Pore Structures of Mesoporous ZSM-5 from Resorcinol-formaldehyde Aerogel and Carbon Aerogel Templating

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Introduction

Template synthesis has been realized for preparation of new designed materials and recently there have been active developments in the template synthesis for the preparation of new nano-structured materials. Many nanoprous carbons have been synthesized with the use of ordered mesoporous silica as molds [1-3], and on the contrary, nanoporous silica materials have been prepared using porous carbons [4.5]. Zeolite molecular sieves are representative of crystalline microporous solids. The main characteristic of zeolites is that the tetrahedral primary building blocks are linked through oxygens, producing a three-dimension network containing channels and cavities of molecular dimensions. They have been found to catalyze a wide variety of chemical reactions [6]. However, in many cases, the sole presence of micropores (width < 2 nm) results in intracrystalline diffusion limitation, which hinders the performance of industrial catalysts. [7,8] Donating mesopores (width 2-50 nm) to zeolites could lead to significantly improved properties as compared to conventional zeolite catalysts, which have very recently been shown in the alkylation of benzene with ethane using mesoporous zeolite single crystals [9]. Previously, these authors prepared zeolites of uniform mesoporous channels by the templating method using carbon aerogels [10,11]. Here, we show that resorcinol-formaldehyde aerogels and carbon aerogels of different mesoporosities can been used as templates for preparing ZSM-5 of tunable mesoporosities. Both resorcinol-formaldehyde aerogels and carbon aerogels are well known as mesoporous materials having great mesopore volume [12,13]. Resorcinol-formaldehyde aerogel is the precursor of carbon aerogel and has a merit of much easier burning.

Experimental

The preparation of mesoprous ZSM-5 is based on our previously established procedures [10]. It consists of three steps: (1) Preparing an aluminosilicate solution from tetraethyl orthosilicate (TEOS) and aluminum isopropoxide [Al(*i*PrO)$_3$], and NaOH, H_2O, and tetrapropylammonium bromide (TPABr) with composition (molar basis) 10 Na_2O:200 SiO_2:Al_2O_3:20 TPABr:16000 H_2O. (2) Introducing the zeolite precursor into the mesopores of resorcinol-formaldehyde aerogels or carbon aerogels of different mesoporosities. The resorcinol-formaldehyde aerogels and carbon aerogels were prepared using the Pekala method. [12,13] Briefly, resorcinol-formaldehyde (RF) gels were derived from the sol-gel polymerization of resorcinol and formaldehyde with a slight amount of sodium carbonate as a basic catalyst. The molar ratio of resorcinol to catalyst was 200. The RF aerogels were dried under a supercritical condition with CO_2, followed by pyrolysis under nitrogen flow at 1323 K. (3) Synthesizing ZSM-5 in the inert mesopores of resorcinol-formaldehyde aerogels or carbon aerogels, and separating the zeolite crystals from resorcinol-formaldehyde aerogels and carbon aerogels by heating the products in O_2 at 823 K for 18 h and at 773 K for 8 h, respectively. The zeolite ZSM-5 was synthesized for comparison.

Results and Discussion

The crystal structures of ZSM-5 and mesoporous ZSM-5 were examined using X-ray diffraction (XRD) and the Fourier transform infrared (FT-IR) absorption spectroscopy. The X-ray diffraction pattern of ZSM-5 were in agreement with that of mesoporous ZSM-5, and in FT-IR spectra of the framework absorption region (1500-300 cm^{-1}) of mesoporous ZSM-5 absorption bands were observed at 1224 (shoulder), 1150-1050 (strong), 795 (weak), 550 (weak to medium) and 455 (strong) cm^{-1}, indicating the MFI-type structures of the products. Our recent work showed the mesoporous ZSM-5 have the same number of acid sites as conventional zeolite ZSM-5. [14]

The nitrogen adsorption isotherm of ZSM-5 as a standard at 77 K basically belongs to IUPAC type I. The predominant adsorption finishes below P/P_0 = 0.02, which is characteristic of uniform microporous solids. All nitrogen

adsorption isotherms of mesoporous ZSM-5 zeolites prepared from resorcinol-formaldehyde aerogels and carbon aerogels templating have a steep uptake below $P/P_0 = 0.02$ and clear hysteresis loop above $P/P_0 \sim 0.6$, suggesting the co-existence of micropores and mesopores. The mesoporous ZSM-5 zeolites have mesopores of 9-25 nm in widths and 0.07-0.2 mL/g in volumes from nitrogen adsorption data analysis. Field emission scanning electron micrograph observations confirmed the presence of mesopores. Experimental results show the mesoporous systems of the finally obtained zeolites can be influenced by proper preparation of resorcinol-formaldehyde aerogels and carbon aerogels through solution chemistry.

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