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A fast organic template-free, ZSM-11 seed-assisted synthesis of ZSM-5 with good performance in methanol-to-olefin

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ABSTRACT

This work demonstrated a novel and efficient route for preparing ZSM-5 zeolite by adding ZSM-11 seeds in a template-free system. Compared to conventional ZSM-5-seeded synthesis using crystallization time of 36 h, ZSM-11 seeds drove the crystallization of ZSM-5 in much shorter time (12–16 h). Particularly, as used hierarchical ZSM-11 seeds with intergrowth morphology, numerous small ZSM-5 crystals with size of 1–2 μm could be obtained in a very short period (12 h). Both the seed and product zeolites were characterized by XRD, XRF, ^{27}Al MAS NMR, SEM, FTIR and N_2 adsorption–desorption analysis. It was found that the existence of terminal Si–OH units on the surface of ZSM-11 seed particles was principally responsible for the fast crystallization of target ZSM-5 zeolites. Moreover, the external surface area provided by the seeds played a vital role in accelerating the nucleation rate by offering specific sites for the formation of nuclei. When applied in the methanol to olefins (MTO) reaction, small ZSM-5 crystals obtained in the hierarchical ZSM-11-seeded system exhibited both a high selectivity to $C_2^=$–$C_4^=$ olefins and a low deactivation rate. In general, this green synthesis route gives enlightenment for designing the synthesis of zeolites with good performance by using seed crystals with special properties.

1. Introduction

Catalysts based on ZSM-5 zeolites have been widely applied in many areas of petrochemical industry due to their excellent catalytic performance, superior mechanical strength and high hydrothermal stability. Particularly, due to the unique pentasil type structure (MFI), ZSM-5 zeolites exhibit preferable selectivity to light olefins in some important catalytic processes such as catalytic cracking of hydrocarbons to olefins [1–3] or converting methanol to olefins (MTO) [4–6]. Thus, synthesis of ZSM-5 with good catalytic performance has become one of hot topics in the domain of catalysis and material science.

As a kind of high-silica zeolite, ZSM-5 is generally prepared from reaction mixtures containing certain amount of organic templates, which are used as structure directing and charge balancing agents [7–12]. By packing into the cages and channels of zeolites, these organic species can induce the formation of some special framework structures [13]. However, organic template methods have obvious disadvantages like poisonous and expensive. Moreover, these organic species enclosed in zeolitic structures can only be removed by calcination at high temperatures, which inevitably puts a burden on both the energetic consumption and environmental pollution [12,14–16].

In view of this, the template-free synthesis method seems to be more ideal since it not only avoids the high temperature calcination process, but also employs cheaper and less toxic reactants and allows easy waste disposal [17]. Nevertheless, there are still some defects including yielding some impurity phases, generating uncontrollable sized crystals and requiring long crystallization time, etc. [18–20]. Introduction of a little bit of seed crystals to the template-free reaction gel can effectively compensate for these defects mentioned above [21]. By adding seed crystals of desired zeolite into the synthesis batches, the crystallization rate is increased and the formation of undesired phases is suppressed as well [7,21,22]. Furthermore, both the particle size and morphology of product zeolites can be well controlled by adding seeds with various properties. For instance, Ren et al. synthesized submicron ZSM-5 with crystal size in the domain of 270–1100 nm by introducing the pre-prepared silicalite-1 seed solution with crystal size of 90–690 nm [23]. In this study, the as-prepared zeolite crystals revealed a novel core (all-silica) – shell (alumina-containing) structure and the thickness of shell could be easily adjusted by changing the amount of silicalite-1 seeds. Based on the similar seed surface crystallization mechanism, ZSM-5 microparticles with an average diameter up to 8.78 μm have been obtained on the basis of

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commercial ZSM-5 submicron particles [24]. Besides, ZSM-5 nanocrystals were also synthesized by using TPA-containing silicalite-1 seed suspension which contained nano-sized crystal aggregates with an average crystal size of about 80 nm [22]. In this process, two types of crystals were observed, which were formed either by the growth of a single isolated bred (10–30 nm) released from the seed aggregates or by direct growth of the complex aggregates into larger aggregates. Although extensive researches have been reported for the synthesis of template-free ZSM-5, it should be noted that the crystals used to synthesize ZSM-5 generally possess the same MFI framework, which can be regarded as homogenous seeds, despite of in the form of silicalite-1 (all-silica) or alumina-containing ZSM-5.

In this study, we tried a new template-free synthesis route to prepare ZSM-5 zeolites in the presence of seeds with a MEL framework. It is well acknowledged that ZSM-11 possesses the similar framework density and pore size as ZSM-5 except for different channels sinuosity [25–27]. Therefore, ZSM-11 was chosen as the seeds to induce the formation of ZSM-5 phase. To the best of our knowledge, this is the first report on the crystallization of ZSM-5 induced by ZSM-11 seeds in completely template-free systems. In order to reveal the function of ZSM-11 seeds in promoting ZSM-5 crystallization, the kinetics of crystallization as well as crystal size distribution was compared with the conventional ZSM-5 seeded process and its corresponding zeolitic products. Meanwhile, catalytic performance of the obtained ZSM-5 is also investigated in MTO reaction.

2. Experimental

2.1. Reagents

The synthesis of both the seed and product zeolites was performed with colloidal silica (40 wt.% SiO_2, 60 wt.% H_2O, Qingdao Haiyang Chemical Co., Ltd.), aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$, Sinopharm Chemical Reagent Co., Ltd.) and sodium hydroxide (96.0 wt.%, Sinopharm Chemical Reagent Co., Ltd.) as silica source, aluminum source and alkali source, respectively. Tetrabutylammonium bromide (TBABr, 99.0 wt.%, Tianjin Bodi Chemical Reagent Co., Ltd.) or 1,8-diaminooctane (DAOT, 97.5 wt.%, J & K Chemical Ltd.) were used as a template for ZSM-11 synthesis. Additionally, n-butylamine (99.0 wt.%, Tianjin BASF Chemical Co., Ltd.) was used to induce the structure of ZSM-5. All chemicals were used as received without further purification.

2.2. Synthesis of seed crystals

Seed crystals with different frameworks and morphologies were prepared in the presence of organic template and designated as S-*nc*, where $n = 5$ or 11 depending on the type of zeolite framework, while $c = h$ or m, indicating the textural properties of hierarchy or micro-porosity.

Hierarchical ZSM-11 zeolite with intergrowth morphology was synthesized according to literature [28]. Aluminum sulfate was dissolved in distilled water followed by addition of sodium hydroxide and got a clear solution. Then a mixture of silica sol and tetrabutylammonium bromide was added to the solution. After a period of vigorous stirring, the resulting homogeneous gel with the chemical composition of 9.0 Na_2O: 1.0 Al_2O_3: 65 SiO_2: 0.53 $(TBA)_2O$: 1300 H_2O was transferred to a stainless-steel autoclave and subjected to hydrothermal treatment first at 90 °C for 24 h and then at 170 °C for another 24 h. After hydrothermal treatment, the insoluble was separated by filtration, washed with distilled water and dried at 100 °C, followed by the template removal by calcination in air flow at 550 °C for 3 h. Both the microporous ZSM-11 and microporous ZSM-5 zeolites were prepared from the reactant mixture with the same composition as that of hierarchical ZSM-11 except for adding the conventional templates of DAOT and n-butylamine to direct the formation of ZSM-11 and ZSM-5, respectively.

2.3. Seed-assisted, template-free synthesis of ZSM-5

ZSM-5 that synthesized by the organic template-free and seed-assisted route was designated as P-*nc* in accordance with the added S-*nc* seeds. Here, all the template-free synthesis of zeolites were carried out by adding different seeds in the starting Na-aluminosilicate gel with a chemical composition of 9.0 Na_2O: 1.0 Al_2O_3: 65 SiO_2: 1300 H_2O, which was the same as that of the seeds preparation except for the absence of templates.

In a typical run for the seed-assisted synthesis of ZSM-5, aluminum sulfate was dissolved in distilled water, followed by the addition of sodium hydroxide to obtain a clear solution. Then, a mixture of seeds and silica sol diluted by distilled water was added to the former solution at a very slow rate. The amount of zeolite seed crystals was 5 wt.% relative to the total solid content of the initial gel. After being vigorously stirred for some time, the obtained seeded Na-aluminosilicate gels were transferred to stainless-steel autoclaves and left to age at ambient temperature for 48 h. Then the autoclaves were put into the preheated oven at crystallization temperature (170 °C) for different periods under autogenous pressure and static conditions. After predetermined crystallization periods, the prepared well-crystallized solid was separated by filtration, washed several times with distilled water and dried at 100 °C.

2.4. Characterization

All samples were characterized by X-ray diffraction on the X'Pert PRO MPD (PANalytical Co.) diffractometer at 40 kV and 40 mA with Cu Kα radiation at a scanning rate of 2 °/min in the 2θ range from 4.5 to 65°. The characteristic vibration bands of the zeolite particles were confirmed by FTIR on a Nexus Model Infrared Spectrophotometer (Nicolet Co, USA). In order to obtain the spectra representing various OH groups, pure zeolite samples were pressed into a self-supporting wafer and dehydrated in an O_2 flow while heating from room temperature to 550 °C at a heating rate of 5 °C/min. After an isothermal period of 1 h at 550 °C, the sample was evacuated for 1 h at 550 °C and cooled to room temperature in vacuum, then followed by the recording of spectra. Particle size and crystal morphology of the samples were examined with a scanning electron microscopy (SEM), which was carried on a S4800. Nitrogen adsorption–desorption experiments at 77 K were conducted in an Autosorb instrument (Quantachrome). The total surface (S_{BET}) was calculated according to the (Brunauer–Emmet–Teller) BET isothermal equation, and the total volume (V_{total}) was determined from the nitrogen adsorbed volume at $P/P_0 = 0.990$. Both the micropore surface area (S_{micro}) and the micropore volume (V_{micro}) were calculated by application of the t-plot method. The external surface area (S_{ext}) and mesopore volume (V_{meso}) were obtained by the calculated total data minus the corresponding micropore data. The acid properties of samples were measured by ammonia temperature programmed desorption (NH_3-TPD) on TP-5078. X-ray fluorescence spectroscopy (Axios) was used to analyze the composition of Si and Al in all the seed and product samples. ^{27}Al MAS NMR spectra were recorded on a Bruker AV-400 NMR spectrometer with spinning rate of 10 kHz and delay time of 7 μs. The solution of $Al(NO_3)_3$ was used as reference.