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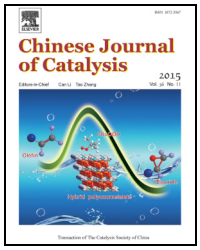

Article

Facile preparation of nanocrystal-assembled hierarchical mordenite zeolites with remarkable catalytic performance

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ABSTRACT

The present study reports a novel strategy to fabricate nanocrystal-assembled hierarchical MOR zeolites. This is the first demonstration of hierarchical MOR without preferential growth along the *c*-axis, which facilitates mass transfer in the 12-membered ring channels of MOR zeolite for the conversions involving bulky molecules. The facile method involves the combined use of tetraethylammonium hydroxide (TEAOH) and commercial surfactants, in which TEAOH is essential for the construction of nanocrystal assemblies. The surfactant serves as a crystal growth-inhibiting agent to further inhibit nanocrystalline particle growth, resulting in enhanced mesoporosity. The hierarchical MOR assembled particles, constructed of 20–50-nm crystallites, exhibit superior catalytic properties in the alkylation of benzene with benzyl alcohol compared with the control sample, as the hierarchical MOR possesses a larger external surface area and longer *c*-axis dimension. More importantly, the material shows improved activity and stability in the dimethyl ether carbonylation to methyl acetate reaction, which is a novel route to produce ethanol from syngas.

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1. Introduction

Zeolites are important heterogeneous catalysts in oil refining and petrochemical industries because of their unique pore structures, large surface area, strong acidity, and excellent hydrothermal stability [1,2]. Mordenite (MOR), one of the most important members in the zeolite family, has exhibited excellent performance in catalysis, such as toluene disproportionation, hydroisomerization, alkylation, dimethylamine synthesis, and dimethyl ether carbonylation [3–5]. The channel system of MOR zeolite consists of a straight 12-membered ring (MR) channel (0.65 nm × 0.70 nm), a compressed 8-MR channel (0.26 nm × 0.57 nm) parallel to the *c*-axis, and an additional 8-MR channel (0.34 nm × 0.48 nm) along the *b*-axis [6]. However, MOR is generally referred to as a one-dimensional zeolite as the 8-MR channels are too small for most molecules to ingress. This unique pore structure may impose severe diffusion limitations in catalytic processes, leading to underutilization of the active sites and resulting in rapid deactivation, especially for the reactions involving bulky molecules [7–9]. In recent years, the quest for enhancing the catalytic efficiency and prolonging catalyst life has stimulated much research on improv-

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ing the mass transport properties.

Integrating mesopores into the zeolite structures or decreasing the crystal size has proven to be an effective way to overcome the inherent diffusion limitations and improve the catalysis efficiency of zeolites [10–23]. Mesoporous MOR zeolites are hitherto mainly synthesized *via* a top-down approach through dealumination or sequential dealumination-desilication treatment [9,24,25]. A one-step, bottom-up synthesis of mesoporous MOR is highly desirable; however, this remains a challenging task, despite the significant developments in the synthesis of hierarchical zeolites, such as ZSM-5 and beta. Recently, Xiao and co-workers [26] successfully synthesized micro-sized MOR nanofiber bundles when assisted by a self-designed cationic copolymer containing quaternary ammonium groups. Jo and Ryoo et al. [27] reported a zeolite-seeding route to synthesize mesoporous MOR zeolite with nanorod-like morphology by employing organosilane surfactants as a mesopore-generating agent. Very recently, Li and co-workers [28] synthesized H-MOR nanosheet assemblies through a conventional hydrothermal reaction in the absence of templating agents. However, the above-mentioned MOR nanofibers and nanorods show a narrowed *a*-*b* cross section, whereas the growth along the *c*-axis direction is less inhibited, suggesting that the 12-MR channels in these hierarchical MOR zeolites have the longest dimension and implying that the mass transport in this direction remains restricted.

Synthesis of zeolite nanocrystals with reduced size in three dimensions decreases the diffusion pathway irrespective of the direction of travel. There are, however, only a few examples reported where nanocrystalline MOR have been effectively synthesized in such a manner. Kubota's group [29] has reported the preparation of MOR nanocrystals of ~80 nm in diameter using a hydrophobic structure-directing agent, *N*,*N*,*N*',*N*'-tetraethylbicyclo[2.2.2]oct-7-ene-2,3:5,6-dipyrrolidinium. In addition, the divalent cation *N*,*N*,*N*,*N*',*N*',*N*'-hexaethylpentanediammonium was also reported to direct the synthesis of nanoscale MOR [30,31]. Recently, Ryoo *et al.* [32] developed a multivalent surfactant-capping route to synthesize nanocrystalline zeolites including MOR, FAU, CHA, and MFI. By using a self-designed prolinol derivative surfactant $C_{18}H_{37}N^+(Me)_2C_6H_{12}N^+(CH_3)_2CH_2C_6H_4CH_2N^+(CH_3)(C_4H_7CH_2OH)$ as a capping agent, MOR nanocrystals could be readily prepared. They attributed the nanocrystal formation to the multiple valencies on the surfactant and thereby the introduction of a strong binding effect of the surfactant molecules on the substrate surfaces compared with monovalent surfactants.

Herein, we report a facile and direct approach to synthesize nanocrystal-assembled hierarchical MOR zeolites by subjecting the crystallization to relatively low temperatures (130 °C) in the presence of tetraethylammonium hydroxide (TEAOH) and commercial surfactant. The role of TEAOH and surfactants in the generation of the hierarchical assembled structure is investigated in detail and the physicochemical properties of the products are well characterized. The catalytic performance of the hierarchical MOR zeolites is evaluated *via* the benzylation of benzene with benzyl alcohol (BA) and compared with the control sample and hierarchical MOR having nanosheet-assembled morphology with a longer *c*-direction dimension. In addition, the hierarchical zeolite is applied as a catalyst for the dimethyl ether (DME) carbonylation to methyl acetate (MA) reaction, which is a novel route to produce ethanol from syngas.

2. Experimental

2.1. Materials and synthesis

The chemical reagents used in the experiments included $NaAlO_2$ (54.5% Al_2O_3, 40.9% Na_2O, Tianjin Guangfu Chemical Co.), colloidal silica (30.1% SiO_2, Qingdao Chengyu Chemical Co.), TEAOH (25.0% in water, Xiamen Pioneer Technology Co., Ltd.), NaOH (Tianjin Kemiou Chemical Reagent Co.), $C_{12}H_{25}$-$N^+(CH_3)_2$-C_2H_4-$N^+(CH_3)_2$-$C_{12}H_{25}Br_2$ ($C_{12\text{-}2\text{-}12}$, Henan Titaning Chemical Technology Co.), hexadecyltrimethylammonium bromide (CTAB, Energy Chemical), sodium dodecylbenzenesulphonate (SDBS, Energy Chemical), and Pluronic F-127 (M_r = 12600 g/mol, Sigma). All the above reagents were used without further purification.

A typical synthesis procedure was as follows. NaOH and surfactant ($C_{12\text{-}2\text{-}12}$) were dissolved in H_2O to prepare a clear solution. Thereafter, TEAOH was added to the solution dropwise followed by the addition of $NaAlO_2$. Then, colloidal silica was added to the mixture under vigorous stirring. The final mixture with a composition of SiO_2:0.033Al_2O_3:0.25Na_2O:0.10TEAOH:0.05$C_{12\text{-}2\text{-}12}$:40$H_2O$ was stirred for additional 3 h to obtain a homogenous gel prior to being transferred into a stainless steel autoclave. The sol-gel was subjected to hydrothermal crystallization at 130 °C for 5–7 d and rotated at 60 rpm. The products were recovered by centrifugation, washed with deionized water, dried overnight at 120 °C and finally calcined at 550 °C for 5 h to remove the organic species. The protonated samples were obtained by ion exchange with NH_4NO_3 aqueous solution (1 mol/L, 1 g calcined sample in 10 mL solution) at 80 °C under stirring. The ion exchange was repeated three times and every ion exchange solution was for 2 h. The samples were recovered by centrifugation, washed with deionized water, and dried at 120 °C before calcination at 550 °C for 4 h.

2.2. Characterization

Powder XRD patterns were recorded on a PANalytical X'Pert PRO X-ray diffractometer with Cu K_α radiation (λ = 0.154059 nm) and a scan step width of 0.026°. The chemical composition of the samples was measured using a Philips fluorescence (XRF, Magix-601 X-ray) spectrometer. Morphology was observed using scanning electron microscopy (SEM, SU8020). N_2 adsorption-desorption isotherms were obtained on a Micromeritics ASAP 2020 system at –196 °C. The total surface area was calculated based on the BET model. Micropore volume and micropore surface area were calculated using the *t*-plot method. Pore size distribution of the mesopores was determined by the BJH method based on the desorption branch of the isotherms.

Solid state NMR experiments were performed on a Varian

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