

Synthesis and Application of Nanofabricated Nanoporous Materials

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ABSTRACT

Nanofabrication of nanoporous materials under microwave irradiation was successfully implemented by the adhesion of crystallites through the condensation of hydroxyl groups on surface via selective adsorption of microwave energy on Ti species as a nanoglue. This microwave technique gave births of both the uniform size of hockey puck shaped crystals and the stacking of these crystals into fiber or rod types in the synthesis of nanoporous materials such as MFI and AlPO-5 zeolites. The formation of these nanostacked MFI-type zeolite crystals having nanorod shape was ascribed to the presence of metal species, which selectively absorbed microwave irradiation. These fibrous MFI zeolites provide exciting and unique physicochemical properties, for example, low packing density, high stability of the fibrous morphology and the enhanced hydrophobicity. The fabricated Ti-MFI and AlPO-5 show preferential adsorption of p-xylene over o-xylene, which may suggest that a longish molecule can be adsorbed preferentially on the longish nanoporous materials.

Keywords: Nanoporous, material, microwave, nanofabrication, TS-1, thin film.

1. Introduction

Nanofabrication of nanostructured materials has been greatly interested for the implementation of miniaturization of chemical system as the application of nanomaterials. Nanoporous materials having micropores or mesopores would be expected to show some advantages of encapsulating molecules in their pores for achieving the integrated systems such as micro-reactors, fuel cells, sensors, batteries and MEMS etc [1]. Zeolitic (molecular sieves) or mesoporous materials are the promising candidates for nanoscopically-engineered materials due to their well-defined pore structures, thermal stabilities and tailor-made synthetic abilities. Recently, many strategies have been tried to fabricate the nanostructured materials to form various shapes of nanofabrication such as fiber, rod, brick, ball and thin film.

In this regards, we recently made an invention of microwave technique which is a novel method to fabricate titanium-incorporated zeolite crystal (Ti-MFI) in which titanium species behave as the inorganic glue [2].

Microwave technique has been often addressed to offer several advantages over conventional synthesis of inorganic materials such as rapid and homogeneous heating throughout the reaction vessel, the possibility of selective heating of desired materials, homogeneous nucleation, and short crystallization time [3]. Although the microwave method has been successively applied to the synthesis of nanoporous materials, it has been mainly focused on substantial reduction in crystallization time. Recently, we found that the microwave technique could provide an efficient way to control particle size distribution and macroscopic morphology upon the synthesis of nanostructured materials [4]. Herein, those kinds of nanofabricated materials made of nanoporous materials are demonstrated to be synthesized by microwave technique for the rapidness and easiness. Moreover, their applications based on the nanofabricated morphologies are illustrated in catalysis.

2. EXPERIMENTAL

2.1. Microporous Materials

Ti-MFI zeolites were synthesized under microwave irradiation with literature method [2]. The final molar composition of the reaction mixture was 1 TEOS : 0.2 TPAOH : 0.05 TPOT : 1 isopropyl alcohol : 22.2 H₂O. For the MFI thin film or membrane, the titania thin film or membrane onto glass were prepared by dip-coating or spin coating. The titania precursors were placed on the surface of a precleaned substrates, and then a drop of a fluid containing a titania solution [5] was coated at 2000rpm. After 2day aging at room temperature, the titania substrates were calcined at 773K for 2h and then blow-dried with air. The TiO₂ substrate was placed horizontally at the bottom of the Teflon autoclave. Subsequently, the mixture was heated for 90 min at 438 K under 600W of microwave power with the microwave. The AlPO-5 molecular sieve with the shape of rod was synthesized under microwave irradiation at 473 K for 2 h. The molar composition of the reaction gel was 1.0Al₂O₃ : 1.1P₂O₅ : 3.5Et₃N : 5HF : 250 H₂O.

2.2. Mesoporous materials

In a typical synthesis, 16 g of a 10% aqueous solution of triblock copolymer, EO₁₀₆PO₇₀EO₁₀₆ (F127) was poured into 26.6 g of distilled water and then 4.71 g of sodium metasilicate (Na₂SiO₃·9H₂O) was added at 313 K with

magnetic stirring to yield a clear solution. To this solution, 13 g of concentrated hydrochloric acid (37.6%) was quickly added with vigorous stirring to obtain a gel. The molar composition of the gel mixture was $1.0 \text{ SiO}_2 : 3.17 \times 10^{-4} \text{ F127} : 6.68 \text{ HCl} : 137.9 \text{ H}_2\text{O}$. The gel solution was irradiated for 120 min at 373 K.

2.3. Characterization

The solid product was isolated by filtration or centrifuge, washed with doubly distilled water, dried in an oven at 373 K for 10 h and calcined in air at 773 K. The prepared samples were characterized by several instrumental analysis techniques. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku diffractometer using $\text{Cu K}\alpha$ radiation. Scanning electron microscopy (SEM) was performed with a Philips scanning electron microscope (model XL30S FEG). UV-DRS spectra were recorded on a Shimadzu spectrophotometer UV-2501PC with quartz flat cell at room temperature.

3. RESULTS AND DISCUSSION

3.1. Fabrication of Nanoporous Materials

Ti-MFI (titanium silicalite-1) [2] and AFI (AlPO-5) [6]

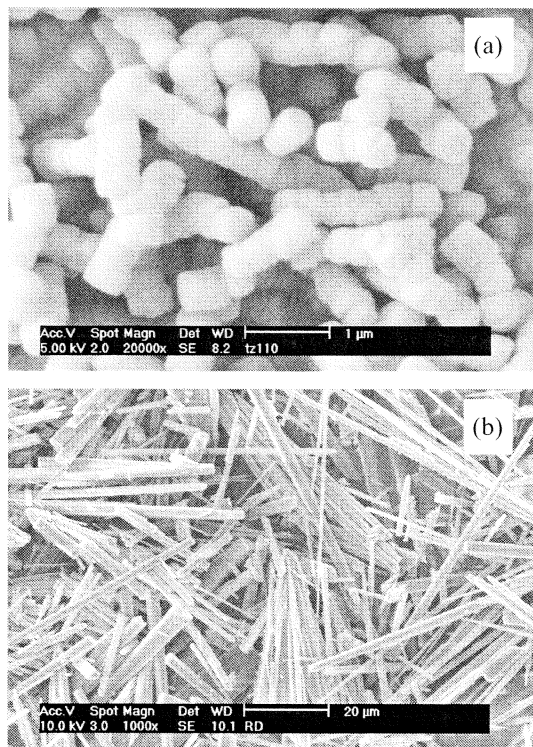
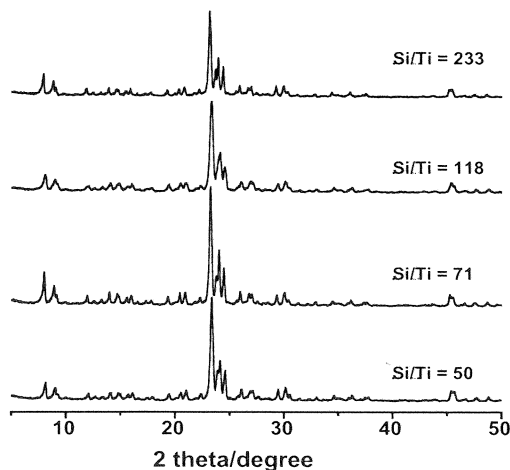


Figure 1. SEM images of (a)Ti-MFI and (b) AlPO-5 with the shape of nanofiber or nanorod.

with the shape of nanorod or nanofiber were synthesized (Figure 1) Firstly, when the silicalites(Si-MFI) was prepared, its shape was uniform with hockey puck shaped platelet crystals by microwave. However, if Ti-MFI(molar ratio of Si/Ti = 118) was synthesized by microwave, it showed similar XRD pattern as silicalite but fibrous morphology. (Figure 1a) These materials exhibit characteristics of the MFI structure with orthorhombic symmetry. (Figure 2) A curve for crystallization kinetics of Ti-MFI zeolite points to virtually 100% crystallinity after 40 min microwave irradiation. Fibrous Ti-MFI crystal seemed to show to be tightly bounded having approximately 400 nm in width and 1-10 microns in length.



der XRD patterns of Ti-MFI zeolites prepared by microwave irradiation for 90 min.

Figure 2. Powder XRD patterns of Ti-MFI zeolite prepared by microwave irradiation at 438K for 90min

The width of this material is very uniform, while its length is affected directly by amount of titanium species, synthetic time, etc. Under microwave environment, metallosilicate-1 having hockey puck or platelet shaped crystals was selectively obtained, and then these crystals were turned out to be fiber types based on same sized crystallites through self-assembly via its hydroxyl bonds. The BET (Brunauer-Emmett-Teller) surface area and pore volume of this material are $423 \text{ m}^2/\text{g}$ and 0.21 cc/g respectively. Figure 1b shows scanning electron microscopic (SEM) image of AlPO-5 synthesized with HF. The aspect ratio is quite of about 40 and has the shape of rod. The XRD pattern of AlPO-5 (not shown) is very similar to, except the relative intensities, the pattern of AlPO-5 with aspect ratio of about 1. The relative intensity of diffraction from the plane of (002) is very low, however, the diffraction from (100) is very high.

Moreover, zeolite monolayer thin film having well-arrays over TiO_2 -coated glass were successfully obtained with by microwave. (Figure 3a) As can be seen, Figure 1a and Figure 3a, titania species having high dielectric constants, which are located on the surface of zeolite crystals or

substrates, behave as nanoglue between various zeolitic crystals through selective absorption of microwave energy. We also have exploited this property to form patterned MFI thin films on a patterned substrate. (not shown) The TiO_2 patterns on a glass substrate were formed by applying the soft lithography technique and TiO_2 sol solution.

In the synthesis of mesoporous materials, as can be seen Figure 3b, spherical or ball shape of mesostructured material was successively synthesized at acidic condition. The XRD pattern of the as-made sample shows a single intense peak of $d = 112 \text{ \AA}$, indicative of a wormhole-like or a disordered mesostructure [7]. The sample shows spheres of a broad size range of $0.5 \sim 5 \text{ \mu m}$. The BET surface areas and pore volume of disordered sample is $672 \text{ m}^2\text{g}^{-1}$ and $0.59 \text{ cm}^3\text{g}^{-1}$, respectively. The ball shape of wormhole mesostructure by a supramolecular templating process

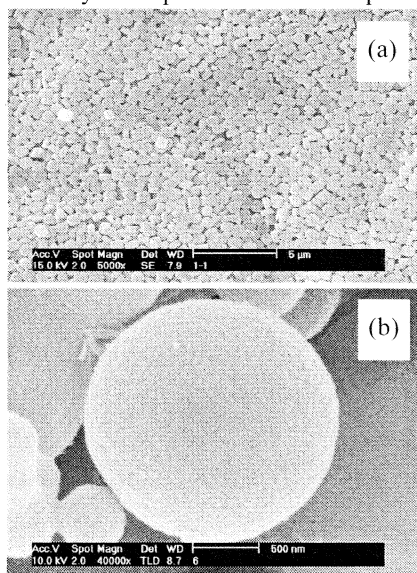


Figure 3. SEM image of (a) Thin film of hockey-puck shaped Si-MFI crystals on TiO_2 nanoglue (MFI/ TiO_2 /glass). (b) ball-shaped mesoporous material.

because the control of the particle morphology and size of mesostructured silicas could open up new possibilities for the application of mesoporous silicas as a packing materials in chromatography or as an easy-to-handle form for catalytic purposes [8].

3.2. Application

The fibrous Ti-MFI zeolites provide exciting and unique physicochemical properties, for example, low packing density, high stability of the fibrous morphology, and the enhanced hydrophobicity. The packing density of fibrous TS-1 powders is 1.9 times lower than that of non-fibrous Ti-MFI powder. We can further ensure that the fibrous Ti-MFI zeolites with a unique morphology as well as the enhanced hydrophobicity can be utilized for a new adsorbent to reveal the morphology dependence to the shape selective adsorption of hydrocarbons. For example,

we found that the fibrous Ti-MFI zeolite exhibits much higher adsorption selectivity for p-xylene (p-xylene/o-xylene = 9.90) than non-fibrous Ti-MFI (p-xylene/o-xylene = 3.76) prepared by hydrothermal method when we measured adsorption preference of the xylene isomers at 293 K. Additionally, another possibility should be addressed on catalytic properties of the fibrous Ti-MFI zeolites obtained by the microwave method. They show very high activity for photocatalytic reduction of CO_2 with H_2O to produce CH_3OH and CH_4 (not shown) as well as high selectivity to styrene oxide in epoxidation of styrene with H_2O_2 as compared with Ti-MFI zeolites prepared by hydrothermal method. Now further studies on characterization as well as the formation mechanism of the fibrous Ti-MFI zeolites are currently underway.

The fibrous AlPO-5 also shows preferential adsorption

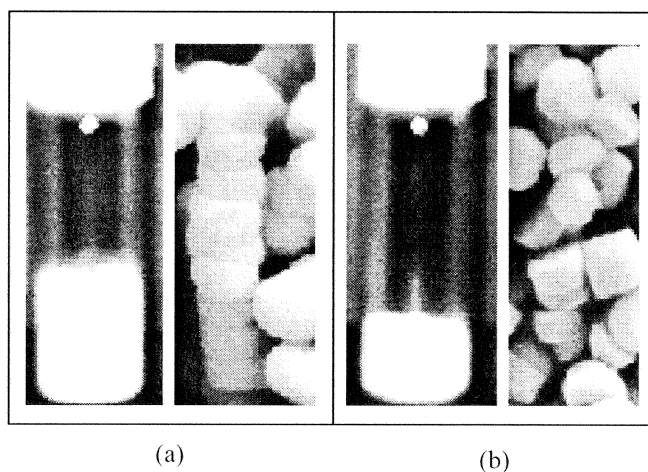


Figure 4. Photographs of sample bottles containing (a) fibrous Ti-MFI (Si/Ti=70) and (b) non-fibrous Si-MFI.

of p-xylene over o-xylene at 278-293K on the contrary to normal AlPO-5, with the aspect ratio of about 1, which shows preferential adsorption of o-xylene over p-xylene.

4. CONCLUSION

This study is illustrating that nanoscopical fabrication of nanostructured materials, as a new technique, could be performed with metallic species as nanoglue under microwave irradiation. The concept of nanoglue, which is the sites for the fabrication induced by the selective absorption of microwave energy, is proposed as a novel technique for the nanofabrication of nanoporous materials. Nanostacking process seemed to be self-assembly process through the dehydration of hydroxyl groups onto surface by converting hydrogen bond ($\text{Si-OH} \cdots \text{HO-Si}$) between adjacent crystallites into covalent bonds (Si-O-Si or Si-O-Ti) under the microwave irradiation with the help of selective absorption of microwave energy onto metal species.

The nanofabricated nanoporous materials with various morphologies by microwave irradiation will be expected to be great interest for many applications. It has great potential as new opening of applications such as novel materials for fabrication of nanofiber and nanowires, films (membranes), microreactors, chemical sensors, non-linear optical molecules, and nanoreactors, and catalysis having shape or length selectivity, photocatalysis and size-selective sensing devices as well.

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