Triblock Copolymer Synthesis of Highly Ordered Titanium-substituted Mesoporous Silica with the Aid of Prehydrolysis Route

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Abstract

Highly ordered titanium-substituted hexagonal mesoporous silica materials (Ti-SBA-15) with various silica/titania (Si/Ti) mole ratios have been synthesized from tetraethyl orthosilicate (TEOS) and titanium isopropoxide by sol-gel method. Poly(ethylene oxide-b-propylene oxide-b-ethylene oxide) was used as the template. Prehydrolysis was applied to synthesize Ti-SBA-15 with high titanium loading. The Ti-SBA-15 with various Si/Ti mole ratios have been characterized using small-angle X-ray scattering (SAXS), nitrogen adsorption, Fourier transform infrared spectroscopy (FT-IR), transmission electron microscope (TEM), and UV-vis spectroscopy. Well-ordered hexagonal arrays of the mesopores were shown in SAXS and TEM measurments. The formation of the Si-O-Ti bond was proved by FT-IR spectroscopy, and the result of N_2 adsorption indicates that a high degree of substitution of Ti for Si did not change the textural properties. UV-vis spectroscopy confirmed successful isomorphous substitution of titanium inside siliceous framework SBA-15.

Key words: Mesoporous, Prehydrolysis, Ti-SBA-15, Block copolymer templating.

Introduction

The mesoporous materials have attracted much interest for their emerging applications in catalysis, ion exchange, encapsulation of transition metal semiconductor cluster, chemical sensing, complex, fabricateon[1-3], and nanomaterials because mesoporous materials have uniform pore size distribution, high surface area, and good thermal stability. Since the mesoporous materials were first disclosed by Yanagisawa et al. [1], surfactantmediated synthesis methods have been paid much attention in the preparation of inorganic mesoporous materials, which incorporate polymeric, can and organometallic 'guest' in organic, inorganic their pores on removal of the surfactant template[1-5].

There has been growing interest in introducing titanium into the wall of mesoporous materials as titanium-substituted mesoporous materials provide higher surface areas (>200 m²/g) than pure titania[6-8].

Many attempts have been made to prepare Ticontaining MCM-41 mesoporous molecular sieve. However, the poor hydrothermal stability of the Ti-MCM-41 limited its potential application[9]. Recently, Zhao et al.[10], reported the synthesis of a novel mesoporous silica, SBA-15 using polyethylene oxideb-polypropylene oxide-b-polyethylene oxide (PEO-PPO-PEO) triblock copolymer (EPE) as a template to organize the structure of a polymerizing silica precursor. The hexagonal SBA-15 silica, which exhibits a remarkable hydrothermal stability, can be synthesized in wide range of pore sizes.

It has been suggested that the titanium has isomorphous substitution and forms highly dispersed titanium sites after calcinations[11]. Such materials may show higher activity for liquid-phase oxidation and have potential as a novel catalyst. Recently, titanium-substituted mesoporous silica (Ti-SBA-15) was also prepared by post-synthesis methods by Luan et al.[11], Wu et al.[12], and Morey et al.[13] Newalker et al. reported on the direct synthesis of Ti-SBA-15 under microwave-hydrothermal conditions at 373 K[14]. We wish to report here on the direct synthesis of Ti-SBA-15 using prehydrolysis technique.

Experimental

A prehydrolysis method was employed in this work in contrast with the conventional one-step sol-gel reaction. In a typical synthesis, 2.03 g of amphiphilic triblock copolymer, EPE(M_w 5800) was dispersed in 80 ml of distilled water under 35~40 °C. In the second bottle, 5ml of distilled water and 2 M HC1 were mixed. To this solution was dropwise added 0.05 mol of TEOS with stirring for 6h to make the solution homogeneous. Then, the solution of the first bottle was poured into the solution of the second bottle. The two-step hydrolysis methodology is referred to as "prehydrolysis" in this work. A given amount of titanium isopropoxide (0.0078, 0.0048, 0.0036, 0.0026, 0.002, and 0 mole) was added into the second bottle and the gel thus obtained was stirred at 35 °C for 24h. The Si/Ti mole ratios of the reaction mixture in this work were adjusted to be 6.4, 10.4, 13.0, 19.0, 25.0, and ∞ , respectively on the bulk basis. The solid product was recovered by filtration, washed with deionized water, dried in the air at room temperature. The assynthesized sample was heated up in air in a furnace at a rate of 1 °C/min from room temperature to 500 °C and calcined at 500 °C for 3h.

Small angle X-ray scattering (SAXS) was performed at Pohang Accelerator Laboratory (PAL), POSTECH, Korea using Co- K $\alpha(\lambda=1.608\text{\AA})$ radiation with the energy range of 4-16 keV. Nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2010 system. Prior to measurement samples were dehydrated at 150°C for 24h. The BET method was used to calculate the specific surface area. The pore size distribution was calculated from the adsorption branch of the isotherm by BJH (Barrett-Joyner-Halenda) method coupled with the apparatus software. FT-IR spectra were recorded on a Recollect impact 400D spectrometer using the KBr pellet technique. UV-vis diffuse reflectance spectra (DRUV) were measured with Kontron Instrument Uvikon 860 spectrophotometer. TEM images were acquired with JEOL 2010 electron microscope operating at 200 kV. The samples for TEM were prepared by dispersing the fine powders of the products onto holey carbon copper grids.

Results and Discussion

The sol-gel process consists of three main steps

including hydrolysis, condensation and redissolution in the case of silicon alkoxide. The three reactions are in competition one another so that the final composition of the reaction mixture depends on the kinetics of those reactions that vary according to the pH. For example, at moderate pH, since the condensation is faster than hydrolysis, highly branched silica species are usually formed. In basic medium, either discrete colloidal silica particles or dense clusters are formed[15]. In the present investigation, the condensation rate of TEOS was adjusted to be restricted in the range of pH< 2~4, so that the hydrolysis rate is comparable to the condensation rate. By using the prehydrolysis method, well-ordered hexagonal T-SBA-15 can be prepared.

Fig.1 (A) shows the SAXS patterns of calcined and as-synthesized samples with Si/Ti mole ratio of 10.0. Fig.1 (B) shows the SAXS patterns of the calcined samples with different Si/Ti mole ratios. In the low 2 θ region of 0.5 –3.5°, there are four peaks indexed as (100), (110), (200), and (210), which is indicative of hexagonal lattice structure. The relatively broad diffraction peak at 0.93° is observed in the assynthesized sample, as shown in Fig.1 (A-b). In Fig. 1 (A-a), the intensities of peaks of the Ti-SBA-15 sample increase significantly after calcination, suggesting that the calcination process may strengthen siloxane crosslinking and thereby improve the ordering of Ti-SBA-15 framework. The diffraction peak of the calcined Ti-SBA-15 shifts towards higher scattering angle in comparison with that of the as-synthesized sample, which indicates a unit-cell contraction of the assynthesized sample after removal of the template upon calcination. From Fig. 1 (B), it can be seen that the (100) peak shifts toward higher angle with the increasing Si/Ti mole ratio of Ti-SBA-15 except for the sample with Si/Ti mole ratio of 6.41. The result can be expected form the fact that the Ti(IV) has an ionic radius (0.68Å) bigger than Si(IV) (0.42Å) and the former substituting for the latter will result in larger lattice parameters while maintaining the symmetry. However, the reason why is the sample with Si/Ti=6.41 exceptional is not clear at moment.

The textural properties of Ti-SBA-15 samples are summarized in Table 1. It is obvious that the textural properties such as BET surface area, pore volume and pore size for Ti-SBA-15 samples are in good agreement with those for siliceous SBA-15 sample[10]. It should be noted that the structural parameters under high titanium loading (Si/Ti = 6.41) are found to be similar to those under low titanium loading, which reveals that a high degree of substitution of Ti for Si in our synthetic approach can not result in the loss of textural properties.



Fig.1. (A) SAXS patterns of (a) calcined and (b) assynthesized Ti-SBA-15 (Si/Ti mole ratio of 10). (B)SAXS patterns of calcined Ti-SBA-15 samples with various Si/Ti mole ratios of (a) 6.41,(b) 10.4, (c) 13.0, (d) 19.0, (e) ∞ .

Sample (Si/Ti moler atio)	BET surface area (m ² /g)	PoreVolume (cm ³ /g)	Pore size D(Å)	d ₁₀₀ -spacing (Å)	a _o ^a (Å)	t ^b (_Å)
6.4	905	0.60	35.0	83	95.8	60.9
10.4	881	0.62	38.0	87	100.4	62.5
14.0	749	0.56	35.0	82	94.6	59.7
19.0	748	0.52	34.1	81	93.5	58.5
25.0	731	0.50	33.5	78	90.1	55.1
0	645	0.43	33.1	74	85.5	50.5

Table I . Textural properties of Ti-SBA-15 samples.

^a Unit cell parameter $a_0 = 2/(3)^{1/2} \times d_{100}$ ^b Pore wall-thickness, t= a_0 - D

Figure 2 displays nitrogen adsorption-desorption isotherms at 77 K for the calcined siliceous SBA-15 and Ti-SBA-15 with various Si/Ti mole ratios. All of the nitrogen adsorption/desorption isotherms are found to be of Type IV in nature according to the IUPAC classification and exhibited a H1 hysteresis loop which is typical of a mesoporous solid[8, 14]. N₂ adsorption at low relative pressure ($P/P_0 < 0.35$) is accounted for monolayer adsorption of N2 on the pore walls and does not indicate the presence of micropores. When P/P_0 is between 0.40 and 0.60, characteristic capillary condensation can be observed within uniform pores. It should be noted, however, that the isothermsof the SBA-15 as well as Ti-SBA-15 samples are not perfect when they are prepared at $pH < 2 \sim 4$ via prehydrolysis, as compared with the SBA-15 reported by the Prof. Stucky's group[10].



Fig.2. Adsorption-desorption isotherms of nitrogen at 77K for various Ti-SBA-15 with different Si/Ti mole ratios of (a) 6.4, (b)10.4, (c)13.0, (d) ∞ .

Figure 3 shows the typical BJH pore size distribution curves for Ti-SBA-15 samples. The BJH data showed



Fig.3. Pore size distribution for Ti-SBA-15 samples with different Si/Ti mole ratios of (a) 6.4, (b)10.4, and (c) ∞

pore diameter of about 35 Å for samples having Si/Ti ratios of 6.41, 13.0, 19.0 and ∞ , except for the sample with Si/Ti ratio of 10.4 with 38 Å. For simplicity, the pore size distribution curves for samples with Si/Ti=13.0 or 19.0 were not shown here, which showed the same trends. Careful inspection of in Fig. 2, and especially the isotherm (d) of pure SBA-15, were slightly different from that of a good quality SBA-15,

which has been prepared under strong acidic condition[10].The pores and the capillary condensation step (mesopore volume) were smaller than that of the SBA-15 prepared under strong acidic condition. The hysteresis loops also indicate that the cylindrical pores. Figure 3 shows that pore size was slightly increased with Ti amounts, even though the difference is not large.



Fig.4. TEM image of (a) TI-SBA-15(Si/Ti mole ratio of 6.4) and (b) Ti-SBA-15(St/Ti mole ratio of 10.4)

Representative TEM images of Ti-SBA-15 mesoporous samples with Si/Ti mole ratios of 6.4 and 10.4 are shown in Fig.4. It can be seen that these samples exhibit highly ordered hexagonal array uniform channels. From the TEM image of Ti-SBA-15 with Si/Ti mole ratio of 10.4, for example, it can be estimated that the pore size and wall thickness are 3.8 nm, and 6.2 nm, respectively. The result is in good agreement with the N₂ adsorption data.



Fig.5. FT-IR spectra of various calcined samples with different Si/Ti mole ratio of (a)6.4, (b)19.4, (c)13.0,(d)19.0, (e)25.0, and (f) ∞ .

Fig.5 shows the spectra of the siliceous and Ti-SBA-15 samples. The IR spectra of Ti-SBA-15 samples show characteristic adsorption bands at ca.1060, 957 and 803 cm⁻¹, corresponding to Si-O-Si asymmetric stretching, Ti-O-Si, Si-O-Si symmetric stretching vibration, respectively. In the siliceous SBA-15 sample (f), the large band near at 1065 cm^{-1} is assigned to the asymmetric stretching of the internal SiO₄ tetrahedra. The adsorption band near at 957 cm⁻¹ is strengthened with the increase of the amount of titanium, which may be attributed to the incorporation of titanium into the framework. A band about 957 cm⁻¹ has been previously observed in the spectra of various titanium-substituted silicalites and recently reassigned from silanol or titanyl (Ti=O) stretching modes to an asymmetric Ti-O-Si stretching mode on the basis of quantum mechanical calculations[16]. In addition, it should be noted that the band near at 960 cm⁻¹ shown in Fig.5 (f), is indicative of the abundance of silanol group present in the calcined samples.



Fig.6. UV-Vis spectra of calcined Ti-SBA-15 samples with different Si/Ti mole ratio of (a)6.4, (b)10.4, (c)13.0, (d)19.0, and (e)25.0.

Fig.6 shows the UV-vis spectra of calcined Ti-SBA-15 samples with various Si/Ti mole ratios. A large absorption band at about 230 nm and a small absorption band at about 270 nm in the form of a shoulder are observed for all Ti-SBA-15 samples. The band at about 230 nm can be assigned to the ligand-tometal charge transfer involving isolated Ti atoms in tetrahedral coordination[11]. The shoulder band at about 70 nm probably corresponds to partially polymerized octahedral Ti species. Absence of a band at ~ 330 nm indicates that all Ti-SBA-15 samples are free of bulk anatase phase. This exhibits successful isomorphous substitution of titanium inside siliceous framework SBA-15 although the intensity of shoulder band at about 270 nm slightly increases with the increase of titanium amount.

It should be mentioned here that the IR and UV-Vis spectra in this work do not prove completely that the Ti is incorporated in the walls, although most of the Ti species are in an isolated tetrahedral environment. The same spectra can be obtained if the Ti species were present on the surface of the walls by a simple grafting method.

Conclusions

Titanium-substituted mesoporous silica materials Ti-SBA-15 were successfully prepared by prehydrolysis and sol-gel method using EPE as the template. SAXS and TEM analyses showed that the mesoporous materials possess well-ordered hexagonal arrays. The result of N_2 adsorption showed that the textural properties of Ti-SBA-15 with various Si/Ti mole ratios are well preserved. FT-IR spectroscopy proved the Si-O-Ti networking structures. From the measurement of UV-Vis spectroscopy, titanium is believed to exist mostly in isolated tetrahedral sites.

Acknowledgements

The work was supported by the National Research Laboratory Program, the Center for Integrated Molecular Systems, and the BK 21 Project. The synchrotron SAXS experiments were carried out at Pohang Accelerator Laboratory (PAL), Korea.

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(Received October 11, 2003; Accepted December 1, 2003)