



Synthesis of mesoporous MOR materials by varying temperature crystallizations and combining ternary organic templates

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ABSTRACT

An approach, which involved perturbations of synthesis conditions in crystallization temperature and organic template composition, has been proposed for derivation of mesopores from bulk structural defects formed in mordenite (MOR) phases, based on the character of intrinsic crystal defects and tensional distortions of two compressed 8-membered rings in MOR framework. Consequently, hierarchically porous materials with MOR structures were prepared by varying temperature synthesis and using ternary organic micelles templates. The synthesized materials were characterized by powder X-ray diffraction, nitrogen adsorption at 77 K and transmission electron microscopy. These crystalline materials combined the advantages of both mordenites with the micropore system and mesoporous materials by featuring an additional intracrystalline mesopore system in MOR single crystals, resulting in a hierarchical pore distribution in range of 1.7–80.0 nm together with the significant specific surface areas. In particular, individual crystal morphologies of typical mesoporous MOR materials showed the defect-rich structures responding essentially to the mesoporosity; the mesoporous materials were substantiated matchable well to normal mordenites in acid capacity and acid strength distribution. Furthermore, several factors acting on intracrystalline mesopore formation were elucidated for explicating the perturbation synthesis approach, and whole reaction routes for synthesizing different solid products under related crystallization conditions were summarized coupling with a demonstration of part TEM micrographs. The overall results suggested that the investigative approach of perturbation imposed on crystal growth provides an alternative route for direct hydrothermal synthesis of mesoporous zeolite materials and implied that bulk structural defects within single crystals lead to the formation of intracrystalline mesopores in various sizes.

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1. Introduction

Development of advanced heterogeneous catalysis is essentially depended on exploitation of new functional zeolite materials. Creation of hierarchical pores has become a huge challenge in the field of porous material synthesis, and from a catalytic perspective, it is of most significance to recognize the methodology and formation mechanism of intracrystalline mesopores in zeolite synthesis [1]. Classical mordenite (MOR), a member of the large-pore zeolite family of silicoaluminates, has an orthorhombic crystal structure attributed to topological space group symmetry *Cmcm*. The MOR zeolite has a pore system consisting of a linear 12-membered ring (MR) channels (0.67×0.70 nm) running along to the *c*-axis and a vertical crossed 8-MR channels (0.26×0.57 nm) along to the *b*-axis, while another one is composed of compressed 8-MR channels (0.34×0.48 nm) paralleled with the 12-MR main channels

[2]. As one of the important zeolite catalysts, mordenite has been used for acid-catalyzed reactions in oil refining or petrochemical processes [3–5]. However, since all the 8-MR channels are unable to access for most molecules to enter, the MOR zeolite is generally considered as a one-dimensional pore system associated with the 12-MR channels, particularly resulting in certain steric inhibitions for most bulky molecular reactions [6]. The pore structure of mordenite evidently restricts its applications as catalysts because of mass transfer limitations.

Zeolite-based materials containing various levels of porosity have a number of potential advantages, e.g., prominent acidities equivalent to conventional zeolites and improvements in overall mass transport including more accesses to acid sites. From early work on the synthesis of the long-range ordered mesoporous materials, synthesis strategies for new materials can be categorized mainly into three types. The first type of approach is obviously expected to create mesopores by post-treatments of given zeolites, e.g., MFI [7], MOR [8], MTW [9] and BEA zeolite [10], which involves steaming and acid leaching treatments of zeolite crystals and recent alkaline-treated desilication from different zeolite frameworks.

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However, the mesopores formed during steaming are predominantly cavities inside the zeolite crystals, rather than cylindrical-like pores with the interior of the crystal, while the method of alkaline-treated desilication provides a broader pore sized distribution due to non-localized extraction of framework silicon-atoms from the zeolite lattice [11,12]. The second type of approach takes a mesostructured replication as its starting point. In fact, a great variety of mesoporous and/or macroporous zeolite materials have been hydrothermally synthesized by either hard templates, viz. carbon nanotubes [13], ultrafine carbons [14] and nanosized calcium carbonates [15], or soft templates, e.g., starch [16,17] and glucose [18]. These disordered pores or caves, depending on the used substrates in size, are left in the crystalline zeolites after removing these templates from the synthesized matrices. A well-known problem is how to effectively eliminate the organic or inorganic substrates without devastation of zeolite structures. In most cases, these methods of mesopore replication are subjected to an insufficient porosity in these synthesized materials [19]. The third type of approach seeks to impose a long-range ordered mesoporosity upon a microporous material, for example, by growing zeolite crystals onto a porous substrate or by controlled packing of zeolite nanocrystals. Various composite materials have already been obtained using these synthesis methods. These materials are usually either composites of certain zeolite with an ordered mesoporous material [20,21] or entire assemblies of inbuilt subcolloidal zeolitic crystals [22]. One common trend relating to the ordering and crystallinity appears for most of the synthesized materials, viz. the ordering nature of materials always decreases with their increasing crystallinity. Hence it is really a difficult alternative between ordering and crystallinity. However, remarkable investigations on synthesis of zeolites with mesoporous structure have been reported very recently [23–27]. It is noteworthy that the combination of crystalline matrices and mesoporous structures are examined for the purpose of manufacturing new porous materials.

As distinct from most zeolites, the two affiliated 8-membered rings in MOR framework are severely compressed and distorted. The strong strain between certain adjacent $[\text{TO}_4]$ tetrahedrons may induce lattice defects including stacking faults and even an intergrowth with a dachiardite phase [28], and the transition in nuclear growth orientation has been investigated in respect to the mordenite matrices [29]. Since the objective seems always to seek intracrystalline mesopores rather than only perfect crystallinities, these structural characters of mordenite allow desilication and dealumination but also may suggest a new idea of deriving mesopores from bulk structural defects in MOR phases. Thereby a novel approach is proposed here to construct intracrystalline mesopore textures by introducing and intensifying crystal defects of MOR zeolites in hydrothermal synthesis. As a consequence, new mordenite materials of hierarchical pore structures are synthesized via two-staged temperature crystallizations and using ternary organic supermolecular micelles as templates. The main intentions in the present work are to discuss the feasibility of the mesopore derivation and to report important factors effected on the formation of intracrystalline mesopores. Furthermore, the crystalline phase, mesoporosity and acidity of synthesized materials are studied using powder X-ray diffraction, nitrogen adsorption at 77 K, transmission electron microscopy, and ammonia temperature-programmed desorption. Finally, mesopore formation is represented based on the observed results.

2. Experimental

2.1. Synthesis of mesoporous MOR materials

To pre-prepare a hydrated silica gel (SiO_2 , ca. 60%) as a low alkaline and concentrated silica source, the commercial water glass

(modulus, 4.0) was repeatedly treated with a mixed solution consisting of 1.0 M ammonium chloride and 0.5 M hydrochloric acid, followed leaching off partial solution until a final pH value of around 10.0. Mordenite materials within/without mesoporous structures were synthesized, respectively, using an initial gels with molar compositions as followings: $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{TEAOH}:\text{CTAB}:\text{CA}:\text{H}_2\text{O} = 1.0:(0.033\text{--}0.067):0.58:(0\text{--}0.23):(0\text{--}0.25):(0\text{--}0.06):105\text{--}120$. In a typical procedure, 16.0 g of the prepared silica gel was diluted with 150 g distilled water for forming silica sol (A); A mixture of 0.67 g NaAlO_2 and 4.1 g NaOH was dissolved into 150 g distilled water for generating mixing solution (B); Another mixing solution (C) composed of tetraethylammonium hydroxide (TEAOH, 35%), cetyltrimethylammonium bromide (CTAB, 98%), and/or *n*-cetylamine (CA, 98%) was prepared with 60 g distilled water according to initiative gel compositions. And then the silica sol (A) were mixed rapidly with the solution (B) by a vigorous stirring at ambient temperature, followed by the addition of mixing solution (C). The homogenized gel was aged overnight at room temperature and examined with the pH of 11.5. The initial gel was statically heated in a Teflon-lined autoclave at 413 K for 3 h and subsequently at 443 K for 196 h by a rate of temperature rise of $0.5\text{ K}\cdot\text{min}^{-1}$. Finally the solid was separated by filtration, washed with distilled water and dried at 383 K for 24 h. For all samples the organic templates were removed by calcinations at 613 K for 3 h and at 823 K for 8 h, and the resulting solid products were defined as S-*n*. In addition, partial mordenite samples were converted into H-MOR zeolites by three successive ion exchanges using 0.1 M NH_4NO_3 solution and calcination at 813 K for 4 h.

2.2. Physicochemical characterization

Solid samples were characterized by powder X-ray diffraction (XRD) on a Rigaku D/max-2400 diffractometer equipped with $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154\text{ nm}$) at 50 kV and 40 mA. The XRD data were gathered in a low angle range of $1.5\text{--}5^\circ$ and successively in a wide angle range of $5\text{--}50^\circ$ (2θ), and scanning step size was 0.02° as counting time of 10 s. Nitrogen adsorption-desorption isotherms of calcined samples were measured on a Micromeritics ASAP 2400 apparatus at liquid nitrogen temperature (77 K). Microporous volume and microporous surface area were determined with the *t*-plot method; the data on mesoporosity and mesopore size distribution were calculated from the adsorption branch of the isotherm using the Barret-Joyner-Hallenda (BJH) model [30]. Transmission electron microscope (TEM) images were obtained with a JEOL 2000 electron microscope operating at 200 kV. Prior to measurements, the material was supersonically dispersed in ethanol and the suspended particulates were deposited onto a perforated carbon foil supported on a copper grid. Ammonia temperature-programmed desorption (NH_3 -TPD) was performed on a Dupont-2000 thermogravimetric analyzer equipped with a thermal conductivity detector (TCD). The Si/Al atomic ratios for the H-MOR zeolites were determined by inductively coupled plasma spectroscopy (ICP).

3. Results

3.1. Synthesis condition and powder X-ray diffraction

All samples were prepared using the hydrated silica-rich gel and sodium metaaluminate. Among the synthesized samples, one set regarding S-1, S-2 and S-3 was related with an increasing CA/SiO₂ molar ratio from 0.04 to 0.06, and another set concerning S-4, S-2 and S-5 was associated with Al₂O₃/SiO₂ molar ratio from 15 to 30. In addition, the normal mordenite (S-0) was synthesized by unique TEAOH template at only 413 K for 196 h. Powder X-ray diffraction patterns of these solid products were shown in Fig. 1 and the relevant synthesis conditions were displayed in Table 1.

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