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Short communication

Controllable synthesis of chainlike hierarchical ZSM-5 templated by sucrose and its catalytic performance

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ABSTRACT

Hierarchical ZSM-5 with controllable chainlike structure was hydrothermally synthesized with sucrose as template, characterized by XRD, FT-IR, N_2 adsorption, SEM and TEM, and used for methylation of 2-methylnaphthalene. Hierarchical ZSM-5 can be rapidly synthesized, and chainlike morphology is stacked with several submicron crystals. With increasing sucrose amount in the precursor, the chain structure became more obvious, and the surface area and pore volume of mesopores increased. Narrow mesoporous distribution was centered at about 7 nm. It is thought that the formation of mesopores is related to the template role of sucrose. Chainlike hierarchical ZSM-5 exhibited high 2-methylnaphthalene conversion and 2,6-dimethylnaphthalene yield.

1. Introduction

Zeolite has been widely used in industry as catalysts for its unique properties, such as high surface area, acidity, and shape selectivity, especially in the fields of oil refining and petrochemistry [1]. However, the micropores in zeolites often impose diffusion limitations that restrict accessibility to the internal surface of zeolites, especially when bulky molecules are involved [2]. To overcome these problems, one of the most promising ways is to prepare composites containing mesopores as well as micropores. These hierarchical materials, which combine the advantages of both zeolites and mesoporous materials, exhibit fast diffusion rates and many exposed active acidic sites [3–7]. For example, in the synthesis of 2,6-dimethylnaphthalene (2,6-DMN) by methylation of 2-methylnaphthalene (2-MN), it was found that catalytic activity and stability could be significantly improved when some mesopores were introduced into ZSM-5 [6]. Templating methods are widely used to synthesize mesoporous materials [8–10]. Therefore, the cost of template and synthesis process should be considered in industrial application.

Sucrose is often chosen as a template for the synthesis of hierarchical zeolite owing to its low cost. Kustova et al. [11] reported that mesopores ZSM-5 and ZSM-11 could be synthesized by mixing silica gel with different concentration solutions of sucrose, carbonization, and crystallization through impregnating a structure-directing agent. Tong et al. [12] reported that monolithic zeolite BEA could be synthesized using the same method as that of Kustova et al. Zhu et al. [13] prepared the mesopore Silicate-1 by using porous carbon from sucrose as the template. Wang et al. [14,15] synthesized hierarchical TS-1 directly using sucrose as the meso/macroporous template by dry gel conversion. However, these processes generally need a long reaction time and several steps to prepare mesoporous zeolite. Here we report a rapid, convenient method to fabricate hierarchical ZSM-5 with a chainlike morphology by using sucrose as the template, and the effect of the sucrose amount on the structure of hierarchical ZSM-5 and catalytic performance in the synthesis of 2,6-DMN by methylation of 2-MN with methanol was examined.

2. Experimental

2.1. Synthesis of chainlike hierarchical ZSM-5 zeolites

Chainlike hierarchical ZSM-5 was synthesized by hydrothermal crystallization. The detailed synthesis procedure is as follows: tetrapropylammonium hydroxide (TPAOH, 25 wt.%, aq; YueyangYutai Chemical Technology Development Co., Ltd., China), sodium aluminate ($NaAlO_2$, Sinopharm Chemical Reagent Co., Ltd.) and distilled water were first mixed and stirred for 30 min until a clear solution is obtained. Then tetraethyl orthosilicate (TEOS, Sinopharm Chemical Reagent Co., Ltd.) was dropwise added to the solution under stirring and agitated for 2 h until a clear gel was obtained. The composition of the resultant precursor is $1SiO_2/0.011Al_2O_3/0.25TPAOH/30H_2O$. Finally, different

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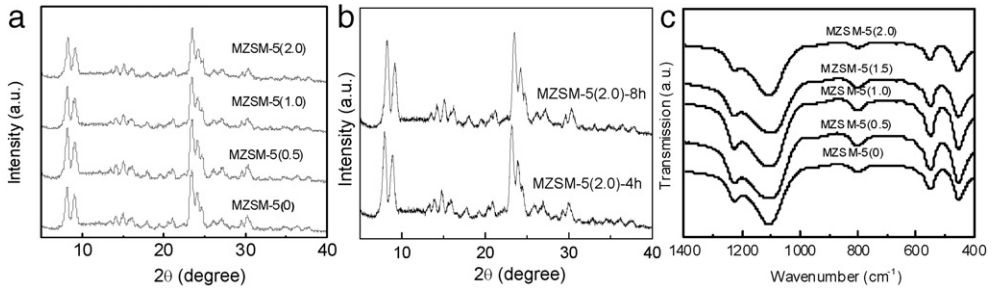

Fig. 1. XRD patterns (a, b) and FT-IR spectra (c) of MZSM-5 (x) samples.

amounts of sucrose were added to the mixture and agitated for another 2 h. The precursor was charged into a stainless-steel autoclave and crystallized at 170 °C for 72 h. The products were filtered, washed with deionized water, dried at 120 °C and calcined at 550 °C for 10 h. Zeolites synthesized with different amounts of sucrose were denoted as MZSM-5(x) (x = 0–2.0), where x represents the mass ratio of sucrose to SiO_2.

To investigate the effect of crystallization time on the structure, the precursor with a ratio of sucrose to SiO_2 of 2.0 was crystallized at 170 °C for 4 h or 8 h. The products were expressed as MZSM-5(2.0)-4 h and MZSM-5(2.0)-8 h, respectively.

2.2. Characterizations

X-ray diffraction (XRD) patterns of the samples were obtained on a D/Max2400 diffractor (Rigaku) with CuKα radiation at 40 kV and 40 mA. FT-IR spectra of the structure band region (1400–400 cm^{-1}) were investigated on an EQUINOX55 spectrometer. The framework SiO_2/Al_2O_3 molar ratio was determined by XRF spectroscopy on a SRS3400X instrument after the sample was washed with 1 M HCl at 80 °C for 4 h to remove extra-framework aluminum. BET specific surface area of the samples was determined by nitrogen adsorption using ASAP 2020 apparatus at −196 °C. The samples were outgassed at 300 °C for

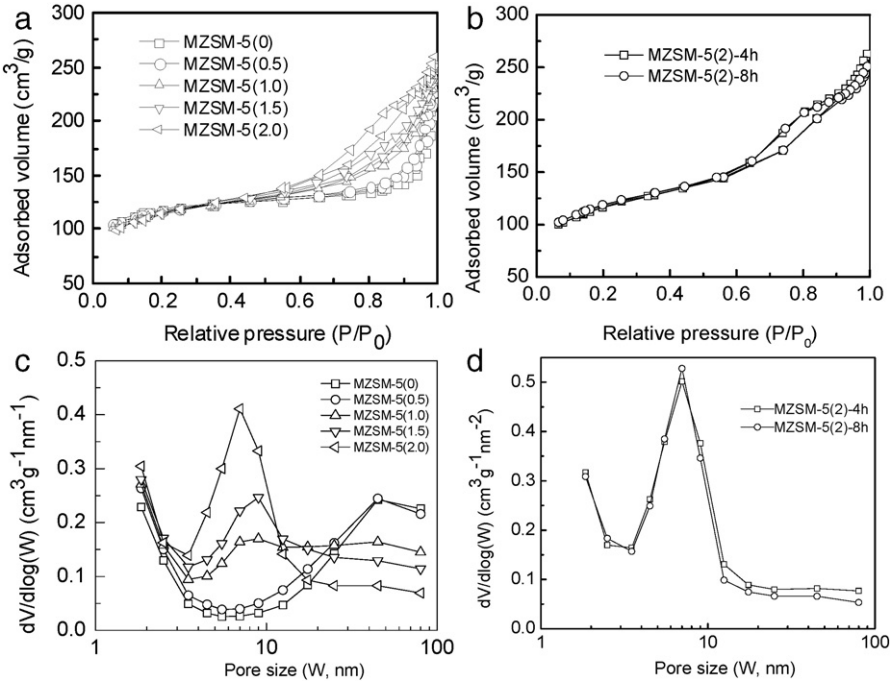

Fig. 2. Nitrogen adsorption–desorption isotherms (a, b) and pore distribution (c, d) of the samples.

Table 1
SiO_2/Al_2O_3 molar ratio and textural properties of MZSM-5(x) samples.

Sample	SiO_2/Al_2O_3 molar ratio[a]	S_{BET} (m^2/g)	S_{mic} (m^2/g)	S_{ext} (m^2/g)	V_{total} (cm^3/g)	V_{mic} (cm^3/g)	V_{meso} (cm^3/g)
MZSM-5(0)	102	405	226	179	0.32	0.10	0.22
MZSM-5(0.5)	108	406	217	189	0.33	0.10	0.23
MZSM-5(1.0)	136	397	202	195	0.36	0.10	0.26
MZSM-5(1.5)	138	397	179	218	0.36	0.08	0.28
MZSM-5(2.0)	141	399	159	240	0.39	0.08	0.31

[a] by XRF.