



Direct synthesis of hierarchically structured MFI zeolite nanosheet assemblies with tailored activity in benzylation reaction



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ABSTRACT

The MFI zeolites with nanosheet morphology were prepared by a seed-assisted strategy using specially designed bolaform surfactant $[\text{C}_6\text{H}_{13}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-(CH}_2\text{)}_{12}\text{-O-(p-C}_6\text{H}_4\text{)}_2\text{-O-(CH}_2\text{)}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{13}] [\text{Br}^-]_4$ ($\text{C}_{6-12}\text{-diphe}$) as a structure-directing agent. The MFI zeolite nanosheet assemblies were composed of MFI nanosheets with randomly organized structure, exhibiting a narrow mesopore distribution. By tuning the Si/Al ratios of MFI zeolite nanosheet assemblies from 60 to 10, the morphology of resultant zeolites changed from nanosheet stacks to house-of-cards-like structures, and to nanosponges. In addition, the porosity and Brønsted acid/Lewis acid ratio exhibited a parabola-type dependence on the Si/Al ratios of obtained zeolites, indicating that meso-/microporosity and acidity of MFI nanosheet assemblies can be systematically tailored by changing the constituents of zeolites. Catalytic performance of MFI zeolite nanosheet assemblies was investigated in the benzylation of benzyl alcohol with mesitylene. The results revealed that MFI zeolite nanosheet assemblies exhibited extraordinary catalytic activity compared to conventional ZSM-5 zeolite. The conversion of benzyl alcohol and selectivity (1,3,5-trimethyl-2-benzylbenzene vs dibenzyl ether) of zeolite catalysts were linearly dependent on the Brønsted acid/Lewis acid ratio, and they exhibited a parabola-type dependence on the $S_{\text{ext}}/S_{\text{BET}}$, indicating that a balance between acidity and porosity of zeolites can be realized to modulate the catalytic properties of MFI zeolite nanosheet assemblies guided by $\text{C}_{6-12}\text{-diphe}$.

1. Introduction

Zeolites are crystalline microporous solids with high surface area and ordered pore and channel system. They are widely used in the field of catalysis, adsorption and separation owing to their well-defined frameworks [1–7]. The sole presence of micropores in traditional zeolites, however, limits its practical application involving large molecules due to the small pore size and narrow channel apertures. Considerable efforts have been placed to overcome the diffusion limitations caused by the sole micropores [8–10]. Hierarchically structured zeolites containing extra mesopores in addition to the inherent micropores of zeolites have been intensively investigated in the past decades [11–16] to improve mass transportability of guest molecules and enhance the accessibility of active sites in zeolite catalysts.

Two dimensional zeolites (2D zeolites), in which the third dimension is limited to ~ 2–3 nm corresponding to 1–2 unit cell [17], are ideal candidates in the field of catalysis owing to their large surface areas, open porous structures and exposed active sites in comparison to conventional three dimensional (3D) zeolites. Unfortunately, up-to-

date, only about 15 zeolites have been found to possess such 2D layered form [18]. Generally, the synthesis routes for 2D zeolites can be categorized into three different approaches [19]: i) hydrothermal synthesis; ii) surfactant-templated synthesis; and iii) 3D to 2D transformation. Among these approaches, surfactant-templated synthesis of zeolites is one of the most important discoveries in zeolite science [20]. In 2009, a breakthrough was made by Ryoo et al. [21] in which an ultrathin MFI zeolite nanosheets with 2.0 nm thickness layer along the b-axis corresponding to one unit cell was synthesized by employing a diquaternary ammonium surfactant. Based on the synthesis condition, the MFI zeolite nanosheets could be obtained in the form of unilamellar MFI nanosheets or multilamellar stacked MFI nanosheets. The unilamellar MFI nanosheets were composed of single MFI layer. After removing the surfactants under high temperature, the calcined samples exhibited a surface area of $710\text{ m}^2\text{ g}^{-1}$. However, they showed a rather broad mesopore size distribution due to the disordered assemblies of the zeolite nanosheets. For multilamellar MFI zeolite nanosheets, these samples were arranged in a regular way along b-axis, resulting in the formation of uniform mesopores between neighboring nanosheets.

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Nevertheless, the ordered mesopores were lost during calcination procedures.

An effective approach to inhibit the collapse of MFI zeolite layers is to introduce pillars in the interlayer space to maintain the ordered mesoporous structure in the zeolite. In 2010, Ryoo and coworkers reported a method to retain the ordered structure of multilamellar MFI zeolite nanosheets through the intercalation of silica pillars in the spacing between neighboring MFI layers [22]. However, these silica pillars were sensitive to humidity and easily disintegrated under ambient condition. Besides, these materials were firstly synthesized by using specially designed bifunctional surfactants as the templates followed by treatment of tetraethoxysilane solution prior to templates removal, and then they can be transformed into pillar through the calcination. Thus, the relatively complicated synthesis process limits its practical application [23]. Recently, Tsapatsis et al. [24] and Che et al. [25] successfully synthesized self-pillared MFI zeolites by employing tetrabutyl-phosphonium hydroxide and bolaform amphiphilic surfactant as the structure directing agents, respectively. Nevertheless, the orthogonally connected MFI zeolite nanosheets reported by Tsapatsis et al. exhibited a broad mesopore distribution. In addition, it is not easy to tune the Si/Al ratio with high Al content. On the other hand, the house-of-cards-like MFI zeolite nanosheets reported by Che et al. collapsed to single crystals after removing the templates under high calcination temperature.

Recently, MFI zeolite nanosponges containing three dimensional disordered networks of nanosheets have been vigorously investigated [23,26–28]. The MFI nanosheets assemble in a self-bridged way to maintain their mesopores with uniform diameters. The MFI zeolite nanosponges can be obtained by seed-assisted method. This method not only produces mesoporous MFI nanosheets with uniform diameters but also shortens the hydrothermal synthesis time. Besides, these MFI zeolite nanosponges showed significantly enhanced hydrothermal and mechanical stabilities than pillared MFI zeolites [23]. Furthermore, MFI zeolite nanosponges exhibited high reaction activity and long life time in the Pechmann condensation reaction and liquid-phase Friedel–Crafts alkylation reaction involving bulk reactants [26,28].

In the present research, inspired by the structure of MFI zeolite nanosponges that have the nanosheet assemblies' structure facilitating the transport of bulk molecules, we report a facile one step synthesis method to fabricate hierarchically structured MFI zeolite nanosheet assemblies. The rigid bolaform quaternary ammonium surfactant with the formula of $[\text{C}_6\text{H}_{13}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-(CH}_2\text{)}_{12}\text{-O-(p-C}_6\text{H}_4\text{)}_2\text{-O-(CH}_2\text{)}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{13}] [\text{Br}^-]_4$ was employed as the bifunctional templates since the strong π - π stacking interactions in the surfactant helps to stabilize the micelle structure, while a small amount of conventional MFI zeolite was used as crystallization-accelerating seeds to induce the formation of MFI zeolite nanosheet assemblies. To the best of our knowledge, synthesis of MFI zeolite nanosheet assemblies using bolaform surfactants as the bifunctional template, has not been reported. The chemical constituent (Si/Al ratio) of MFI zeolite assemblies was systematically modulated and their consequences on zeolite morphology and porosity were also studied. Furthermore, the effect of hierarchical structure and constituent of MFI zeolite nanosheet assemblies on the catalytic activity of benzylolation of mesitylene with benzyl alcohol were investigated to reveal the relationship between MFI zeolite nanosheet assemblies' structure and catalytic properties.

2. Experimental

2.1. Materials for catalyst synthesis and reaction

Tetraethyl orthosilicate (TEOS, 98%, analytical reagent), Ethanol (> 99%, analytical reagent), Acetonitrile (> 98%, analytical reagent), Toluene (> 99%, analytical reagent), Ether (> 98%, analytical reagent), Benzyl alcohol (> 98%, analytical reagent) and N-dodecane

(> 98%, analytical reagent) were purchased from Damao Chemical Reagent Factory. Ammonium nitrate (> 98%, analytical reagent) was purchased from Guangzhou Chemical Reagent Factory. Potassium hydroxide (> 90%, analytical reagent), Sodium hydroxide (> 97%, analytical reagent), Sodium aluminate (44.7 wt% Na_2O , 52 wt% Al_2O_3) and 1,3,5-Trimethylbenzene (> 97%, analytical reagent) were purchased from Aladdin. 4,4'-Biphenol (> 98%), 1,12-Dibromododecane (> 98%), N, N, N, N-tetramethyl-1,6-hexanediamine (> 98%) and 1-Bromohexane (> 98%) were purchased from Energy Chemical.

2.2. Synthesis of bolaform quaternary ammonium surfactant

The rigid bolaform quaternary ammonium surfactant was synthesized using the method described in our previous research work [29]. First, 0.01 mol 4,4'-dihydroxybiphenyl (99%, J&K) was dissolved in 80 mL hot ethanol consisting of 0.02 mol potassium hydroxide. After that, 0.05 mol 1,12-dibromododecane was slowly added to the mixture above under stirring in N_2 environment. The mixture was then refluxed under stirring for 20 h at 80 °C. After the mixture has been cooled down to room temperature and solvent has been evaporated, the precipitated product with the formula of $\text{BrCH}_2(\text{CH}_2)_{10}\text{CH}_2\text{-O-(p-C}_6\text{H}_4\text{)}_2\text{-O-CH}_2(\text{CH}_2)_{10}\text{CH}_2\text{Br}$ (denoted as $\text{C}_{12}\text{-diphe-12}$) was collected by filtration and washed repeatedly with hot ethanol, and dried in a vacuum oven at 50 °C for 12 h. Next, 0.03 mol $\text{C}_{12}\text{-diphe-12}$ and 0.06 mol N,N,N',N'-tetramethyl-1,6-hexanediamine (99%, J&K) were dissolved in 50 mL acetonitrile/toluene mixture (1:1 v/v) and refluxed at 70 °C for 10 h under N_2 environment. After cooling to room temperature and solvent evaporation, solid product with the formula of $[\text{C}_6\text{H}_{13}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-(CH}_2\text{)}_{12}\text{-O-(p-C}_6\text{H}_4\text{)}_2\text{-O-(CH}_2\text{)}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{12}\text{-N}^+(\text{CH}_3)_2\text{-C}_6\text{H}_{13}] [\text{Br}^-]_4$ was formed, designated as $\text{C}_{6-12}\text{-diphe}$.

2.3. Synthesis of the MFI zeolite nanosheet assemblies

MFI zeolite nanosheet assemblies were synthesized through a seed-assisted hydrothermal approach using $\text{C}_{6-12}\text{-diphe}$ as dual functional template. In a typical synthesis of MFI zeolite nanosheet assemblies, 0.05 g conventional MFI zeolite (Si/Al = 14, Nankai University Catalyst Co., LTD) was dispersed in 8.8 mL of 1.0 M NaOH solution. The mixture was stirred at 60 °C for 10 h. Then 2.1 g $\text{C}_{6-12}\text{-diphe}$ surfactant was added to the mixture, and the solution was stirred at 60 °C for 1 h (solution A). Meanwhile, 0.13 g NaAlO_2 (44.7 wt% Na_2O , 52 wt% Al_2O_3 , J&K) was dissolved in 21.3 mL deionized water, and this mixture was stirred at ambient temperature for 2 h (solution B). Solution A was slowly added to the solution B under magnetic stirring condition. This mixture was stirred for 1 h at room temperature to obtain solution C. After that, solution C was added to 8.3 g tetraethylorthosilicate (TEOS, 98%, J&K) and the mixture was vigorously stirred at 60 °C for 10 h to form the final gel. The final synthesis gel had a molar composition of 16.28 Na_2O : 125 SiO_2 : x Al_2O_3 : 5 $\text{C}_{6-12}\text{Br}_4$: 500 EtOH: 5000 H_2O , where x = 1.25, 2.00 and 4.00. The resultant gel was transferred to Teflon-lined stainless steel autoclave and was heated to 150 °C for 4 days under rotating condition. After crystallization, the products were filtered, washed with DI water, and dried in an oven at 100 °C for 10 h. Finally, the organic templates were removed by calcination at 550 °C for 6 h. The MFI zeolite nanosheet assemblies were denoted as MZA-n, in which n corresponded to the molar ratio of Si/Al (n = 15, 31 and 50). For comparison, the commercial ZSM-5 zeolite (CZSM-5) was purchased from Nankai University Catalyst Co., Ltd.

2.4. Characterization

Powder XRD patterns were collected on a Bruker D8 Advance Diffractometer equipped with $\text{CuK}\alpha$ radiation (40 kV, 40 mA and $\lambda = 0.15418$). Infrared spectrum of zeolite catalysts were recorded on a FT-IR spectrometer (Nicolet 6700). N_2 adsorption/desorption isotherms were measured on an ASAP 2020 analyzer under liquid nitrogen

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