Microporous and Mesoporous Materials 224 (2016) 17–25

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Mordenite zeolite with ultrahigh SiO_2/Al_2O_3 ratio directly synthesized from ionic liquid-assisted dry-gel-conversion

Zhipan Ma, Jingyan Xie, Jianlin Zhang, Wei Zhang, Yu Zhou**, Jun Wang*

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Chemical Engineering, Nanjing Tech University, Nanjing 210009, China

ARTICLE INFO

Article history:
Received 7 September 2015
Received in revised form
30 October 2015
Accepted 5 November 2015
Available online 14 November 2015

Keywords:
High-silica mordenite
Zeolite synthesis
Dry-gel-conversion
Ionic liquid
Microporous materials

ABSTRACT

SiO_2/Al_2O_3 ratio (SAR) is one of the most important parameters for zeolite materials, and tuning of SAR towards required topology is crucial for applications of zeolites. Mordenite (MOR) zeolites normally possess the moderate SARs of about 4–32. In this work, a breakthrough for straightforward synthesis of high-silica MOR zeolites was achieved without using seed or fluoride additive, attaining well crystallized MOR with wide window of SARs in the range of 11–263, in which the ultrahigh SAR of 263 represented the highest value for MOR up to date. The synthesis relied on the gel preparation by acidic hydrolysis of the silica precursor with the ionic liquid (IL), 1-butyl-3-methylimidazolium bromide ([BMIm]Br), as the structure-direct-agent, followed by dry-gel-conversion (DGC). Besides mordenite, ZSM-5 could be also obtained from this route. Thermal stability tests demonstrated that the obtained ultrahigh-silica MOR zeolites preserved the crystalline structure up to 800 °C, and the higher SAR, the better thermal stability. Our synthesis largely expands the SAR range of MOR zeolites and provides a series of highly thermal stable high-silica MOR zeolites as promising catalyst supports.

1. Introduction

Zeolites are a series of crystalline aluminosilicates built by regular assembly of corner-shared SiO_4- and AlO_4-tetrahedra [1–4]. Their unique well-defined uniform and tunable micropores enable them widely industrial applications as adsorbents, ion-exchangers and catalysts [5,6]. The topologies, morphologies, chemical compositions such as SiO_2/Al_2O_3 ratio (SAR) are all related to the actual performance of zeolites in practical applications [7–10]. Thereinto, SAR significantly affects physicochemical properties of zeolites, such as acid/base properties, coke resistance capability, hydrothermal stability, and catalytic activity and selectivity. Many efforts have been devoted to studying the SAR of zeolites, as well as the structure-performance relationship [11–13]. Existing research results indicate that high-silica zeolites favor better coke resistance, higher intrinsic activity (yield and selectivity) and superior thermal stability [14–18]. Nevertheless, it is still one challenge to directly synthesize high-silica zeolites on target topologies.

Among hundreds of zeolite topologies, mordenite (MOR) zeolites with parallel 12-membered ring (0.65 × 0.70 nm) and *Cmcm* space group have attained great industrial applications as green and effective catalysts for alkylation, reforming, hydroisomerization, dewaxing, cracking, and so on. Normally, SAR of MOR zeolites is in the range of 4–32 [19–22]. High-silica MOR zeolites can be obtained through both direct synthesis and post-modification [23–30]. For example, MOR zeolites with various SARs were prepared through acid extraction, calcination-acid extraction, high temperature steaming treatment combined with acid extraction, clathrate dealumination, etc. Alternatively, straightforward synthesis is preferred because of the following advantages: 1) simplifying the preparation process, 2) avoiding the usage of additional acid or base solutions that may increase the waste release, 3) resisting the formation of lattice defects and skeleton fragments [31], and 4) favoring higher thermal stability than post-dealuminated counterparts [32]. However, direct synthesis of high-silica MOR zeolites in early attempts was usually proceeded in the presence of additional additives (fluoride, zeolitic seed, benzene-1,2-diol chelate agent, etc.) [31–34], and the actual SAR in the final solid was restricted to below 74.2 [31]. To our knowledge, no MOR zeolite with higher SAR has been reported with a straightforward synthesis. Therefore, it is still very difficult to facilely control the SAR of MOR in a wide range for achieving the high-silica MOR zeolites.

* Corresponding author. Tel.: +86 25 83172264; fax: +86 25 83172261.
** Corresponding author. Tel.: +86 25 83172264; fax: +86 25 83172261.
E-mail addresses: njutzhouyu@njtech.edu.cn (Y. Zhou), junwang@njtech.edu.cn (J. Wang).

http://dx.doi.org/10.1016/j.micromeso.2015.11.007
1387-1811/

In this work, we develop a novel direct synthesis approach towards ultrahigh-silica MOR zeolites. The synthesis involves a dry-gel-conversion (DGC) route, in which the dry gel is prepared by acidic hydrolysis of silica precursor [35] with the ionic liquid (IL) of 1-butyl-3-methylimidazolium bromide ([BMIm]Br) being used as the structure-direct-agent (SDA). It is known that zeolite topology depends excessively on the chemical composition of the synthetic mixture and template/SDA [36]. Imidazolium-based ILs have been used as the synthetic media and/or templates and sometimes showed enumerated advantages including high thermal stability, nonflammability, and essentially zero vapor pressure compared with conventional organic templates [37–39]. For example, as the mixed SDA, imidazolium-based ILs with fluoride led to successful synthesis of multiple topologies of pure-silica or silica-rich zeolites [40,41]. Pure-silica ZSM-22 was rapidly synthesized by using [BMIm]Br as the SDA in DGC route [42]. Alkyl-substituted imidazolium-based IL as SDA was utilized to synthesize high-silica Y zeolites with SARs of 6.20–6.40 [43]. For MOR, it is rarely reported using ILs as template/SDA. Herein, straightforward synthesis of ultrahigh-silica MOR is achieved through the IL-assisted DGC route in an unseeded fluoride-free system. Highly crystallized high-silica MOR zeolites with a wide window of SARs (11–263) are prepared, remarkably breaking through the upper limit of SAR (74.2) from the traditional synthesis approach for MOR zeolites. Systematical investigations over the synthetic parameters are performed. Besides, well crystallized ZSM-5 can be also synthesized from this route. The thermal stability of the obtained high-silica zeolites is assessed by TG and XRD analyses. The results indicate that the obtained high-silica MOR zeolites possess superior thermal stability.

2. Experimental

2.1. Materials

Silicic acid (H_2SiO_3, 75 wt% SiO_2), Tetraethoxysilane (TEOS, 28.4 wt% SiO_2) and Sodium hydroxide (NaOH, 96 wt%) were purchased from Sinopharm Chem. Reagent Co., Ltd. Column-layer chromatographic silica gel (SiO_2, 98 wt%, 100 mesh) was from Branch of Qingdao Haiyang Chem. Co., Ltd. Colloidal silica ($SiO_2 \cdot nH_2O$, 40 wt%) was provided by Zhejiang Yuda Chem. Co., Ltd. Concentrated hydrochloride acid (HCl, 36.5 wt%) and Sodium aluminate ($NaAlO_2$, 41 wt% Al_2O_3) were provided by Shanghai Chem. Reagent Co., Ltd. Aluminum sulfate ($Al_2(SO_4)_3 \cdot 18H_2O$, 99 wt %) was provided by Xilong Chem. Reagent Co., Ltd. 1-Butyl-3-methylimidazolium bromide ([BMIm]Br, 99 wt%) was purchased from Lanzhou Greenchem ILS, LICP of Chinese Academy of Sciences. Tetraethylammonium bromide (TEABr, 99 wt%) was supplied by Jintan Huadong Chem. Res. Institute. All the chemicals were of analytical grade and employed as received.

2.2. Synthesis

High-silica mordenite (MOR) zeolites were prepared in a dry-gel-conversion (DGC) route by using ionic liquid as the structure directing agent (SDA). A typical synthetic procedure was carried out as follows. First, the silica source of silicic acid was mixed with deionized water in a glass beaker, followed with slowly dropping of concentrated hydrochloric acid to reach the pH value of ca. 1.0. The obtained mixture was stirred at 25 °C for 24 h, then the alumina source of $NaAlO_2$ and SDA of [BMIm]Br were added one by one. After that, NaOH was added to get the required alkaline environment of the slurry. The obtained slurry was then aged at room temperature for 12 h. The final molar composition of the gel was 1 SiO_2: x Al_2O_3: 0.2 [BMIm]Br: y H_2O: w Na_2O (x, y and w denote the molar ratios of Al_2O_3/SiO_2, H_2O/SiO_2 and Na_2O/SiO_2, respectively). After aging, the gel was oven-dried at 100 °C to remove water, and the resultant solid was further ground to the powder-state dry gel. Finally, 0.5 g dry gel was placed on a raised Teflon holder and sealed inside a 50 mL Teflon-lined stainless steel autoclave involving 0.5 g deionized water at the bottom for static crystallization at 140 °C for 4 days under autogenous pressure. The final product was obtained by calcining at 550 °C for 5 h in air stream to remove the ionic liquid.

Various samples were synthesized with the similar procedure by varying the silica source, aluminum source, crystallization temperature and time, etc. The obtained high-silica MOR and ZSM-5 (MFI phase) zeolites using silicic acid were named as HMn and HZn, in which $n = 1/x$ (n means molar ratio of SiO_2/Al_2O_3 in initial gel). Samples obtained by using TEOS were named as TMn and TZn for MOR and MFI phase.

2.3. Characterization

The crystalline structure of the prepared samples were characterized by X-ray diffraction analysis (XRD) with a SmartLab diffractometer from Rigaku equipped with a 9 kW rotating anode Cu source at 45 kV and 100 mA, from 5° to 50° with a scan rate of 0.2° s^{-1}. Morphologies of the samples were tested with a field-emission scanning electron microscope (SEM) instrument of Hitachi S-4800. EDS analysis was obtained on this instrument with an acceleration voltage of 20 kV. Specific surface areas and pore volumes of the calcined samples were obtained from N_2-adsorption–desorption isotherms using multipoint BET and t-plot methods. The samples were outgassed at 300 °C to a vacuum of 10^{-3} Torr prior to the measurements. Isotherms were obtained at liquid nitrogen temperature with a BEL SORP-MAX analyzer. FT-IR spectra were recorded on a Nicolet iS10 FT-IR instrument (KBr disks) in the 4000–500 cm^{-1} region. Morphology and microstructure of zeolites were determined by transmission electron microscopy (TEM) using a JEM-2100 F. Thermogravimetric (TG) analysis was carried out with a STA 409 instrument in dry air at a heating rate of 10 °C min^{-1}. The chemical compositions of samples were obtained using Jarrell-Ash 1100 inductively coupling plasma (ICP) spectrometer and ADVANT'XP X-ray fluorescence (XRF) spectrometer (ZSX Primus II). The C and N elemental analysis was performed on an elemental analyzer Vario EL cube. The ^{29}Si and ^{27}Al MAS NMR spectrum were recorded on a Bruker Avance 400 D multinuclear solid-state magnetic resonance spectrometer.

3. Results and discussion

3.1. Formation of ultrahigh-silica MOR

Fig. 1A shows the XRD patterns of the as-synthesized samples obtained with different SiO_2/Al_2O_3 molar ratios in the initial gel's composition of 1 SiO_2: x Al_2O_3: 0.2 [BMIm]Br: 8H_2O: 0.25 Na_2O (x = 0.01, 0.005, 0.0038, 0.0031, 0.0025, 0) at the crystallization temperature of 140 °C and time of 4 days. Pure MOR phase with high-resolution XRD diffracting peaks is observed over the samples of x = 0.01, 0.005, 0.0038 and 0.0031, in spite of the slight decline of the peak intensity with the decrease of the Al content in the gel. Further reducing the Al amount to x = 0.0025 causes emerging a little impurity peak belonging to ZSM-5 zeolite at 2θ = 7.94° (Fig. 1A, curve e). Pure phase assigned to ZSM-22 rather than MOR forms in the absence of aluminum source $NaAlO_2$, suggesting that the small amount of Al^{3+} is crucial for the formation of MOR phase. Fig. 1B gives the XRD patterns of the as-calcined MOR zeolites named as HMn series (n = 1/x, meaning the molar ratio of SiO_2/Al_2O_3 in initial gel). Similar XRD diffraction peaks attributable to MOR structure are observed over the HMn (n = 100, 200, 260 and