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Post-transformation of MWW-type lamellar precursors into MCM-56 analogues

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Abstract

A postsynthesis method has been developed to prepare various metallosilicates structurally analogous to MCM-56 from corresponding lamellar precursors made up of MWW sheets. The precursors were converted into high crystalline MCM-56 analogues readily by a controlled acid treatment. Acid-treating the MWW precursors at lower temperatures (<353 K) led to MCM-56 analogues even after further calcination, whereas the acid treatment at higher temperatures such as refluxing only resulted in conventional three dimensional (3D) MWW structure. In addition, the construction of MCM-56 structure depended greatly on the crystal size of the precursors, that is, the structural transformation of MCM-56 was achieved only for the precursors with a relatively smaller crystal size. The formation of MCM-56 analogues was however neither dependent of the types of metallosilicates (containing B, Al, Ti, Ga or Fe ions) nor the amount of framework metal ions. Compared with 3D Ti-MWW, the Ti-MCM-56 analogue had a larger external surface, which mitigated effectively the steric restrictions to bulky molecules imposed by the intracrystal micropores. The Ti-MCM-56 analogue was then superior to Ti-Beta, 3D Ti-MWW and TS-1 in the epoxidation of a wide range of bulky alkenes with *tert*-butyl hydroperoxide as well as in the oxidative desulfurization of dibenzothiophene with hydrogen peroxide.
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1. Introduction

Zeolites are useful microporous materials in a number of chemical processes; their applications range from effective heterogeneous catalysts to separation/sorption agents. The pore sizes of zeolites are the same scale as the molecular dimensions of many organic reactants, which gives rise to so-called shape-selective catalysis [1,2]. This unique property implies that it is impossible to process those organic molecules larger than the pores of zeolite catalysts. From the viewpoint of petrochemical and fine chemical applications, it is thus desirable to develop zeolites with larger porosity but still containing highly active and stable catalytic sites. Therefore, how to develop zeolitic porous materials which are accessible to large organic molecules is of continual research interests.

Many porous materials with larger pores have been hydrothermally synthesized, for example, crystalline UTD-1 [3], CIT-5 [4,5], and ordered mesoporous silicates (M41S type materials) [6]. For example, UTD-1 with one dimensional (1D) 14-membered ring (MR) pores is a promising catalyst for large molecules. Nevertheless, the pore sizes of these zeolites are still not large enough for processing bulky reactants [7]. In comparison to zeolites, the mesoporous materials do have much larger pores with tunable sizes, but they are thermally less stable and catalytically less active. Therefore, to make the most of the active sites on the exterior of zeolite crystals would be an alternative

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way to find highly active catalysts which are capable of overcoming the shortcomings shown above. Post modification of those zeolites originated from lamellar precursors is considered to be suitable for preparing the catalysts for processing large molecules because they have structural diversity.

As one of the most representative lamellar zeolite, MCM-22, with the MWW structure and the same topology as PSH-3 [8], SSZ-25 [9], ERB-1 [10], ITQ-1 [11] and MCM-49 [12], is comprised of two independent channel systems. One contains the 12-MR supercages of $0.7 \times 0.7 \times 1.8$ nm dimension connected to one another through 10-MR windows, while the other is a sinusoidal 2D 10-MR pore system [13,14]. Another feature of MWW structure is that there are 12-MR half cups or side pockets exposed to the crystal exterior. Since the crystals of MCM-22 are made up of very thin sheets with a hexagonal morphology, the 12-MR cups are abundant on the crystal exterior. An easy accessibility of the side cups to reactant molecules has made MCM-22 an active catalyst for a wide variety of reactions [15–17].

In order to make full use of intracrystal supercages, a microporous and mesoporous hybrid material, MCM-36, has been postsynthesized from MCM-22 lamellar precursor through swelling with surfactant first and subsequent interlayer pillaring with silica [18–20]. MCM-36 is shown to be catalytically active for the alkylations of *iso*-butane with *n*-butene [19,20]. Following a similar line, MCM-22 is further delaminated by combining surfactant-swelling and sonic treatment, which results in ITQ-2 with 12-MR cups exposed to a maximum extent [21]. ITQ-2, structurally containing single layer of MWW sheet, is reached readily by large molecules. It is then superior to MCM-22 in gas–oil cracking as a solid acid catalyst. From the sense of industrial application, it is have to say that both MCM-36 and ITQ-2 are facing some disadvantages such as a troublesome multistage preparation as well as using expensive surfactant. It is thus desirable to prepare a material with the 12-MR cups exposed to the crystal exterior in a more feasible way.

As an important member of the MWW family, MCM-56 is synthesized from the same synthetic gel as MCM-22 but within a shorter crystallization time [22]. Only few reports deal with the properties and catalytic applications of MCM-56. Sharing the same basic structure with MCM-22, MCM-56 has more 12-MR cups exposed to the crystal surface and is characteristic of large pore zeolites [23–25]. Although its real structure is still waiting for further resolution, MCM-56 is presumed to be a partially delaminated zeolite comprising a disordered collection of MWW monolayers and having a large portion of exposed external surface. Up to date, MCM-56 is prepared only by hydrothermal synthesis, in which it is needed to control carefully the crystallization extent. Furthermore, MCM-56 is still limited to aluminosilicates.

In this paper, we present for the first time a universal postsynthesis method for preparing various metallosilicates structurally analogous to MCM-56, containing B, Al, Fe, Ga or Ti in the framework. Using titanosilicate as a representative, the formation conditions and catalytic properties of Ti-MCM-56 analogue in the liquid-phase oxidation have been studied in detail.

2. Experimental

2.1. Preparation of materials

The MWW lamellar precursors containing Ti, Al, B, Fe or Ga ions were hydrothermally synthesized using piperidine (PI) or hexamethyleneimine (HMI) as an SDA. Following the procedures reported previously [26], Ti-MWW and B-MWW lamellar precursors were crystallized from the gels with the molar compositions of $1SiO_2:(0–0.05)TiO_2:1.4PI$ or $HMI:0.67B_2O_3:19H_2O$ at 443 K for 7 days. The samples prepared using PI and HMI were denoted Ti-MWW-PI and Ti-MWW-HMI, respectively. A Ti-containing precursor was also prepared with fluoride method from the gel of $1SiO_2:0.03TiO_2:1.0PI\ 0.50B_2O_3:1.0HF:10H_2O$ at 443 K for 10 days, which is denoted Ti-MWW-PI-F. Other precursors of MWW metallosilicates were synthesized from the gels of $1SiO_2:0.033M_2O_3:0.9HMI:0.15Na_2O:45H_2O$ at 423 K for 7 days, where M represents Al, Ga or Fe [27–29]. The crystallization was carried out all under rotation at 100 rpm.

The postsynthesis of MCM-56 analogues included the acid treatment of as-synthesized MWW precursors in 2 M HNO_3 solution at desirable temperatures (303–353 K) for 0.5–18 h and subsequent calcination at 803 K for 6 h. For control experiments, the MWW precursor was also refluxed with HNO_3 solution. Other titanosilicates such as TS-1 and Ti-Beta were also prepared by hydrothermal synthesis method. According to the original patent [30], TS-1 (Si/Ti = 40) was synthesized using tetraethyl orthosilicate (TEOS), tetrabutyl orthotitanate (TBOT) and tetrapropylammonium hydroxide (TPAOH). After burning off the organic species, TS-1 was further washed with 1 M HCl solution to remove any extraframework Ti species and alkali ions contaminated in TPAOH solution. Al-free Ti-Beta (Si/Ti = 40) was prepared with seeding method according to the literature [31].

2.2. Characterization methods

The samples were characterized by X-ray powder diffraction (XRD) patterns measured on Bruker D8 ADVANCE diffractometer using Cu-Kα radiation. UV–visible diffuse reflectance spectra were recorded on a Shimadzu UV-2400PC spectrophotometer using $BaSO_4$ as a reference. Scanning electron microscopy (SEM) was performed on a Hitachi-4800 microscope after suspending the sample in ethanol. Surface area was measured by N_2 adsorption at 77 K on an Autosorb Quancachrome 02108-KR-1 analyzer after evacuation at 573 K for 5 h. IR spectra were collected at room temperature on a Shimadzu FTIR-8100 spectrometer with a spectral resolution of 2 cm^{-1} after evacuating the self-supported wafer (30 mg