



Synthesis, characterization and catalytic activity of a novel mesoporous ZSM-5 zeolite

Yuanyuan Ma^{a,b}, Jing Hu^a, Lihua Jia^b, Zhifang Li^a, Qiubin Kan^{a,*}, Shujie Wu^{a,*}

^a College of Chemistry, Jilin University, Changchun 130023, PR China

^b Key Laboratory of Fine Chemicals of College of Heilongjiang Province, Qiqihar University, Qiqihar 161006, China

ARTICLE INFO

Article history:

Received 4 August 2012

Received in revised form 25 December 2012

Accepted 10 January 2013

Available online 25 January 2013

Keywords:

A. Structural materials

C. Electron microscopy

C. Nuclear magnetic resonance (NMR)

D. Catalytic properties

ABSTRACT

A novel mesoporous ZSM-5 zeolite was hydrothermally synthesized using glucose as a template. Characterizations by XRD, TEM and nitrogen isotherms indicated that ZSM-5 possessed worm-like mesoporous. ²⁷Al-MAS-NMR and NH₃-TPD showed that the mesoporous ZSM-5 preserved tetrahedral coordination aluminum and stronger acidity than conventional mesoporous material. As-prepared mesoporous ZSM-5 was successfully used in alkylation reaction of phenol with *tert*-butanol and exhibited significantly high phenol conversion and 2,4-DTBP selectivity. In addition, the hydrothermal stability was also studied by boiling in water for 7 days and displayed good results.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Zeolites are crystalline aluminosilicates with ordered micropores ($d_{\text{micro}} < 2 \text{ nm}$) which are applied to adsorption, catalytic and ion exchange properties. However, the sole presence of micropores in these materials often confines intracrystalline diffusion, resulting in low utilization of the zeolite active volume in catalyzed reactions. The pore width of mesopores ($2 \text{ nm} < d_{\text{meso}} < 50 \text{ nm}$) are bigger than micropores, thus they induce new properties and reveal unexpected applications. The major drawbacks in most industrial reactions are the low thermal, hydrothermal stability and weak acidity due to their amorphous pore wall. Therefore, micro/mesoporous materials which combine microporosity of zeolite units with mesoporous of amorphous phases have been received much attention due to their potential applications in recent years.

Indirect templating method and post-synthetic treatment are in more common use at present to produce micro/mesoporous materials. During the crystallization of the zeolite, the templates are either introduced to form mesopores. Templates include supramolecular [1–3], porous carbons [4–6], resins [7], organic aerogels [8,9], and polymers [10,11], biological templates [12–14] and purely inorganic compounds such as Mg(OH)₂ [15] and

Ca(OH)₂ [16]. The post-synthetic treatment mainly refers to alkaline treatment [17–19] which creates intracrystalline porosity in channel-type zeolites such as ZSM-5, ZSM-12, mordenite, and beta.

This paper mainly presents glucose as template to synthesize mesoporous ZSM-5. Glucose is inexpensive, readily available and nontoxic, so that the synthetic process is pollution-free. Through two-step crystallization procedure we synthesize a novel mesoporous ZSM-5 zeolite. Firstly, zeolite nonparticles were obtained by hydrothermal crystallization. Then these small zeolite particles and glucose were assembled into mesoporous materials during the hydrothermal treatment. Upon calcinations, glucose and TPAOH were removed to form micro/mesoporous composites materials.

2. Experimental

2.1. Catalyst preparation

In a typical synthesis, 0.28 g Aluminum sulfate octadecahydrate (Al₂(SO₄)₃ · 18H₂O) and 6.25 mL tetrapropylammonium hydroxide solution (TPAOH, 20%) were dissolved in 3.75 mL of distilled water under stirring to form a clear solution. Then, 5 mL tetraethyl orthosilicate (TEOS) was dropped into the homogeneous solution under vigorous stirring that was continued for 6 h. The homogeneous solution with the molar composition of 1 Al₂O₃: 50 SiO₂: 8 TPAOH: 1500 H₂O was aged at 100 °C for 16 h. The obtained precursor of ZSM-5 was mixed with glucose aqueous solution (15 mL, 1.5 g glucose). After stirring for another 30 min, the resulted suspension was transferred into Teflon-lined autoclave

* Corresponding author at: Jiefang Road 2519, Changchun 130021, PR China. Tel.: +86 431 88499140; fax: +86 431 88499140.

E-mail addresses: catalysischina@yahoo.com.cn (Q. Kan), wusj@jlu.edu.cn (S. Wu).

and kept at 100 °C for 48 h. The resulting solid was filtered, washed with distilled water and dried at 60 °C over night. Finally, the powder was calcined in air at 550 °C for 6 h to completely remove the organic surfactants.

The protonated form of sample was obtained from ion exchange with NH_4NO_3 for three times, followed by calcination at 773 K for 5 h.

For comparison, we also prepared the conventional ZSM-5. The synthesis steps were similar to those described above, with the exception that glucose aqueous solution were not been used. Al-MCM-41 (Si:Al = 25) was also synthesized according to the literature [20].

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer system equipped with Ni-filtered Cu target Ka-ray (operation at 40 kV, 30 mA, wavelength $\lambda = 0.15418$ nm). Diffractions were carried out in the 2θ range of 5°–40° at the scanning speed of 4°/min. Transmission electron micrograph (TEM) was analyzed with a JEOL JEM-2010 transmission electron microscope operated at an accelerating voltage of 200 kV. N_2 adsorption/desorption isotherm was recorded at 77 K with a Micromeritics ASAP 2020. Before measurements, sample was out gassed at 573 K for 3 h. BET surface areas (S_{BET}) were calculated from adsorption branch in the relative pressure range from 0.05 to 0.30. The mesopore surface area and pore volume were calculated by *t*-plot method. ^{27}Al -MAS NMR spectrum was determined on a Varian Unity-400 spectrometer operating at a magnetic field of $B_0 = 0.94$ T with NMR frequencies of 104 MHz. The chemical shifts were referenced to $\text{Al}(\text{H}_2\text{O})_6^{3+}$. NH_3 -TPD spectra were measured using a fixed-bed reactor connected to a thermal conductivity detector (TCD). The catalysts (0.05 g) were activated at 773 K for 1 h with nitrogen, then cooled down to 373 K, followed by ammonia adsorption for 40 minute. Ammonia desorption measurements were achieved in the temperature range of 373–773 K at an increasing the temperature at 10 K min^{-1} .

The hydrothermal stability was tested by treating the samples in boiling water for 7 days.

2.3. Catalytic test

Alkylation of phenol with *tert*-butanol was carried out at atmospheric pressure in a continuous flow fixed quartz bed reactor (i.d. 6 mm). Prior to catalytic reaction, 0.5 g catalyst were activated in N_2 at 773 K for 1 h to eliminate physically and chemically adsorbed water, then the reactor was cooled to 418 K under a N_2 flow of 20 mL/min. The reaction mixture was injected from the top using a syringe pump. Products were quantified by gas chromatography (GC-8A, Shimadzu) and confirmed by gas chromatography–mass spectrometry (GC–MS).

3. Results and discussion

3.1. X-ray diffraction analysis

Fig. 1 shows the XRD patterns of the conventional ZSM-5 and mesoporous ZSM-5. As expected, the conventional ZSM-5 presents the X-ray pattern (Fig. 1a) typical of ZSM-5 zeolite with well defined reflections. In the case of the mesoporous ZSM-5 obtained using glucose as additive, the same X-ray reflections are clearly identified (Fig. 1b) but are less resolved with lower intensities, suggesting that amorphous aluminosilicate mesoporous walls were not entirely converted into MFI structure. In fact, when this meso-structured zeolite is used as catalyst, not all the skeletons need to be completely converted into a zeolite structure [21]. If

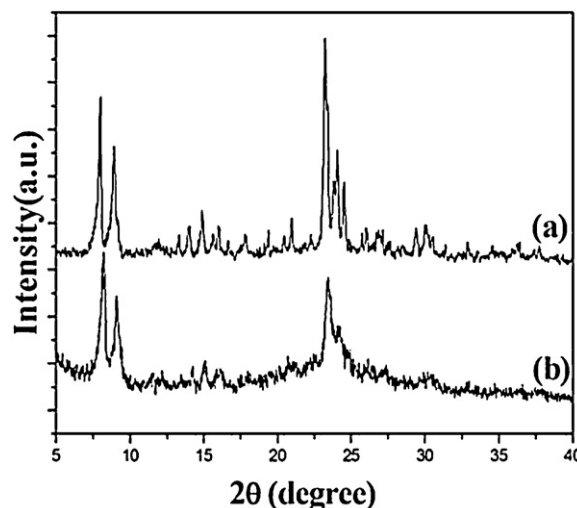


Fig. 1. XRD patterns of as-synthesized zeolite materials prepared under different conditions: (a) conventional ZSM-5 and (b) mesoporous ZSM-5.

zeolites are crystallized fully by prolonging the crystallization time, the pore connectivity of the mesoporous ZSM-5 zeolite is decreased, which is disadvantageous for the mass transport [22].

3.2. Pore structure analysis

As observed by transmission electron microscopy (TEM, Fig. 2a) of the mesoporous ZSM-5 zeolite, ZSM-5 nanoparticles seem to assemble into stacks in a “wormlike” manner and the interconnected pores are disordered arrangements. We can also observe that there is small amount of bulk ZSM-5 in Fig. 2a, which is formed by aluminosilicate nonparticles mixed incompletely with glucose. As revealed by the corresponding HRTEM image (inset Fig. 2a), a well interconnected and densely packed nanocrystal network was observed within mesoporous ZSM-5 zeolite. The total aluminum content of the mesoporous ZSM-5 zeolite was determined by elemental analysis with the EDX mounted on the TEM. The result show that the Si/Al molar ratio of the mesoporous ZSM-5 zeolite is 25.23, which is in good agreement with the raw synthesis gel (Si/Al = 25).

The N_2 adsorption isotherm of the conventional ZSM-5 (Fig. 2b) basically belongs to IUPAC type I, which is a characteristic of microporous materials. However, the isotherm of mesoporous ZSM-5 zeolite (Fig. 2b) reveals microporosity as a sharp knee at P/P_0 lower than 0.1 due to filling of micropores. Furthermore it shows capillary condensation as an adsorption H_2 hysteresis loop at higher P/P_0 which is characteristic of Type IV isotherms and confirms the presence of “ink-bottle” type mesopores in the material [23]. The pore size of the mesoporous ZSM-5 is about 6.3 nm. The total pore volume of the mesoporous ZSM-5 zeolite is $0.79 \text{ cm}^3/\text{g}$, which consists of micropore volume of $0.03 \text{ cm}^3/\text{g}$ and mesopore volume of $0.76 \text{ cm}^3/\text{g}$. The BET surface area of the mesoporous ZSM-5 zeolite is about $599 \text{ m}^2/\text{g}$, consisting of a micropore area of $69.5 \text{ m}^2/\text{g}$ and the external surface area of $529.5 \text{ m}^2/\text{g}$. The mesoporous ZSM-5 zeolite can conquer pore size limitation of ZSM-5 zeolites and makes their pore size distributed from micro scale to meso scale. The formation of mesopores in the sample is probably due to the facts as follows. The aggregation or assembly of the aggregates of the glucose molecules could play an important role and the hydrogen bonding between the aggregated templates and the zeolite nonparticles in solution and/or during the gelation may direct mesophase formation in a manner similar to the neutral surfactants [24].

Download English Version:

<https://daneshyari.com/en/article/1489200>

Download Persian Version:

<https://daneshyari.com/article/1489200>

[Daneshyari.com](https://daneshyari.com)