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Syntheses of Mesoporous Silicas Containing Titania (Ti-SBA-15) by Block Copolymer Templating

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A series of titania modified mesoporous silica (Ti-SBA-15) with various Ti/Si mole ratios were prepared by sol-gel method from tetraethoxysilane (TEOS) and titanium ethoxide. In this work, Poly(ethylene oxide-b-propylene oxide-b-ethylen oxide) was used as a surfactant to make highly ordered mesoporous materials by templating. The samples were characterized by small angle x-ray scattering (SAXS), N_2 adsorption-desorption measurement (BET), and FT-IR spectroscopy.

Keywords: Poly(ethylene oxide-b-propylene oxide-b-ethylene oxide), Templating, Mesoporous and nanoporous materials. Ti-SBA-15

1. Introduction

Since the discovery of M41S family[1], numerous studies have been performed extensively on modifications of the MCM-41 to increase the potential applicability of these materials. These materials have attracted much interest because of their high surface area, large pore volume and well defined pore size. Ordered mesoporous titanium-containing MCM-41 type materials have been a suite of organosilanes. The stability of these materials under various different conditions is a crucial factor in the potential application. Unfortunately, MCM-41 has poor hydrothermal stability because its organic oxide wall is disordered at

the molecular level[2]. SBA-15 is a newly discovered mesoporous silica molecular sieve with uniform tubular channels variable from 50 to 300Å[3]. Incorporation of either framework titanium or titanium nanoparticles into SBA-15 by direct synthesis appears unlikely, because SBA-15 is synthesized in strong acidic media. In this work, poly(ethylene oxide-b-propylene oxide-b-ethylene oxide)[5] was used as a surfactant to make highly ordered mesoporous titanium modified SBA-15(Ti-SBA-15) by templating.

2. Experimental

In our typical synthesis, 2.03g of poly (ethylen oxide)-block-poly(propylene oxide)-block-poly (ethylen oxide) (PEO_{20}-PPO_{70}-PEO_{20}: Mw 5,800, Aldrich) was dispersed in 80g of de-ionized water to make a templating solution. The resultant solution was mixed with 2M HCl (PH=0.7) with stirring, followed by addition of 10.4g tetraethyl orthosilicate, TEOS(Aldich) and titanium ethoxide(Aldich). The mixture was stirred at 35℃ for 2 days. The solid precipitate was filtered, washed with de-ionized water, and dried in air at room temperature, then was calcined at 500℃ for 3h.

N_2 adsorption and desorption experiments were carried out on a Micrometeritics Instrument corporation ASAP 2010 with accelerated surface area and porosimetry system at 77K. FT-IR analyses were performed with a Recollect impact 400D spectrometer. Thirty-two scans were signal-averaged. small angle x-ray scattering (SAXS) experiments at Pohang Accelerator Laboratory (PAL) were performed at POSTECH, Korea.

3. Results and discussion

Figure 1 shows small angle X-ray diffraction patterns of SBA-15(a) and two different Ti-SBAS-15's with different Ti/Si mole ratios (b) Ti/Si=0.14, (c) Ti/Si=0.17. The patterns show several Bragg peaks at low reflection angles about between 1.08 and 5.5 ° which are typical of SBA-15. The strongest peak is indexed as the (100) reflection. SBA-15 samples suggest retain of long range order in the hexagonal phases. When titanium was added, however, the patterns suggest a lower crystallinity than those of SBA-15, regardless of Ti/Si ratios since the

other Bragg peaks indexing (110), (200) and (210) cannot be clearly observed.

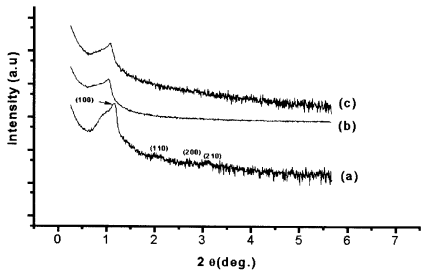

Figure 1. Small angle X-ray diffraction patterns of (a) SBA-15, (b) Ti SBA-15 (Ti/Si=0.13), and (c) Ti SBA-15 (Ti/Si=0.17).

Figure 2 shows FT-IR spectra of the siliceous and Ti-SBA-15 samples in the range of 1580-400cm^{-1}. The IR spectra exhibit specific adsorption bands at 461, 803, 960, and 1085 cm^{-1}. A band at 960cm^{-1} is clearly visible in all spectra except SBA-15, which appeared due to the Si-O-Ti linkage stretching for both the Ti-SBA-15's with different Ti/Si ratios.

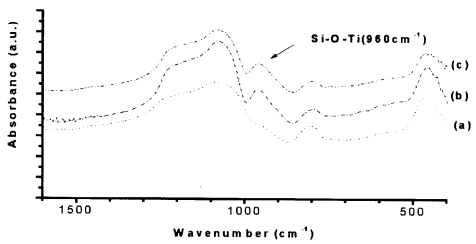

Figure 2. FT-IR spectra of (a) SBA-15, (b) Ti-SBA-15(Ti/Si=0.13), (c) Ti-SBA-15(Ti/Si=0.17).

The FT-IR spectra, therefore, proves the formation of Si-O-Ti networking structures for the Ti-SBA-15 series. However, it should be noted that the 960cm^{-1} band also occurs in the spectra of Ti-free mesoporous molecular sieves due to the abundance of silanol groups present in the calcined silica samples[4]. Figure 3 shows N_2 sorption isotherms at 77K of SBA-15 (a) and Ti-SBA-15's with various Ti/Si ratios. Condensation step can be observed at the relative pressure (P/P_0)

of 0.2-0.4 and a hysteretic loop appears in the desorption curve. For both cases, at low relative pressure (P/P_0) the adsorbed volume is due to monolayer coverage and filling of the micropores. An inflection point occurs at relative pressure between 0.4 and 0.6. This corresponds to capillary condensation in the mesoporous systems and the sharpness of this inflection indicates a uniform pore size distribution.

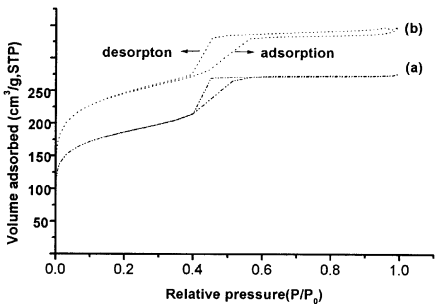

Figure 3. Nitrogen adsorption-desorption isotherms at 77K of (a) SBA-15 and (b) Ti-SBA-15 (Ti/Si=0.13).

Acknowlegement
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