Microporous and Mesoporous Materials 235 (2016) 135–142

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Syntheses of SSZ-39 and mordenite zeolites with *N,N*-dialkyl-2,6-dimethyl-piperidinium hydroxide/iodides: Phase-selective syntheses with anions

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ARTICLE INFO

Article history:
Received 23 June 2016
Received in revised form
30 July 2016
Accepted 3 August 2016
Available online 4 August 2016

Keywords:
AEI zeolite
Anion effect
Ethylene-to-propylene
Phase-selectivity
SSZ-39

ABSTRACT

SSZ-39 and mordenite zeolites were obtained from the conversion of zeolite Y in the presence of the same reaction precursors (organic templates, NaOH, water, etc.) under a wide range of reaction conditions. The applied templates were *N,N*-dialkyl-2,6-dimethyl-piperidinium-OH and -I (alkyl: ethyl or methyl). Curiously, SSZ-39 and mordenite were obtained from hydroxides and iodides, respectively, showing firstly the importance of the anion in the selective crystallization of zeolites. Reactions were also performed at the same set of pH values (achieved by adding small amounts of NaOH to the iodide-based precursors) to investigate the effect of basicity; the results did not vary appreciably with the pH of the synthesis precursors. Based on the phase conversion (MOR – > AEI or ANA with increasing reaction time and pH), the selective formation of SSZ-39 and mordenite from hydroxides and iodides, respectively, could be explained in terms of zeolite-promoting and -preventing anions (hydroxide and iodide, respectively). The phase conversion of zeolites could be explained on the basis of the maximum pore size of zeolites, rather than the framework densities. The obtained zeolites (SSZ-39 and mordenite), in their protonated forms, were employed in ethanol dehydration and direct ethylene-to-propylene conversion, and the results showed that the two zeolites have potential application in acid catalysis. In particular, the SSZ-39 with an AEI structure can be applied in the direct production of propylene from ethylene or ethanol.

1. Introduction

Considering the versatile applications of porous materials such as zeolites and mesoporous materials in catalysis, separation, and adsorption, the phase-selective and facile syntheses of useful porous materials, especially at low cost, are very important [1–10]. So far, the selection of organic templates or structure-directing agents (usually cationic or neutral) has proved important for attaining the desired zeolite [11,12]. In particular, the molecular shape and size of the organic templates play a crucial role in zeolite syntheses [11,12]. There are a few reports showing the importance of metallic cations (especially alkali metals of hydroxides) in zeolite syntheses [13–17].

However, only a small number of studies [18] have been conducted on the effect of anions on zeolite syntheses, as anions have traditionally been regarded as bystanders in syntheses or as simple neutralizers for cations. Toktarev and coworkers [19] studied the syntheses of beta zeolites in the presence of various anions and ranked a variety of anions in order of zeolite-promoting effect (F^-, SO_4^{2-}, PO_4^{3-}, $(CH_2COO)_2^{2-} > HCOO^- > (COO)_2^{2-}$, $CH_3COO^- \gg Cl^- \sim NO_3^- \gg Br^- \gg I^- \gg ClO_4^-$). Similarly, a few reports [20–22] have shown the importance of anions, mainly in terms of the reaction rates of zeolite syntheses. However, thus far, there have been no reports on the phase-selective syntheses of zeolites with different anions.

Additionally, the substitution of hydroxide, which is traditionally used, with bromide or iodide (for example, tetraethyl

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http://dx.doi.org/10.1016/j.micromeso.2016.08.003
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ammonium-Br or -I) might be economically viable [23] considering the lack of a need for ion-exchange for hydroxide and the generally lower cost of bromide or iodide templates. Therefore, zeolite syntheses using different anions are interesting and important for commercial applications.

SSZ-39 (IZA code: AEI) zeolite is characterized by a Cmcm space group and a 3-dimensional channel system (maximum pore size of 8-membered rings, 8-MRs) [24]. The syntheses of SSZ-39 zeolite have been studied [25–27] since the first report in 1997 by Zones and coworkers [28]. SSZ-39 has several catalytic applications, such as the selective catalytic reduction of NOx [29,30] and methanol-to-olefin (MTO) conversion [31]. Mordenite (IZA code: MOR) is a traditional zeolite featuring a space group of Cmcm and a 1-dimensional channel system with a maximum pore size of 12-MRs [24]. Mordenite has been used as a catalyst in various chemical processes [32].

In this study, the phase-selective synthesis of SSZ-39 and mordenite zeolites with *N,N*-dialkyl-2,6-dimethyl-piperidinium hydroxide/iodide (alkyl: ethyl or methyl) was undertaken. Moreover, the selective synthesis was explained based on the contribution of anions to the acceleration of the zeolite synthesis and phase conversion of zeolites. The phase conversion was also discussed in terms of the crystal structures (such as pore size) of the studied zeolites. The synthesized zeolites were applied in ethylene-to-propylene (ETP) conversion and ethanol dehydration to estimate the possible applications of the zeolites in acid catalysis.

2. Experimental

2.1. Materials

All chemicals and materials used were collected from commercially available sources and used without further purification. cis-2,6-Dimethylpiperidine ($C_7H_{15}N$, 98%), iodomethane (CH_3I, 99%), iodoethane (C_2H_5I, 99%), potassium bicarbonate ($KHCO_3$, 99.7%), potassium carbonate (K_2CO_3, 99.5%), sodium silicate solution ($Na_2O(SiO_2)_x \cdot xH_2O$), and sodium hydroxide (NaOH, 98%) were purchased from Sigma-Aldrich. Methanol (CH_3OH, 99.6%), chloroform ($CHCl_3$, 99.5%), and diethyl ether (C_2H_6O, 99%) were procured from OCI chemicals. Y zeolites (hydrogen or ammonium form) having various SiO_2/Al_2O_3 ratios (SARs) (CBV 300, CBV 712, CBV 720, and CBV 760 with SARs of 5.1, 12, 30, and 60, respectively) were acquired from Zeolyst. Amberlite®IRN-78 hydroxide anion exchange resin was purchased from Alfa Aesar.

2.2. Syntheses of zeolites

2.2.1. Synthesis of organic templates

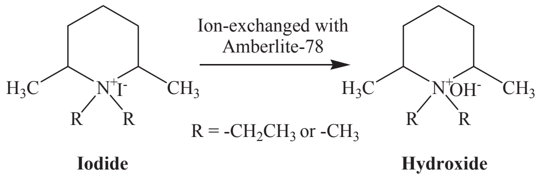
The organic templates *N,N*-diethyl-2,6-dimethyl-piperidinium hydroxide/iodide (DEDMP-I/-OH) and *N,N*-dimethyl-2,6-dimethyl-piperidinium hydroxide/iodide (DMDMP-I/-OH) were prepared from cis-2,6-dimethylpiperidine using a previously reported method [28]. A mixture of cis-2,6-dimethylpiperidine (12.0 g) and potassium bicarbonate ($KHCO_3$; 21.3 g) in 110 mL of dry methanol was placed in a two-necked round-bottom flask, and then iodoethane (66.7 g) was added dropwise under stirring. The resulting mixture was heated at reflux for three days under magnetic stirring. After the reaction reached completion, the reaction mixture was cooled to room temperature, and $KHCO_3$ was removed by filtration. The solution containing piperidinium salt was concentrated by evaporation and precipitated by the addition of diethyl ether. The inorganic salt was completely removed by extracting the piperidinium salt with $CHCl_3$. The obtained piperidinium salt (DEDMP-I) was purified by recrystallization from hot acetone and diethyl ether with a small amount of methanol. Similarly, the DMDMP-I salt was prepared by using potassium carbonate (K_2CO_3) and iodomethane at room temperature under stirring for 7 d. Then, the quaternary DEDMP-I and DMDMP-I salts were converted to hydroxide forms by treatment with Amberlite®IRN-78 hydroxide ion-exchange resin (Scheme 1), and the final concentration of hydroxide ions was confirmed by titration with 0.01 M HCl.

2.2.2. Synthesis of MOR/AEI zeolites

The syntheses of zeolite samples were conducted following a previously reported method [28], and the detailed reaction conditions (typical gel compositions, templates, pH, reaction temperatures, and reaction times) are shown in Table 1. The required amount of template (DEDMP-I/-OH or DMDMP-I/-OH) was mixed with aqueous NaOH solution in a Teflon liner. Then, the Y zeolite crystals were introduced into the solution, and the sodium silicate solution was added and stirred for 1 h. The liner with a specific gel composition was then transferred into a stainless-steel autoclave. The prepared reaction vessel was then placed in an electric oven and heated at a predetermined temperature (135–180 °C) for a predetermined duration (2 h–7 d). After the reactions reached completion, the solid products were collected by filtration, followed by washing with water and drying in an oven at 100 °C overnight. Finally, obtained samples were calcined at 550 °C for 6 h to remove the organic templates from the as-synthesized zeolite samples. The yield of the obtained zeolites was estimated based on the amount of zeolites obtained with respect to the total weight of the applied Y zeolite and silica (from sodium silicate) used in each reaction. The protonated form of selected MOR/AEI samples (samples 1, 2, 5, and 6) was obtained by ion-exchange of the organic-free samples with 1.0 M NH_4NO_3 solution (80 °C and a liquid-to-solid ratio of 100) for 6 h. Finally, the NH_4-form samples were calcined at 500 °C for 3 h in air. The entire ion-exchange procedure was repeated three times.

2.3. Characterization of zeolites

X-ray diffraction (XRD) measurements were conducted on a diffractometer (D2 Phaser with CuKα radiation, Bruker). The morphology of the zeolites was observed with an FE-SEM (field emission scanning electron microscope, Hitachi, SU-8220). Nitrogen adsorption experiments were conducted at −196 °C using a surface area and porosity analyzer (Micromeritics, Tristar II 3020). Before measurements, the samples were evacuated at 150 °C for 12 h. Thermogravimetric analyses (TGA) of the selected materials were performed at a programmed temperature ramp (10 °C/min) under N_2-flow with a PerkinElmer TGA 4000 system. The composition (i.e., SAR) was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES) (Thermo Scientific Co./iCAP 6300 Duo). The acidity of the zeolites was determined using an NH_3 temperature-programmed desorption instrument (TPD, Micrometrics, AutoChem II 2920) equipped with a thermal conductivity detector. After desorption of the physisorbed ammonia at 150 °C, the adsorbed ammonia was desorbed by increasing the



Scheme 1. Chemical structures of N,N-dialkyl-2,6-dimethyl-piperidinium (dialkyl is diethyl or dimethyl) templates. The hydroxides were obtained via ion-exchange of iodides.