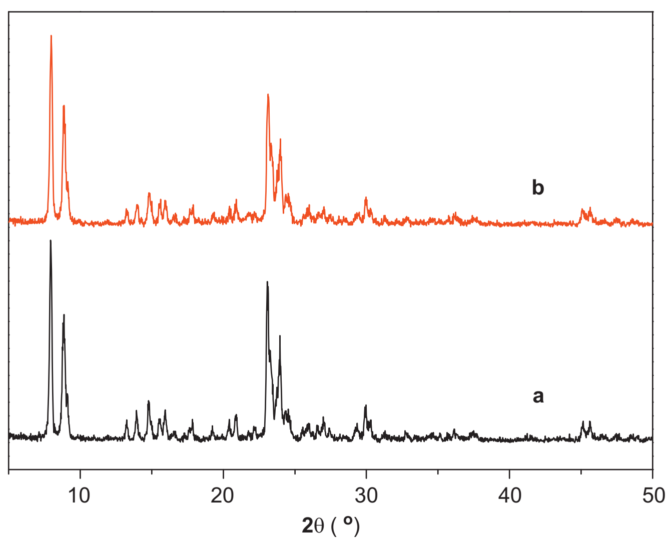

Fig. 1. XRD patterns of mesoporous silicalite-1: (a) S-Silicalite-1 and (b) C-Silicalite-1.

2. Experimental

2.1. Synthesis

The synthesis of mesoporous zeolite was conducted directly under hydrothermal conditions. All the reagents including tetrapropylammonium hydroxide (TPAOH, 20–25 wt%), tetraethyl orthosilicate (TEOS), NaOH, $NaAlO_2$, tetrabutylorthotitanate (TBOT), acetylacetone, soluble starch, sodium carboxymethyl cellulose (CMC) were reagent grade and used without further purifications.

2.1.1. Synthesis of mesoporous zeolites using soluble starch as porogen

In a typical synthesis of mesoporous silicalite-1, 0.032 g of NaOH, 4.8 g of TPAOH, 4.2 g of TEOS and 10.8 g of deionized water were mixed and stirred at 353 K for 4 h, then, 2 g of soluble starch was added. After stirring at 353 K overnight, the mixture was transferred into an autoclave and aged at 453 K for 2 d for further crystallization. The product was collected by filtration, dried in air and calcined at 873 K for 10 h. The obtained mesoporous silicalite-1 was designated as S-Silicalite-1. Furthermore, mesoporous ZSM-5 and mesoporous TS-1 were also synthesized with the similar procedure by introducing aluminum (0.083 g $NaAlO_2$, Si/Al=20) and titanium source (0.174 g TBOT, Si/Ti=40) in the initial synthesis composition. They were designated as S-ZSM-5 and S-TS-1, respectively.

2.1.2. Synthesis of mesoporous zeolites using CMC as porogen

In a typical synthesis of mesoporous silicalite-1, 0.032 g of NaOH, 4.8 g of TPAOH, 4.2 g of TEOS and 10.8 g of deionized water were mixed and stirred at 353 K for 4 h, then, 1.2 g of CMC was added. The other procedures are the same as above. The obtained mesoporous silicalite-1 was designated as C-Silicalite-1. Furthermore, mesoporous ZSM-5 and mesoporous TS-1 were synthesized

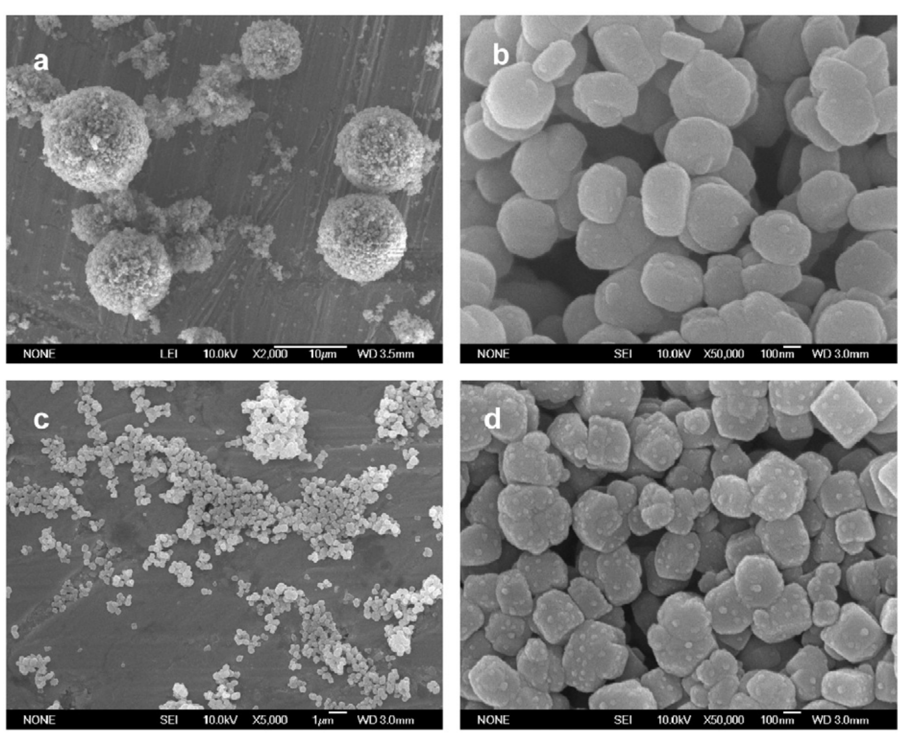

Fig. 2. SEM images of mesoporous silicalite-1: (a, b) S-Silicalite-1 and (c, d) C-Silicalite-1.