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使用双子表面活性剂合成纳米层状 MFI 分子筛

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摘要: 使用双子表面活性剂($C_{18\text{-}6\text{-}6}Br_2$)合成了纳米层状 MFI 分子筛,这种表面活性剂是由溴代十八烷合成。对沸石样品用 X-射线衍射(XRD),低温 N_2 吸附–脱附,扫描电子显微镜(SEM)和透射电子显微镜(TEM)进行了表征。由 N_2 物理吸附的数据可以得出由双子表面活性剂制备的样品具有高的 N_2 吸附量和外比表面积。其比表面积 (454 $m^2 \cdot g^{-1}$)远高于传统 MFI 分子筛,同时它的外表面积占了比表面积的 50%以上。纳米层状分子筛在 *a-c* 平面拥有清晰且广阔的平面区域, 但是沿着 *b* 轴的骨架的厚度却相当小。纳米层状 NSUCH MFI(Nano hierarchical MFI)分子筛的催化性能以氮氧化物的催化净化来评估。结果表明,样品有着很好的去除氮氧化物的催化性能,在 350 ℃时氮氧化物的转化率达到了 100%。

关键词: 层状 MFI; 溴代十八烷; 双子表面活性剂; 氮氧化物
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Synthesis of Nano Hierarchical MFI by Using a Gemini Surfactant

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Abstract: Nano hierarchical MFI zeolite (NSUCH MFI) was synthesized using a gemini surfactant ($C_{18\text{-}6\text{-}6}Br_2$) prepared from 1-Bromooctadecane and characterized by XRD, low temperature N_2 adsorption-desorption, SEM and TEM. As revealed by N_2 physisorption, The title MFI samples exhibit significantly higher amounts of N_2 adsorption. And the BET surface area of the material is 454 $m^2 \cdot g^{-1}$ with more than 50% of the overall surface area being external surface area. The synthesized MFI nanosheets are wide in the *a-c* plane and 2 nm thick along the b axis. The catalytic removal of nitrogen oxides was used to evaluated the catalytic properties of the NSUCH MFI zeolite. The results show that the sample exhibits an excellent catalytic performance for nitrogen oxides removal. The conversion of nitrogen oxides at 350 ℃ is 100%.

Key words: hierarchical MFI; 1-bromooctadecane; gemini surfactant; nitrogen oxides

0 Introduction

Zeolites are a family of crystalline aluminosilicate materials widely used as shape-selective catalysts, ion exchange materials, and adsorbents for organic compounds[1-3]. Zeolites have usually been synthesized with crystal sizes in the micrometer range and, therefore, with negligible external surface area. These properties impose severe limitations for their use in the conversion of bulky compounds[2-4]. Nano-zeolite with a high surface area and higher rates of the intracrystalline diffusion, has shown superior performance[5]. At present the nano-zeolite is synthesized by hybrid zeolitic-ordered mesoporous materials[6-7], delaminated zeolites[8] and zeolites with a secondary porosity prepared by steaming[9], by desilication[10] or by the confined space

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approch [11-12]. The addition of mesopore-generating agents such as carbon nanoparticles [13-16], polymer beads [17-18], and organosilane surfactants [19-20] is also effective for the synthesis of zeolite with intracrystalline mesopores. Microporous zeolites with mesopores generated in this manner are often referred to as "hierarchically microporous-mesoporous" or "hierarchical" zeolites. Hierarchically porous zeolites have the advantage of a facile diffusion into (and also out of) catalytic active sites to permit reactions to take place inside micropores [21-23]. The mesopore walls also provide sufficient catalytic active sites for the conversion of bulky molecules[24]. The term hierarchical zeolites has been applied for designating zeolites containing a bimodal porosity and showing reduced steric and diffusional restrictions.

It is possible to synthesize MFI zeolite nanosheets with a thickness of 2 nm as a fully disordered assembly possessing a large mesopore volume between neighboring nanosheets using the($C_{18}H_{37}$-$N^+(CH_3)_2$-C_6H_{12}-$N^+(CH_3)_2$-C_6H_{13})Br_2 (designated by $C_{18\text{-}6\text{-}6}$ Br_2) surfactant prepared from 1-bromooctadecane. This material has a small size, short channel, small diffusion resistance, larger surface area, and strong adsorption capacity [25]. The NSUCH MFI based Fe/ MFI can also improve the catalytic activity for the catalytic reduction of nitrogen oxides.

1 Experimental

1.1 Synthesis of zeolite samples

Synthesis of organic surfactant: $C_{18\text{-}6\text{-}6}Br_2$ was synthesized from 1-bromooctadecane as follows: 3.33 g (0.01 mol)1-Bromooctadecane and 8.62 g (0.05 mol) *N*, *N*,*N*′,*N*′-tetramethyl-1, 6-diaminohexane were dissolved in 100 mL acetonitrile/toluene mixture (1∶1, *V*/*V*) and heated at 90 ℃ for 10 h. After cooling to room temperature, the product was filtered, washed with diethyl ether, and dried in a vacuum oven at 50 ℃. 5.14 g (0.01 mol)of the product and 3.30 g (0.02 mol)1-bromohexane were dissolved in 300 mL acetonitrile and refluxed for 10 h. After cooling to room temperature, the product was filtered, washed with diethyl ether, and dried in a vacuum oven at 50 ℃.

Synthesis of hierarchical MFI zeolite: Water glass (an aqueous solution of sodium silicate, n_{SiO_2}/n_{Na}=1.75, 29wt% SiO_2), $Al_2(SO_4)_3\cdot 18H_2O$, NaOH, $C_{18\text{-}6\text{-}6}Br_2$, H_2SO_4 and distilled water were mixed to obtain a gel composition of $30Na_2O$ ∶$1Al_2O_3$ ∶$100SiO_2$ ∶$10C_{18\text{-}6\text{-}6}Br_2$ ∶$18H_2SO_4$∶$4000H_2O$. The resultant gel was transferred to a teflon-coated stainless-steel autoclave, and heated at 150 ℃ for 5 d with the autoclave set to tumble at 60 r·min^{-1}. After crystallization, the zeolite product was filtered, washed with distilled water and dried at 120 ℃. The product was calcined at 550 ℃ for 4 h under flowing air.

The MFI zeolite based catalysts, Fe/ MFI catalyst were prepared by wet impregnation method. MFI powders were impregnated with aqueous solutions cotaining given amount of ferric chloride, then dried at 80 ℃ for 8 h. After calcination at 500 ℃ for 5 h, the catalysts were crushed and sieved to 40~60 mesh(250~420 μm) granules.

1.2 Characterization

The powder X-ray diffraction measurement of the MFI were performed on a Rigaku D/max2500 diffractometer using Ni-filtered Cu $K\alpha$ radiation (λ = 0.154 18 nm) [40 mA, 40 kV, 1°(2θ)·min^{-1}, 2θ=5°~35°] at room temperature.

Surface areas of zeolites material were measured using the BET method on a SORPTOMATIC 1990 Nitrogen adsorption instrument. Typically, 100 mg of zeolite powder was dried overnight at 120 ℃ in vacuum. A 7-point isotherm was then recorded and the specific surface area was calculated for the samples before and after calcination in order to obtain the external (S_{ext}) and total specific surface areas (S_{tot}), respectively. A 50 point adsorption/desorption isotherm was measured and used for the calculation of micropore and total pore volume as well as the average diameter of mesopores. Total pore volume (V_{tot}) was calculated by measuring the amount of adsorbed nitrogen at 0.97P/P_0. The *t*-plot method was used to calculate the micropore volume (V_{micro}). The pore size distribution in the zeolite samples was calculated using a BJH model.

Transmission electron micrographs were recorded with a Tecnai G^{2}F20, operating at 200 kV. The sample was suspended in ethanol and dispersed on a copper

grid coated with a lacey carbon film. The surface morphology of the MFI was observed using a JSM-6700F field emission scanning electron microscope with an accelerating voltage of 10.0 kV.

The catalytic activity for NO reduction of MFI catalysts was evaluated in a conventional fixed-bed quartz reactor at 8 mm i.d. and 350 mm in length. Before entering the reactor, four feed gases ($NO+N_2$, NH_3+N_2, air, N_2) controlled separately by mass flow controllers were mixed in a chamber filled with glass wool. The compositions of the feed and effluent of the reactor were continuously analyzed using an online Combustion Gas Analyser (KM9006 Quintox, Kine International Limited), which is capable of monitoring NO, NO_2, O_2, and CO simultaneously.

2　Results and discussion

Double dialkyl quaternary ammonium cationic surfactant used in this work is very different from traditional surfactant in structure, it can be regarded as two or more of the same or different amphiphiles, in their hydrophilic or near the hydrophilic group connection formed by chemical bonds. The surfactant is composed of a long-chain alkyl group (C_{18}) and two quaternary ammonium groups spaced by a C_6 alkyl linkage [26-27]. The diammonium head group acts as an effective structure-directing agent for the MFI zeolite, while the hydrophobic interaction between the long chain tails induces the formation of a mesoscale micellar structure. With the surfactant, an ultrathin zeolite framework could be formed in the hydrophilic part of the micelles while the hydrophobic tail restricted the excessive growth of zeolites.

As illustrated in Fig.1, the peak position of NSUCH MFI is consistent with the standard MFI, indicating that nano-sheets MFI sample is obtained. Under the same conditions, the peaks of NSUCH MFI are wider than that of conventional MFI. The use of $C_{18\text{-}6\text{-}6}Br_2$ as a template agent can effectively extend the time of crystallization which is favorable to the formation of the single-cell nano-layer. The samples obtained after the final hydrothermal treatment are highly crystalline. For the materials prepared from 1-

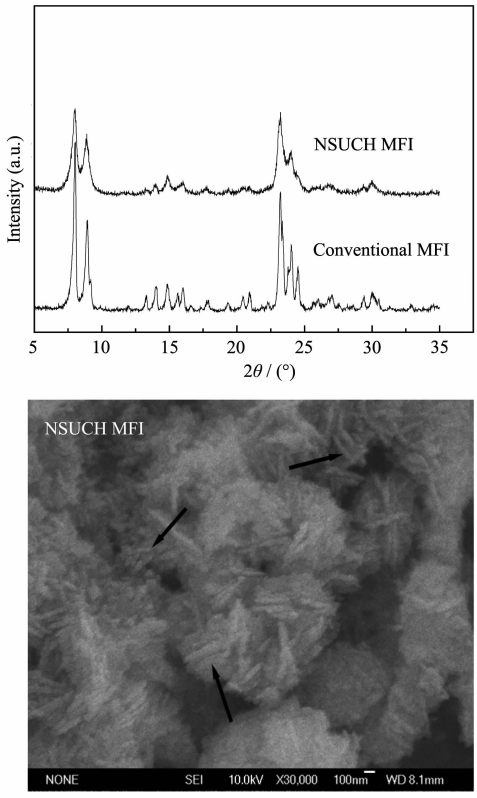

Fig.1　XRD patterns and SEM micrograph of the samples

bromooctadecane, the peaks are less intense compared to those of the conventional zeolites, suggesting that the former presents smaller crystalline domains.

Surfactant is removed in the calcination process leaving free space for catalysis and adsorption. As illustrated in Fig.2, the materials prepared with the $C_{18\text{-}6\text{-}6}Br_2$ exhibit significant higher N_2 adsorption than those of the samples prepared from conventional surfactant. For the MFI zeolite, this enhanced adsorption is originated from the presence of mesopores resulted from the nanocrystals (maximum at 20 nm). However, the increase in the N_2 adsorption occurs mainly at the relative pressure below 0.2, showing the presence of a secondary porosity within the supermicropore region (maximum at 2 nm). The data in Table 1 indicate that the materials obtained from $C_{18\text{-}6\text{-}6}Br_2$ present enhanced BET specific surface area and external surface area. Thus, the BET surface area of NSUCH MFI ($455\ m^2 \cdot g^{-1}$) is exceptionally higher than that of the convention MFI zeolites, while its external surface area accounts for more than 50% of the overall surface area. For NSUCH MFI zeolite,

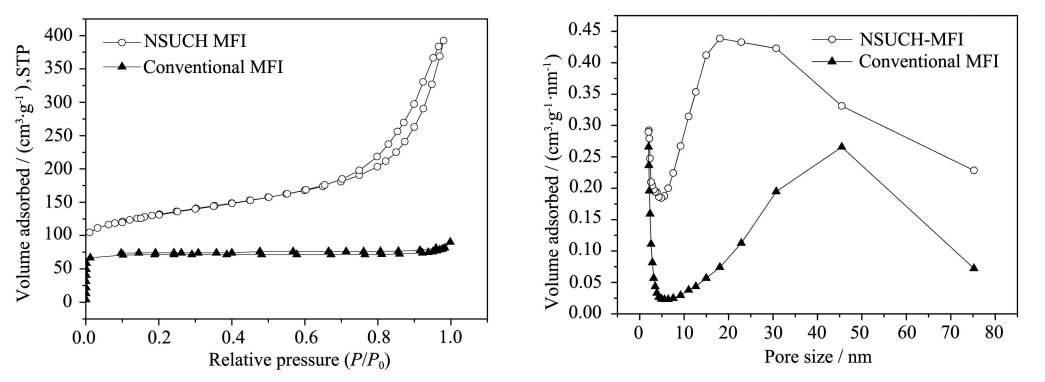

Fig.2 N_2 adsorption-desorption isotherms (A) and pore size distributions (B) at 77 K for the calcined samples

Table 1 Pore characteristics of NSUCH MFI and Conventional MFI

Samples	S_{BET} / ($m^2 \cdot g^{-1}$)	S_{micro} / ($m^2 \cdot g^{-1}$)	$S_{external}$ / ($m^2 \cdot g^{-1}$)	V_{tol} / ($cm^3 \cdot g^{-1}$)	V_{micro} / ($cm^3 \cdot g^{-1}$)	$D_{average}$ / nm
Conventional MFI	206.7	163.5	43.2	0.140	0.110	2.71
NSUCH MFI	454.5	216.9	237.6	0.607	0.099 7	5.34

the $C_{18\text{-}6\text{-}6}Br_2$ causes also an increase in the micropore volume, which confirms the presence of a secondary microporosity.

The average particle size of NSUCH MFI is 100 nm as estimated by TEM. These particles are polycrystalline as shown by the TEM images. Although NSUCH MFI exhibits lower macroscopic particle shape, the small particles of macro-crystals in the TEM image is clearly visible.Figure 3 shows that the MFI sample obtained from tetrapropyl ammonium bromide is formed by 15~25 nm sized nanocrystals. However, the MFI sample crystallized from $C_{18\text{-}6\text{-}6}Br_2$ consists of irregular lamellar crystals formed by aggregates of ultrasmall primary units with size below 2 nm. The crystalline nature of the latter is clearly demonstrated by the lattice fringes observed in the transmission electron microscopy (TEM) images despite their extremely small size. It is interesting to note that the adjacent nanocrystals exhibit the same crystalline orientations, which suggest that they present a significant degree of intergrowth. This fact has been also observed in the crystallization of other nanozeolites[28], and it may explain the relatively well-defined X-ray patterns corresponding to these samples. The NSUCH MFI can thus be considered to be composed of essentially the same building blocks as the multilamellar form. The transmission electron microscope (TEM) investigation of the cross-section (Fig.3a) reveals that the stacking is composed of alternated layers of 2.0-nm-thick MFI zeolite framework and about 2.8-nm-thick surfactant micelles. The MFI zeolite has a plate-like morphology composed of three-dimensionally intergrown nanosheets [25]. The thickness of nano-layers is 20~40 nm.

It suggests that the whole assembly of the nanoparticle is highly oriented, leading to the

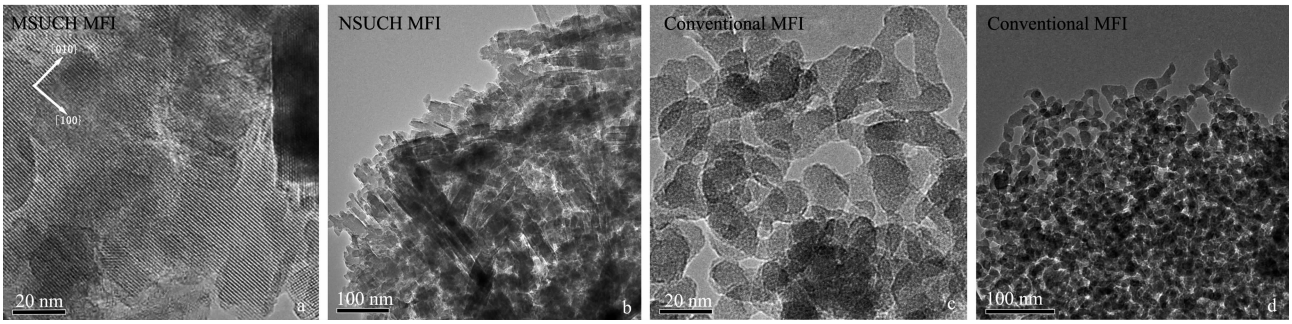

Fig.3 TEM micrographs of the samples

formation of the hierarchical-like particle elongated along the (001) direction. There is a small lattice mismatch between the boundaries of the nanoparticles when they are assembled in the same orientation, typical for mesocrystals. The internal porosity of the particle is revealed by the TEM image taken on a microtomed sample (Fig.3a), showing the existence of evenly distributed nanopores inside the particle and thus supporting the formation of nanoporous mesocrystals. This result is confirmed by the corresponding nitrogen adsorption/desorption measurement, which indicates the presence of rather uniform nanopores with an average diameter of 5.34 nm (Fig.2b). Fig.3a shows a TEM image of the particle shown in Fig.3b, further confirming its single-crystal-like nature. The clear lattice fringes can be well assigned to the (010) and (100) planes of zeolite. A careful TEM observation of the end of the spindle-shaped particle suggests the existence of some (100)-oriented planes.

The catalytic activity of MFI based Fe/ MFI catalysts from NSUCH MFI and conventional MFI is shown in Fig.4. It can be seen that the activity of the sample crystallized from $C_{18\text{-}6\text{-}6}Br_2$ is higher than that of the conventional MFI zeolite at lower temperature (100~450 ℃). This is particularly pronounced at 350 ℃ to 450 ℃, the conversion of nitrogen oxide on NSUCH MFI based catalyst reaches nearly 100% at 350 ℃, suggesting that the NSUCH MFI based catalyst is beneficial to the catalytic reaction of NO_x reduction.

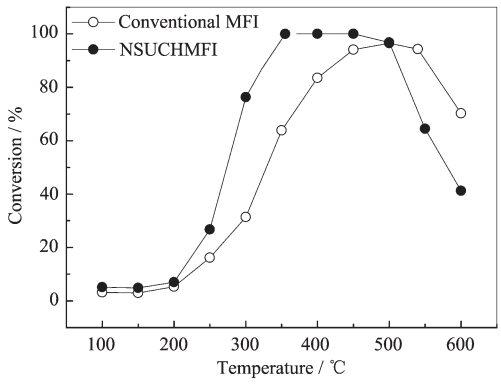

Fig.4　Catalytic activity of MFI based Fe/ MFI catalysts from NSUCH MFI and conventional MFI

3　Conclusions

Nano hierarchica l MFI was synthesized using a double dialkyl quaternary ammonium cationic surfactant ($C_{18\text{-}6\text{-}6}Br_2$) prepared from 1-bromooctadecane. Disordered assembly of MFI zeolite nanosheets could be generated in 5 d at 150 ℃. The effective crystallization can not be ensured when the temperature is lower than 150 ℃. However, single cell nano-layers can not be formed when the temperature is above 180 ℃ due to the decomposition of the double dialkyl quaternary ammonium cationic surfactant. The zeolite has especially a high BET surface area, a large total pore volume.

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