Three-dimensional Mesoporous TiKIT-6 with *Ia*3*d* Symmetry Synthesized at Low Acid Concentration and Its Catalytic Performances

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Here we report for the first time on the preparation of well-ordered titanium substituted KIT-6 at low acid concentration using polymeric surfactant. The characterization results show that the pore diameter and the unit cell constant of Ti-KIT-6 increase with increasing Ti incorporation. UV–vis results reveal that most of the Ti are in tetrahedral coordination. In addition, the materials showed higher activity in the epoxidation of styrene than TiSBA-15.

Mesoporous silica materials have received much attention in recent years owing to their excellent textural characteristics such as large surface area, pore volume, and uniform and large pores.[1–3] Although the materials exhibit interesting structures and textural parameters, which helped them to find applications in adsorption, separation, and hard templating,[4–6] unfortunately, they exhibit neutral framework charge which does not provide any acid sites for acidic or redox catalytic applications. However, the acidity and the redox function can be introduced by the incorporation of di- or trivalent metals in the framework. The preparation of metal-substituted mesoporous silica materials in a highly basic medium is rather easy.[7] However, the incorporation of metal ions in the three-dimensional (3D) mesoporous materials prepared in a highly acidic medium is extremely difficult. In a highly acidic medium, the solubility of the metal source is very high, which limits the incorporation of metal ions in the silica framework and often causes the formation of metal oxide particles.

One of the fascinating materials in the mesoporous family is KIT-6, which is synthesized by using tetraethyl orthosilicate (TEOS) as a silica source, Pluronic P123 as a structure directing agent, and *n*-butanol as a cosolvent in a highly acidic medium.[8] The material possesses well-ordered 3D structure with a cubic space-group symmetry of *Ia*3*d*. It is really worth exploring the possibility of metal incorporation in the silica matrix of KIT-6 as materials with 3D pore systems, which can offer many advantages especially in catalysis because they allow a faster diffusion of reactants than a 1D array of pores and tender easy access to all adsorption sites. However, unfortunately, there has been no report on the direct synthesis of metal-incorporated KIT-6. Here, we report for the first time on the successful preparation of highly ordered mesoporous TiKIT-6 with a high loading of Ti in a low acidic medium. This has been achieved by simply changing the concentration of the HCl in the synthesis mixture. Moreover, the material also demonstrated an excellent catalytic performance in the epoxidation of styrene.

A typical synthesis procedure of TiKIT-6 is as follows: 4.0 g of P123 is dissolved in 146 g of 0.11 M HCl with stirring at 35 °C. It must be noted that the amount of HCl added in the mixture was six times less than that required for the synthesis of pure KIT-6 silica (0.66 M of 150 g of HCl). Then, 4.0 g of *n*-butanol, 8.6 g of TEOS, and the required amount of titanium isopropoxide were added, and the mixture was stirred at 35 °C for 24 h. Subsequently, the reaction mixture was heated for 24 h at 100 °C. The solid product was filtered and calcined at 540 °C. The samples were denoted as TiKIT-6(x) where x denotes the $n_{\mathrm{Si}}/n_{\mathrm{Ti}}$ molar ratio.

All the TiKIT-6 samples exhibit a sharp well-resolved (211) reflection and several higher order reflections at 2θ angles below 4°, which are in good agreement with the XRD pattern of pure KIT-6 silica (Figure 1A). This indicates that the TiKIT-6 materials exhibit highly ordered porous structure with the symmetry of the body-centered cubic *Ia*3*d* space group, even though the synthesis was carried out at a low concentration of HCl. Highly ordered linear arrays of pores which are arranged in regular intervals and the 3D orientation of the well-ordered mesopores of TiKIT-6(21) are confirmed by HRTEM images (Figures 1B and 1C). The $n_{\mathrm{Si}}/n_{\mathrm{Ti}}$ atomic ratio of the TiKIT-6 materials decreases with decreasing the $n_{\mathrm{Si}}/n_{\mathrm{Ti}}$ ratio in the synthetic gel (Table 1S). It was also found that the $n_{\mathrm{Si}}/n_{\mathrm{Ti}}$ atomic ratios in the products are close to the ratios in the corresponding gel, indicating a successful incorporation of titanium added in the

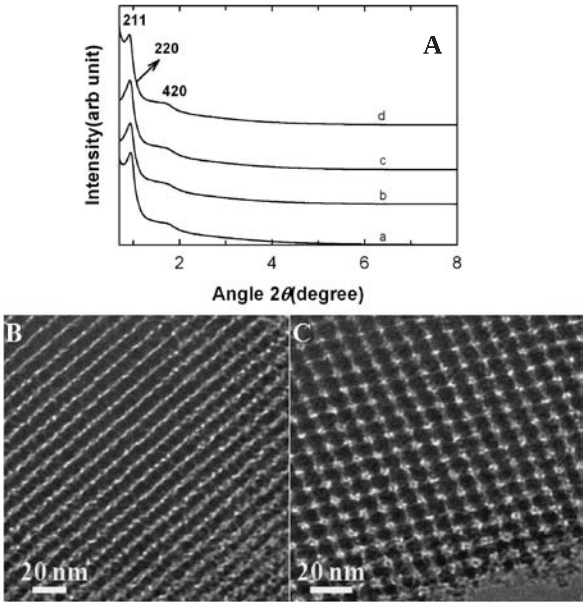

Figure 1. A) Powder XRD patterns of TiKIT-6 prepared at different $n_{\mathrm{Si}}/n_{\mathrm{Ti}}$ ratios: (a) TiKIT-6(39), (b) TiKIT-6(34), (c) TiKIT-6(28), and (d) TiKIT-6(21); B and C) HRTEM images of TiKIT-6(21).

synthesis gel. The higher amount of Ti incorporation in KIT-6 can be explained as follows: it is a well-known fact that the hydrolysis of titanium alkoxides is virtually instantaneous in an acidic medium, whereas the hydrolysis of silicon precursors is much slower. Lowering the local concentration of H^+ ions in the solution by reducing the amount of HCl in the synthesis mixture helps to decrease the hydrolysis rate of the titanium precursors to match that of the silicon precursors. This might enhance the interaction between the Ti–OH and Si–OH species in the synthesis gel resulting in a higher amount of Ti incorporation when a lower amount of HCl was used. Noteworthy, when the amount of HCl is increased, only a low amount of Ti was incorporated into the silica matrix of KIT-6. The specific surface area (A_{BET}) and the specific pore volume (V_{p}) of the materials decrease from 1032 to 786 $\mathrm{m^2/g}$ and 1.2 to 1.0 $\mathrm{cm^3/g}$, respectively, with decreasing the $n_{\mathrm{Si}}/n_{\mathrm{Ti}}$ from 39 to 21 (Figure 1S).[9] Interestingly, the incorporation of Ti in KIT-6 causes a significant increase in the value of the pore diameter ($d\mathrm{p}_{\mathrm{ads}}$; 8.2 to 9.1 nm) and the unit cell constant (a_0; 22.8 to 23.5 nm). This could be mainly due to the fact that the atomic radius of Ti^{4+} (0.56 Å) is larger as compared to that of the Si^{4+} (0.40 Å) by assuming the coordination number of both the atoms is 4, leading to a longer Ti–O distance (Ti–O 0.2 nm; Si–O 0.16 nm). The longer Ti–O bonds are responsible for the increase of the pore diameter and the unit cell constant of TiKIT-6. We also surmise that the isopropanol molecules generated from the Ti source is responsible for the pore size enlargement. To prove this, KIT-6 silica was prepared under similar conditions without Ti source and found to have the pore diameter much smaller than that of TiKIT-6 (Table 1S).[9]

In order to confirm the nature and the coordination of the Ti in the TiKIT-6 materials, the materials were analyzed by UV–vis diffuse reflectance spectroscopy. All the samples exhibit three broad peaks centered around 207, 260, and 310 nm, respectively (Figure 2). It is important to note that the intensity of the peaks increases with decreasing the $n_{\mathrm{Si}}/n_{\mathrm{Ti}}$ ratio in the synthesis mixture, confirming the incorporation of Ti in KIT-6. The peaks around 207 and 260 nm are attributed to a ligand-to-metal charge-transfer transition in isolated TiO_4 or $HOTiO_3$ units, and penta or hexacoordinated Ti species, which are most likely generated through hydration of the tetrahedrally coordinated sites, respectively.[10] This band can be the direct evidence for titanium atoms incorporated into the framework of the mesoporous KIT-6 silica. However, the broad band at 310 nm can be assigned to bulk titania species in the TiKIT-6. The catalytic activity of the TiKIT-6 was studied in the epoxidation of styrene by hydrogen peroxide (H_2O_2) and *tert*-butylhydroperoxide (TBHP) as oxidants, and the results are compared with those of TiSBA-15,[11] which has a 2D porous structure (Table 1). It was found that the conversion and the epoxide selectivity for TiKIT-6 samples are higher than those for the TiSBA-15. This could be mainly due to the 3D porous structure of TiKIT-6 where the reaction molecules can easily diffuse inside the channels and access the active sites, leading to a high conversion of styrene. The high epoxide selectivity may be attributed to the fact that the materials contain a lot of isolated Ti species which are tetrahedrally coordinated with the silicon in the TiKIT-6 and are accessible to the reactant molecules easily.

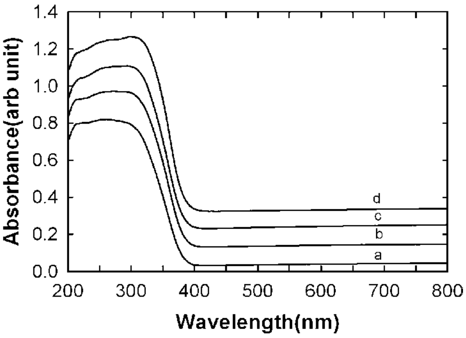

Figure 2. UV–vis DRS spectra of calcined TiKIT-6 samples prepared at different $n_{\mathrm{Si}}/n_{\mathrm{Ti}}$ ratios: (a) TiKIT-6(39), (b) TiKIT-6(34), (c) TiKIT-6(28), and (d) TiKIT-6(21).

Table 1. Comparison of the catalytic activity of the TiKIT-6 in the epoxidation of styrene using H_2O_2 or TBHP with TiSBA-15[a]

Catalysts	Conversion /mol %		Product Selectivity			
			Benzaldehyde		Styrene epoxide	
	H_2O_2[b]	TBHP[c]	H_2O_2	TBHP	H_2O_2	TBHP
TiKIT-6(21)	18.8	13.5	65.4	35.2	34.6	64.8
TiKIT-6(34)	17.5	12.5	68.3	39.3	31.7	60.7
TiSBA-15(6)	16.7	10.1	70.4	52.7	29.6	47.3

[a]Conditions: styrene 7.5 mmol, catalyst 50 mg, MeCN 10 mL, reaction time 4 h; reaction temperature 60 °C. [b]31 wt % H_2O_2. [c]70 wt % TBHP.

In summary, we strikingly demonstrate the succesfull preparation of 3D mesoporous TiKIT-6 with *Ia*3*d* symmetry using soft-templating approach wherein a low amount of HCl was used. The materials exhibit excellent structural order and textural parameters even after the high loading of Ti in the silica matrix of TiKIT-6. Moreover, the oxidation ability of the TiKIT-6 catalysts is higher than TiSBA-15, with the high conversion of styrene and selectivity to epoxide in the epoxidation of styrene. We strongly believe that this simple approach could be applied for the fabrication of various other metal-substituted KIT-6, which could be used for several applications including redox catalysis and photocatalysis.

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References and Notes

1 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka, G. D. Stucky, *J. Am. Chem. Soc.* **1998**, *120*, 6024.
2 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710.
3 T. Yanagisawa, T. Shimizu, K. Kuroda, C. Kato, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 988.
4 A. Vinu, K. Ariga, T. Mori, T. Nakanishi, S. Hishita, D. Golberg, Y. Bando, *Adv. Mater.* **2005**, *17*, 1648.
5 A. Vinu, M. Terrones, D. Golberg, S. Hishita, K. Ariga, T. Mori, *Chem. Mater.* **2005**, *17*, 5887.
6 A. Vinu, V. Murugesan, M. Hartmann, *J. Phys. Chem. B* **2004**, *108*, 7323.
7 R. Schmidt, D. Akporiaye, M. Stöcker, O. H. Ellestad, *J. Chem. Soc., Chem. Commun.* **1994**, 1493.
8 T.-W. Kim, F. Kleitz, B. Paul, R. Ryoo, *J. Am. Chem. Soc.* **2005**, *127*, 7601.
9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/.
10 a) J. Klaas, G. Schulz-Ekloff, N. I. Jaeger, *J. Phys. Chem. B* **1997**, *101*, 1305. b) G. Tozzola, M. A. Mantegazza, G. Ranghino, G. Petrini, S. Bordiga, G. Ricchiardi, C. Lamberti, R. Zulian, A. Zecchina, *J. Catal.* **1998**, *179*, 64.
11 A. Vinu, P. Srinivasu, M. Miyahara, K. Ariga, *J. Phys. Chem. B* **2006**, *110*, 801.