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n-$C_{22}H_{45}N^+(CH_3)_2CH_2(CH_2)_4CH_2N(CH_3)_2Br^-$: A new effective one-step structure directing agent to synthesize hierarchical MFI zeolite with ordered hexagonal mesopores

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ABSTRACT

Hierarchical MFI/MCM-41 composites (HMCs) had been synthesized by a one-step hydrothermal method using $C_{22\text{-}6}N$ as single structure directing agent. The results indicated that the hierarchical mesoporous-microporous composites had been synthesized successfully with ordered hexagonal mesopores and partially crystallized MFI zeolite domains. These materials are characterized by a sharp distribution of mesopore diameters and high specific surface area. Catalytic tests in Claisen-Schmidt condensation of bulky reactants showed that the samples possessed outstanding performance over conventional MFI zeolite and MCM-41, making them promising acid catalysts for catalytic reaction involving large organic molecules.

1. Introduction

Zeolites are a family of crystalline silica or aluminosilicate materials with regular micropores, which have been widely used in adsorption, catalysis and ion exchange [1,2]. When used as catalysts, zeolites exhibit excellent catalytic properties in many reactions due to their strong acidity, high thermal and hydrothermal stability, and optimized pore sizes [3,4]. But the micropores also cause diffusion limitation and then reduce reaction rate and selectivity [5,6]. MCM-41, a typical mesoporous material, on the other hand, has much larger pore size than zeolites [7]. Moreover, its one-dimensional regular pore diameter (ranged from 1.5 to 6.5 nm), high specific surface area and large pore volume manifest itself as a very promising candidate in catalysis [8]. However, compared with zeolites, the relative poor hydrothermal stability and insufficient acidity caused by its amorphous frameworks are still bottlenecks for further applications of MCM-41 [9,10].

It is much desirable to construct hierarchical mesoporous-microporous structures that retain the advantages of strong acidity and hydrothermal stability of zeolites, and introduces the larger pore size of mesoporous materials, so that its diffusion performance can be greatly improved [11,12]. Researchers have come up with several ideas to synthesize the hierarchical mesoporous-microporous materials, including forming mesopores inside the zeolite crystals [13,14], and synthesizing mesoporous materials with crystalline pore walls [15,16].

Ryoo et al. used $C_{22\text{-}6}N_2$ as a single template, and successfully synthesized the hierarchical zeolites by hydrothermal method [17,18]. The unique bifunctional structure of multi-quaternary ammonium surfactants began to draw much attention [19,20]. The multi-ammonium heads in the surfactant served as SDA to direct crystalline microporous zeolite while the C_{22} alkyl tails were intermolecularly assembled to direct lamellar-type nanosheets. Park et al. investigated the effect of multi-quaternary ammonium surfactants with different structures on the MFI synthesis, and they had concluded that at least two ammonium groups were needed for the formation of hierarchical structure [21]. In our previous works, however, we found that $C_{22\text{-}6}N$ [n-$C_{22}H_{45}N^+(CH_3)_2CH_2(CH_2)_4CH_2N(CH_3)_2Br^-$], C_{22} alkyl tail with only one ammonium head, could induce the formation of mesopores at 150 °C, which is exactly the suitable temperature for MFI crystal growth [22]. Hence, in this work, with some modifications, hierarchical MFI/MCM-41 composites, HMC-x in short (x represents the reaction days, in this work, x are 4, 6 and 10 respectively), were successfully synthesized by using $C_{22\text{-}6}N$ as template in one-step hydrothermal condition. The catalytic performance involving large organic molecules in the aldol condensation between benzaldehyde and 2′-hydroxyacetophenone of the samples was also tested.

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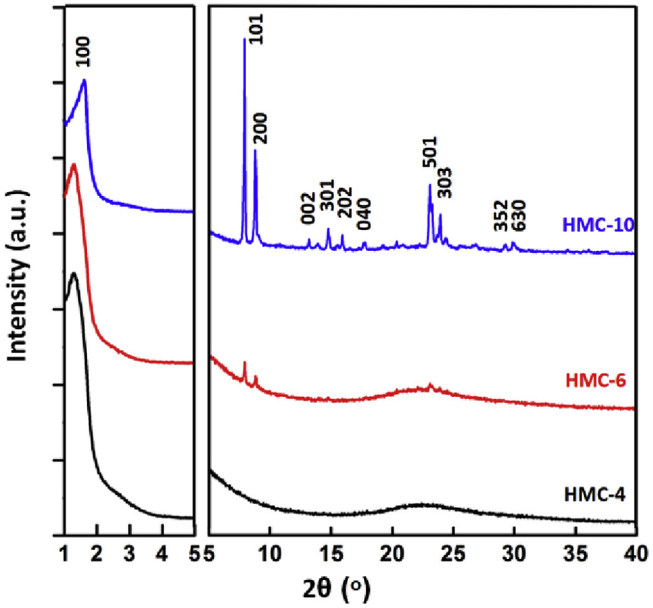

Fig. 1. XRD patterns of HMCs.

2. Experiment

2.1. Preparation of structure-directing agent

0.05 mol of 1-bromodocosane and 0.5 mol of *N,N,N′,N′*-tetramethyl-1,6 -diaminohexane were dissolved in an acetonitrile/toluene mixture (600 mL, 1:1 v/v) and heated at 60 °C for 12 h under magnetic stirring. After being washed by diethyl ether, the solid product was dried at 50 °C in vacuum for 6 h.

2.2. Synthesis of hierarchical MFI/MCM-41 composites

1.23 g of $C_{22\text{-}6}N$ was dissolved in DI water at 70 °C for 2 h, followed by adding 4.0 g of NaOH (2 M) aqueous solution, 3.8 g of TEOS and 2.76 g $Al_2(SO_4)_3{\cdot}18H_2O$ into the mixed solution. After stirring at room temperature for 1 h, the gel was heated at 160 °C in Teflon-lined stainless steel autoclaves for 4, 6 or 10 days. The final molar composition of the synthesis mixture was 6 $C_{22\text{-}6}N$: 50 SiO_2: 20 NaOH: 6350 H_2O: 0.83 $Al_2(SO_4)_3$. The products were centrifuged and washed repeatedly with DI water, and then dried at 50 °C overnight and calcined at 550 °C for 6 h (heating rate 0.75 °C/min).

2.3. Catalytic reaction

Before the catalytic reaction, the ion-exchange procedure was conducted. The samples were treated with ammonium acetate (1 M) aqueous solution at 90 °C under magnetic stirring for 6 h, centrifuged and washed with DI water repeatedly, and then dried at 50 °C overnight. Repeat the procedure mentioned above twice. The materials were finally converted to H^+ form after calcined at 550 °C in air for 6 h.

The catalysts were pre-activated at 150 °C for 2 h before the catalytic reaction. The catalytic reaction was carried out at liquid phase, where the reaction mixtures (1 mmol 2′-hydroxyacetophenone, 1.5 mmol benzaldehyde, 0.5 mL DMF and 0.015 mg catalyst) were heated at 150 °C and stirred simultaneously in heat-resistant glass bottle under N_2 atmosphere for 24 h. The two main products were 2′-hydroxychalcone and flavanone. The selectivity and conversion rate were analyzed by High Performance Liquid Chromatography (HPLC) after the catalytic reaction.

2.4. Characterization

X-ray diffraction (XRD) pattern was obtained with D8-A-Ddvance (Bruke AXS) using CuKα radiation. Fourier transform infrared (FT-IR) spectroscopy was measured by Nicolet 6700 using the KBr wafer technique. Scanning electron microscopy (SEM) experiment was operated at 3 kV on Hitachi S-4800 electron microscope. Transmission electron microscopy (TEM) with electron diffraction (ED) image was collected on JEM-2100 F at an accelerating voltage of 200 kV. The nitrogen adsorption-desorption isotherm was measured at 77 K on Micrometrics ASAP2020 volumetric adsorption apparatus, the sample was degassed at 300 °C for 8 h before measurement. The catalytic products were analyzed by LC3000 High Performance Liquid Chromatography (HPLC) system equipped with an UV detector at 215 nm. Kromasil 100-$5C_{18}$ (250 × 4.6 mm) column was used. The sample injection size was 10 μL and the mobile phase was 85% methanol and 15% water at a flow rate of 1 mL/min.

3. Results and discussion

The XRD patterns in Fig. 1 showed that all the samples possessed a peak corresponding to the (100) reflection of ordered 2D hexagonal MCM-41 in the small-angle scattering range ($2\theta < 5°$), indicating the presence of mesoporous structure [23]. The positions of these peaks were listed in Table 1.

It maintained well but slightly shifted to the right and sharpened with the increase of reaction time. The characteristic peaks of ZSM-5 zeolite ($2\theta = 5°–8°$ and 22°–25°) gradually formed as time increased, which indicated the successful formation of mesoporous material with microcrystalline ZSM-5 zeolite structure at 160 °C.

The evidence of crystalline formation could also be observed from the FT-IR spectra in Fig. 2. Only HMC-10 had a distinct peak at 554 cm^{-1} which was related to the crystalline MFI framework [24,25]. It indicated that the microcrystalline MFI zeolite gradually formed as time increased, which was in accordance with the XRD results.

SEM image of the samples was displayed in Fig. 3. For HMC-4, it demonstrated a typical MCM-41 morphology with small crystal

Table 1
Textual properties of HMCs zeolites.

	V_{mic}[a] [cm^3/g]	V_{mes}[b] [cm^3/g]	V_{tot}[c] [cm^3/g]	S_{BET}[d] [m^2/g]	S_{mic}[a] [m^2/g]	S_{ext}[a] [m^2/g]	2θ[e] [°]	$D_{(100)}$[f] [nm]
HMC-4	0.247	0.939	1.186	567.4	52.1	515.3	1.24	7.14
HMC-6	0.233	0.809	1.042	536.2	31.1	505.1	1.27	6.95
HMC-10	0.206	0.604	0.810	483.3	32.5	450.8	1.61	5.48

[a] The value of micropore volume, micropore surface area and external surface area were determined by *t*-plot method.
[b] The volume of mesopore was calculated by subtracting V_{mic} from V_{tot}.
[c] Total pore volume was determined at $P/P_0 = 0.984$.
[d] BET surface area was determined by multipoint BET method in a relative pressure range (P/P_0) of 0.05–0.30 of N_2 adsorption isotherm.
[e] "2θ" was the position of the maximum intensity peak (100) in the low-angle XRD pattern.
[f] "$D_{(100)}$" was the d-spacing of the diffraction peak (100) calculated from Bragg Equation.