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Regular Article

Synthesis and catalytic performance of hierarchically structured MOR zeolites by a dual-functional templating approach

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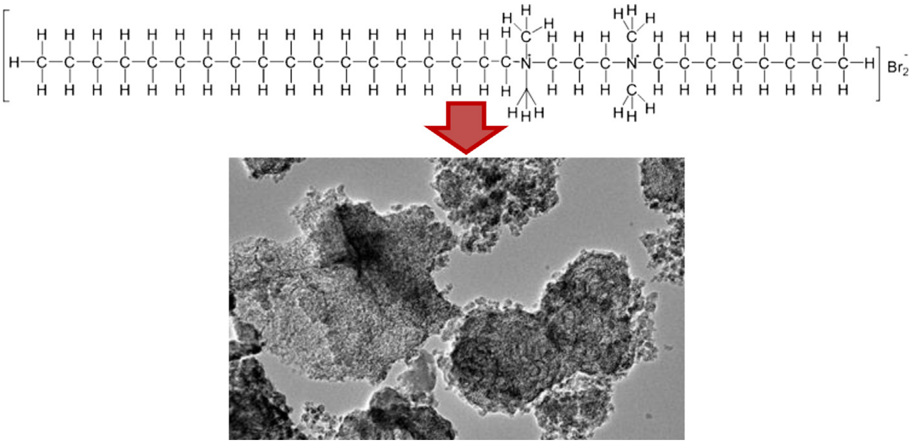
GRAPHICAL ABSTRACT



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ABSTRACT

Novel hierarchical MOR zeolites have been successfully synthesized via a one-step dual-functional templating strategy utilizing gemini organic surfactant ($C_{18\text{-}2\text{-}8}$) through hydrothermal process. After a period of ~96 h for crystallization, the hierarchy MOR zeolite with a larger BET (412.0 m^2/g), abundant intracrystalline mesopores (average mesopore size distribution of 4.55 nm), and more accessible acid sites can be synthesized. The XRD study revealed a long range structural ordering of mesoporous and a good crystallinity of microporous structure. The results indicated that the surfactant acted as a dual-functional template for generating both micropores and mesopores simultaneously. Compared with conventional MOR zeolite, hierarchically structured MOR zeolite not only has higher activity and stability, but also can avoid side-reaction taking place in ethanol dehydration reactions. This hierarchical micro/mesostructured mordenite zeolite may be a candidate for practical industrial applications especially in those reactions where bulky molecules are involved.

1. Introduction

Hierarchy refers to the presence of at least one accessional pore system [1–5]. That refers to form hierarchical zeolites containing both micropores and mesopores [6], which could accelerate access

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of bulky reactants to catalytical active sites while mataining the crystallinity and acidity of the micropore simultaneously. In view of this, they are generally used in adsorption-separation, catalysis and ion-exchange and so on [7–13]. Therefore, quite attentions have been payed to the synthesis of hierarchical zeolites in recent decades [14–16].

A number of synthesis strategies could improve the approachability of zeolites, mainly including the decrease in the size of the crystalline zeolite domains or the increase in the size of the micropores [17,18]. They can all be classified into two primary categories, which are "top-down" and "bottom-up" approaches [1]. The former includes dealumination, desilication by alkaline treatments [19]. However, mesopores from post-demetallation are uncontrollable and their formation is undesirable. The "bottom-up" approach refers to templating strategy [20,17]. Specially, soft-templating is used as templates for mesopores allowing more accurate control of the mesopore size as well as maintaining better integrity of the zeolite structures. A breakthrough in the synthesis of hierarchical zeolites was the application of gemini quaternary ammonium surfactants in the crystallization process, which led to the coherent assembly of the zeolite layer. Several attractive features such as pore size control, large surface areas, interconnected mesopores, and facile synthesis on a large scale could be achieved by this method. It is worth noting that the soft-templating method related studies are mainly centered around on MFI, BEA, and CHA. However, mordenite, one of the several zeolites having realized successful industrial application, has rarely been prepared using this method. Herein, a feasible route, preparing hierarchical mordenite directly by using a diquaternary ammonium-type surfactant as a dual-functional template, was presented in this work. By using the new gemini surfactant $[C_{18}H_{37}(CH_3)_2N^+(CH_2)_2N^+(CH_3)_2C_8H_{17}][Br^-]^2$ ($C_{18\text{-}2\text{-}8}$), hierarchically structured mordenite zeolites were synthesized successfully. The results of characterization demonstrated that the short hydrophobic chain act as a structure-directing agent (SDA) for the crystalline microporous MOR zeolite frameworks, whereas the long hydrophobic surfactant tails lead to generate mesopores.

2. Experimental

2.1. Materials

homogeneous sodium metaaluminate ($NaAlO_2$, 99.9%), NaOH (6 mol/L), DI water, 1-bromooctadecane (99.9%), N,N,N′,N′-tetramethyl-1,2- ethanediamine (99.9%), acetonitrile (>99%, extra pure), fumed silica ($SiO_2{\cdot}nH_2O$, 99.0%), ethylacetate (99.0%), octane (99.0%).

2.2. Synthesis of diquaternary ammonium surfactant $[C_{18}H_{37}(CH_3)_2N^+(CH_2)_2N^+(CH_3)_2C_8H_{17}][Br^-]^2$ ($C_{18\text{-}2\text{-}8}$)

Diquaternary ammonium surfactant $[C_{18}H_{37}(CH_3)_2N^+(CH_2)_2N^+(CH_3)_2C_8H_{17}][Br^-]_2$ ($C_{18\text{-}2\text{-}8}$) was synthesized as follows: 2 mol of 1-bromooctadecane and 1 mol of N,N,N′,N′-tetramethyl-1,2-ethanediamine were dissolved in the acetonitrile. The mixture then reacted at 343 K under magnetic stirring for 24 h. After cooling to the room temperature, the product was filtered, washed with cold ethylacetate and dried in a vacuum oven at 283 K overnight. The as-obtained product was the intermediate. Then the 1 mol of intermediate and 3 times of octane were dissolved in the acetonitrile. The mixture then reacted at 363 K under magnetic stirring for 24 h. Finally, the product was filtered, washed with cold ethylacetate and dried in a vacuum oven at 323 K overnight [21]. The as-obtained product was the $C_{18\text{-}2\text{-}8}$. Scheme 1 shows the structure model of $C_{18\text{-}2\text{-}8}$.

2.3. Synthesis of hierarchical MOR zeolites

Typically, the hydrothermal synthesis was performed by dissolving 0.630 g $NaAlO_2$ and 3.00 mL NaOH in 9.25 mL DI water, and subsequently adding 0.250 g $C_{18\text{-}2\text{-}8}$ to the mixture vigorously at the room temperature for 60 min using a magnetic stirrer. Finally, fumed silica was added to the gel at the room temperature to produce a white gel with the following composition: $1NaAlO_2/50SiO_2/1.14C_{18\text{-}2\text{-}8}/850H_2O/3.8NaOH$. The gel was transferred to a Teflon-lined stainless-steel autoclave, which was set to crystallize in a preheated oven at 403 K for 96 h. After crystallization, the zeolite product was filtered, washed with DI water, and dried at 373 K overnight. The as-obtained samples were named MMOR. For comparison, conventional mordenite zeolite was also synthesized under the same condition just without adding $C_{18\text{-}2\text{-}8}$. The as-synthesized sample was designated as CMOR. All zeolite samples were calcined in dry air at 673 K and hold for 6 h.

2.4. Characterization

The powder X-ray diffraction (PXRD) data were obtained on a Rigaku Dlmax-2500 instrument (40 KV, 100 Ma). The Cu/Kα radiation was at a scanning rate of $8^\circ{\cdot}min^{-1}$ with the scanning range of 0.5–40°.

N_2 adsorption and desorption isotherms (BET) were obtained using a Micromeritics ASAP-2020 instrument. The mesoporous structure was determined from the adsorption branch of isotherms by using Barrett-Joyner-Halenda (BJH) model. The microporous distribution was calculated by using HK model. And the cumulative pore volume curves and pore size distributions (PSD) were estimated by applying the NLDFT method to the adsorption branch of the isotherms, assuming cylindrical pore geometry.

Scanning electron microscope (SEM) was performed on a scanning electron microscope (type SU-1500) with an acceleration voltage of 30 KV.

The acidic properties of the samples were activated for 60 min in a flow of helium at 500 °C (the heating rate was $10\,°C{\cdot}min^{-1}$), after being cooled to 100 °C, saturated with NH_3 for 40 min; (30% NH_3 + 97% Ar); physical bound NH_3 was desorbed by venting with He at 100 °C; the remaining NH_3 was desorbed by heating in the temperature range of 100–800 °C ($10\,°C{\cdot}min^{-1}$) and using a TCD detector.

Transmission electron microscopy (TEM. JEM-1011) was used to study the channel of hierarchical-pore structure.

Thermogravimetry-differential thermogravimetry (TG-DTG) was performed using a NETZSCH STA 449F5 analyzer with a heating rate of $10\,°C{\cdot}min^{-1}$.

2.5. Catalytic performance testing

The reactivity of acid sites in MOR were evaluated by ethanol dehydration reactions under strict kinetic control conditions. It was carried out at 573 k under atmospheric pressure in a laboratory unit constituted by a fixed bed tubular reactor containing 0.3 g of the as-obtained samples diluted in 1.5 g of ground quartz (40 mesh). N_2 was used as carrier gas ($0.4\ mL{\cdot}min^{-1}$) and the deionized water, alcohol ($V_{H_2O}:V_{EtOH} = 7:3$) fed continuously at a flow rate of $0.050\ mL{\cdot}min^{-1}$. The reactor effluent was analyzed by online gas chromatography using a Shimadzu GC-2010 instrument.

Not considering the coke formation, the EtOH conversion (C_{EtOH}) were close estimated through a carbon balance as is indicated in Eq. (1). The yield of $CH_2=CH_2$ ($Y_{CH_2=CH_2}$) were calculated according to Eq. (2).

$$C_{EtOH} = \left[\frac{n_{EtOHr} - n_{EtOHp}}{n_{EtOHr}}\right] \times 100\% \qquad (1)$$