

Synthesis of Bimodal Mesoporous Titania with High Thermal Stability via Replication of Citric Acid-Templated Mesoporous Silica

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We first synthesized the mesoporous titania, designated KRICT-MT, via replication of the citric acid (CA)-templated mesoporous silica, composed of the silica-nanosphere framework. The KRICT-MT showed the extremely high thermal stability and bimodal mesostructure with the small primary mesopores of 4–5 nm and the large secondary mesopores of 50 nm in mean pore diameter, which are three-dimensionally interconnected. In general, the anatase is transformed into the rutile by thermal treatment in the temperature range of 600–800 °C, and the mesostructure of the mesoporous titania is collapsed above 600 °C along with a significant decrease in pore properties such as specific surface area and pore volume. In contrast, the anatase–rutile phase transformation of the KRICT-MT was not observed up to 900 °C, resulting in the maintenance of its high pore properties at high temperature. In addition, we employed the KRICT-MT as a catalyst support for water–gas shift reaction. The Pt-impregnated KRICT-MT showed much higher catalytic activity than the Pt-impregnated Degussa P25. The remarkably high catalytic activity of the Pt/KRICT-MT is attributed to the three-dimensionally interconnected and bimodal mesostructure.

Introduction

Since the first reported synthesis of MCM-41 in 1992,¹ there has been intense research activity in synthesizing various mesoporous materials using supramolecular assembly of surfactant molecules as a template.^{2–6} Recently, the approach has been extended to prepare transition-metal oxides due to their special optical, electronic, and magnetic properties.⁷ As one of the most important transition-metal oxides, titania is an extremely attractive material for diverse applications such as catalyst, photocatalyst, membrane, controlled delivery, and energy conversion.^{8,9} Mesoporous titania has been synthesized using a variety of templates, such as an alkyl phosphate,¹⁰ amine,^{11–13} ionic,^{14,15} block

polymer,^{7,16,17} nonionic surfactants,¹⁸ and nonsurfactants.^{19,20} However, it is quite difficult to fabricate thermally stable mesoporous titania. When postsynthesis thermal treatment at high temperature is employed for elimination of the various templates and crystallization of the anatase, the mesoporous titania readily loses its structural order and surface area. In other words, the relatively low thermal stability of the titania-based mesoporous materials is often attributed to their phase transformation and pore shrinkage derived from elimination of the structure-directing agents.²¹ From a viewpoint of catalytic application, it is very significant to synthesize the mesoporous titania with high thermal stability. Another important research area in the mesoporous titania as a catalyst support is to fabricate three-dimensionally interconnected mesopores because the reactant molecules easily access active sites in the mesopores. Recently, Aronson et al. synthesized titania-grafted MCM-41 and FSM-16 to improve

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the thermal stability by reacting TiCl_4 in hexanes with as-synthesized silicate powder in which surfactant remained.²² More recently, Yoshitake et al. improved thermal stability of template(primary amine)-extracted titania through CVD treatment of titanium isopropoxide.²³ Cassiers et al. synthesized NH_3 -treated titania, which is stable up to 600 °C.²⁴

Here, we report the novel synthesis of bimodal mesoporous titania, designated KRICT-MT (Korea Research Institute of Chemical Technology-Mesoporous Titania), via replication of citric acid (CA)-templated mesoporous silica, composed of silica-nanosphere framework. The KRICT-MT showed the extremely high thermal stability and bimodal mesostructure, which is three-dimensionally interconnected. In our previous papers, we first synthesized the nonsurfactant-templated mesoporous materials using silica nanospheres as a framework.^{25,26} In the current report, we first employed the CA-templated mesoporous silica with thermally stable silica-nanosphere framework to synthesize mesoporous titania by means of replication. In addition, the KRICT-MT was used as a catalyst support and showed the high catalytic activity for water–gas shift (WGS) reaction.

Experimental Section

Synthesis of CA-Templated Mesoporous Silica. Transparent colloidal silica sol was synthesized from base-catalyzed condition via hydrolysis of tetraethyl orthosilicate (TEOS) and condensation reaction. A TEOS: NH_3 : H_2O :EtOH molar ratio was 1:0.086:53.6:40.7. Prior to addition of a $\text{NH}_3/\text{H}_2\text{O}$ mixture, a TEOS/ethanol mixture was stirred vigorously at 50 °C. The addition of the $\text{NH}_3/\text{H}_2\text{O}$ mixture was carried out dropwise, followed by refluxing the final mixture for 3 h, resulting in the stable colloidal silica sol including silica nanospheres with about 5 nm in diameter.²⁵ Subsequently, 8 g of citric acid (CA) as a nonsurfactant template was added to 100 mL of the as-prepared colloidal silica sol (a CA/Si molar ratio = 0.97), and the mixture was stirred vigorously for 10 min at room temperature to obtain the silica nanosphere–CA nanocomposite solution. After the nanocomposite solution was dried at 70 °C for 12 h and calcined at 500 °C for 2 h, the CA-templated mesoporous silica (CMS) was successfully obtained.

Synthesis of Mesoporous Titania via Replication of CA-Templated Mesoporous Silica. The CMS was used as a silica template for synthesis of mesoporous titania. A titanium(IV) isopropoxide (TIP)/ethanol mixture (a volume ratio = 1) was incorporated into the CMS as a silica template, which was degassed in a vacuum oven at 90 °C, using the excess impregnation technique with vigorous stirring at room temperature for 20 h. For sol–gel reaction of the TIP, the TIP–CMS composite was transferred into a water/ethanol mixture (a volume ratio = 1). The vigorous stirring at room temperature for 20 h gave amorphous titania inside the CMS template. The process above was repeated once more for enough incorporation of the titania into the CMS. The amorphous titania–CMS nanocomposite was then calcined at 500 °C in air for 2 h, resulting in the formation of the nanocrystalline anatase. After elimination of the silica from the anatase titania–CMS nanocomposite by stirring in 2.5 wt % NaOH aqueous solution at

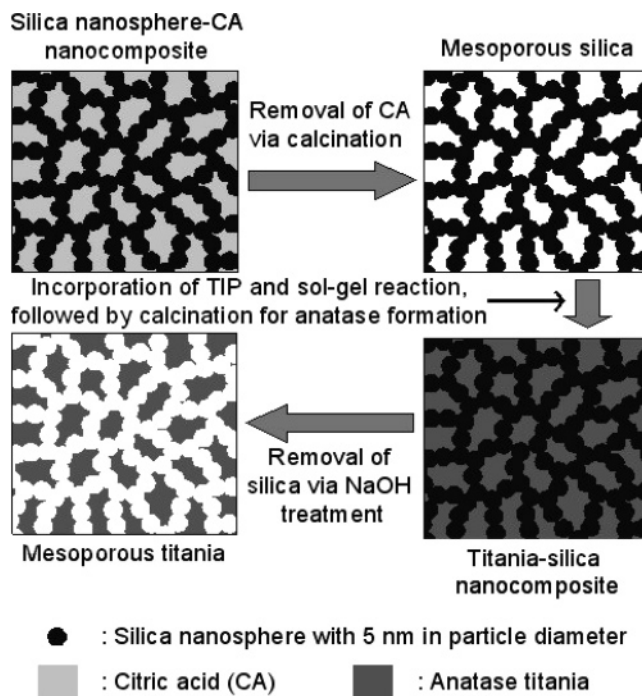


Figure 1. A schematic diagram for synthesis of the KRICT-MT via replication of the CA-templated mesoporous silica.

50 °C, we successfully obtained the mesoporous titania, designated KRICT-MT (Korea Research Institute of Chemical Technology-Mesoporous Titania).

Characterization. Nitrogen adsorption/desorption isotherms of the KRICT-MT were taken by a micromeritics ASAP 2020 instrument. Pore size distribution curves were obtained from desorption branch by using the Barrett–Joyner–Halenda (BJH) method. X-ray diffraction (XRD) patterns were collected using a Rigaku D/MAX-2200V instrument (operated at 1.6 kW). Transmission electron microscopy (TEM) analysis was carried out using a FEI/TECNAI G2 instrument (operated at 200 kV). A scanning electron microscopy (SEM) image was taken using a Philips XL 30S FEG instrument.

Catalytic Activity Test. The KRICT-MT was employed as a catalyst support for water–gas shift (WGS) reaction to observe its catalytic activity. The Pt (1 wt %)/KRICT-MT was prepared by impregnating the KRICT-MT with tetraammineplatinum(II) hydroxide by means of the incipient wetness method. Drying and calcination were carried out at 80 and 500 °C in air, respectively. For comparison, we also prepared the Pt(1 wt %)/Degussa P25 via the incipient wetness method. Drying and calcination were conducted under the same conditions as the Pt/KRICT-MT. The WGS reaction was carried out at a fixed-bed reactor at atmospheric pressure. Five hundred milligrams of the Pt/KRICT-MT or the Pt/Degussa P25 was loaded into the reactor. The catalysts were reduced in a hydrogen flow (25 mL/min) at 200 °C for 1 h and then purged with He (purity, 99.9999%). The feed gas was a CO(1%)/He(99%) binary gas, and the total space velocity was 7500 h⁻¹. The water was fed by a pump (307 pump, GILSON) with 0.03 mL/min of a liquid flow rate and vaporized through a preheating line. The product gas stream was analyzed by a Shimadzu GC-14B gas chromatograph, equipped with a thermal conductivity detector (TCD) and packed molecular sieves 5 Å column.

Results and Discussion

Figure 1 shows a schematic diagram for the synthesis procedure of the mesoporous titania via replication of the

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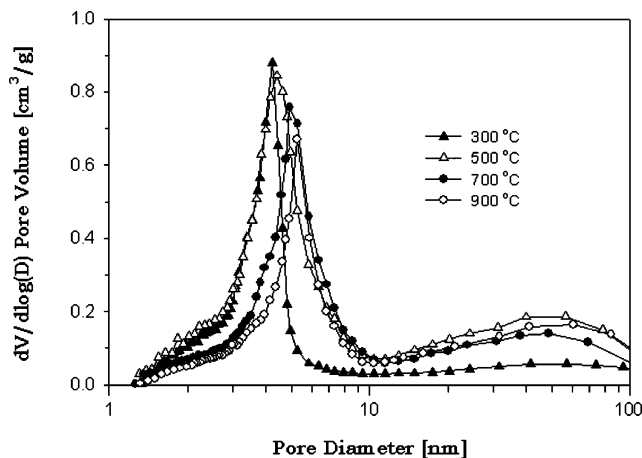


Figure 2. Pore size distributions of the KRICT-MT with different calcination temperatures.

CA-templated mesoporous silica (CMS). To synthesize the silica nanosphere–CA nanocomposite solution, citric acid was added to the colloidal silica sol including silica nanospheres with about 5 nm in particle diameter. After drying and calcination, the CMS was obtained. We employed the CMS as a silica template for synthesis of the mesoporous titania. A titanium(IV) isopropoxide (TIP)/ethanol mixture solution was incorporated into the CMS using the excess impregnation technique with vigorous stirring. The sol–gel reaction of TIP inside the CMS was conducted in a water/ethanol mixture solution, resulting in the formation of the amorphous titania–CMS composite. Calcination of the composite led to the formation of the nanocrystalline anatase inside the CMS. After elimination of three-dimensionally interconnected silica nanospheres by NaOH treatment at 50 °C, we successfully obtained the KRICT-MT with three-dimensionally interconnected mesostructure.

As reported in our previous paper, the pore diameter of the CMS was easily controlled from 2 nm up to 15 nm by simply varying the CA concentration.²⁵ In addition, the CMS showed a high pore volume (1.4 cm³/g) and surface area (750 m²/g). We employed the CMS with the maximum pore diameter of 15 nm to facilitate the penetration and sol–gel reaction of the TIP in mesopores of the CMS and to obtain thicker titania framework leading to high thermal stability of the KRICT-MT. If the mesoporous silica with small pore size is used as a silica template, the incorporation and reaction of the TIP can be suppressed due to the extreme reactivity of the TIP in the presence of water. That is, prior to enough penetration and reaction of the TIP, the entrances to the silica mesopores can be plugged by titania particles reacted in advance.

Figures 2 and 3 show the pore size distributions and N₂ sorption isotherms of the KRICT-MT with different calcination temperature. The KRICT-MT exhibited bimodal pore size distributions with small primary mesopores and large secondary mesopores. The mean pore size of the primary and secondary mesopores was about 4–5 and 50 nm, respectively. The isotherms of the KRICT-MT showed two major capillary condensation steps. The first hysteresis loop at a lower relative pressure is attributed to primary mesopores inside the titania secondary particles. The second hysteresis

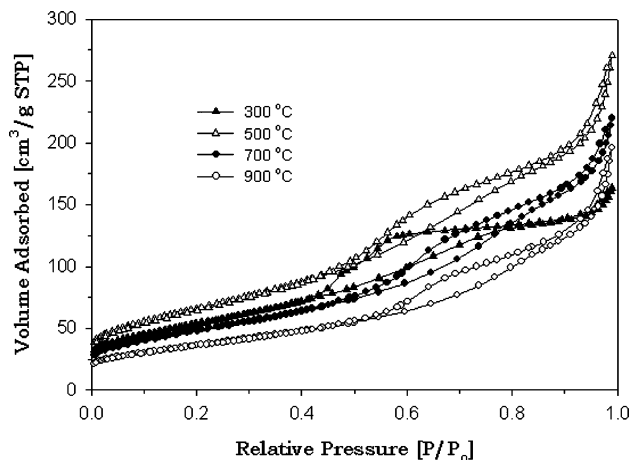


Figure 3. N₂ sorption isotherms of the KRICT-MT with different calcination temperatures.

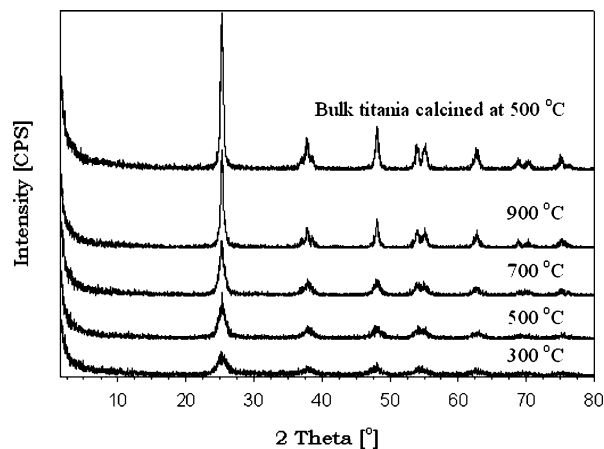


Figure 4. XRD patterns of the KRICT-MT with different calcination temperatures.

Table 1. Pore Properties of the KRICT-MT with an Increase in Calcination Temperature

	calcination temperature of the KRICT-MT			
	300 °C	500 °C	700 °C	900 °C
BET surface area [m ² /g]	240	300	230	180
pore volume [cm ³ /g]	0.26	0.45	0.37	0.33

loop at a higher relative pressure indicates the presence of the secondary mesopores, which are derived from the interstitial void among the interconnected secondary particles.

Despite an increase in the calcination temperature up to 900 °C, the bimodal pore structure of the KRICT-MT was maintained and a substantial change in the pore diameter was not observed. As shown in Table 1, the pore volume was sustained in the range of 0.26–0.45 cm³/g, and the specific surface area was also maintained in the range of 180–300 m²/g with the increase in the calcination temperature from 300 to 900 °C. The KRICT-MT calcined at 500 °C showed the maximum surface area and pore volume. Even after the calcination at 900 °C, the KRICT-MT still gave high pore properties, such as the pore volume of 0.33 cm³/g and the specific surface area of 180 m²/g. A significant falloff in the pore properties of the KRICT-MT was not observed up to 900 °C. Figure 4 presents XRD patterns of the KRICT-MT with different calcination temperature. While the XRD pattern of bulk titania calcined at 500 °C showed strong

anatase peaks with small fwhm, the KRICT-MT showed weak anatase crystal peaks with large fwhm. The result implies that the pore wall of the KRICT-MT prepared by replication of the CMS was composed of the nanocrystalline anatase. In addition, the anatase to rutile transformation was not observed up to 900 °C. Generally, the anatase is transformed into a rutile by thermal treatment in the temperature range of 600–800 °C,²⁷ resulting in the mesostructure collapse of the mesoporous titania above 600 °C along with a significant decrease in pore properties such as specific surface area and pore volume.^{28–30} In contrast, the KRICT-MT had the stable anatase crystal up to 900 °C, resulting in the maintenance of its high pore properties at high temperature. Moreover, the intensity and the fwhm of the anatase peaks were not significantly changed with increasing the calcination temperature until 700 °C, which demonstrates that there was not substantial growth of the anatase crystallites. After the calcination even at 900 °C, the anatase crystal size of the KRICT-MT was smaller than that of the bulk titania calcined at 500 °C. The results in Figures 2 and 4 corroborate the conclusion that thermal stability of the KRICT-MT is extremely high.

Mesoporous titania can be synthesized by using various surfactant or nonsurfactant templates. Whether thermal treatment or extraction is employed to eliminate the templates, the thermal treatment for crystallization of the anatase should be conducted after formation of the mesopores. In this case, the high pore properties of the mesoporous titania can be significantly lost.^{11,28–30} However, in our synthetic method, the thermal stability of the mesoporous titania is extremely high because the anatase crystallization via thermal treatment was conducted before the removal of the silica template and the silica template was eliminated through the NaOH treatment at low temperature. Moreover, the silica-nanosphere template, which proved thermally stable in our previous study,^{25,26} successfully maintained the distance between the anatase clusters incorporated into the mesopores of the CMS template, resulting in the suppression of the anatase–rutile phase transformation up to 900 °C. In other words, a lower coordination of the primary anatase clusters reduces the chance of a rutile nucleus reaching the critical size.

A SEM image of the KRICT-MT indicates that the secondary titania particles were below 100 nm in diameter and the large secondary mesopores were formed among the interconnected secondary particles (inset in Figure 5a). A TEM image of the secondary particle in Figure 5a reveals that the secondary titania particle is composed of the small primary mesopores and the nanocrystalline-titania framework. The primary mesopores are three-dimensionally interconnected and disordered. The wormhole-like mesostructure inside the secondary titania particle is almost consistent with the schematic diagram in Figure 1. Figure 5b is a local enlarged TEM image of Figure 5a. The presence of clearly resolved lattice fringes demonstrates that the framework of

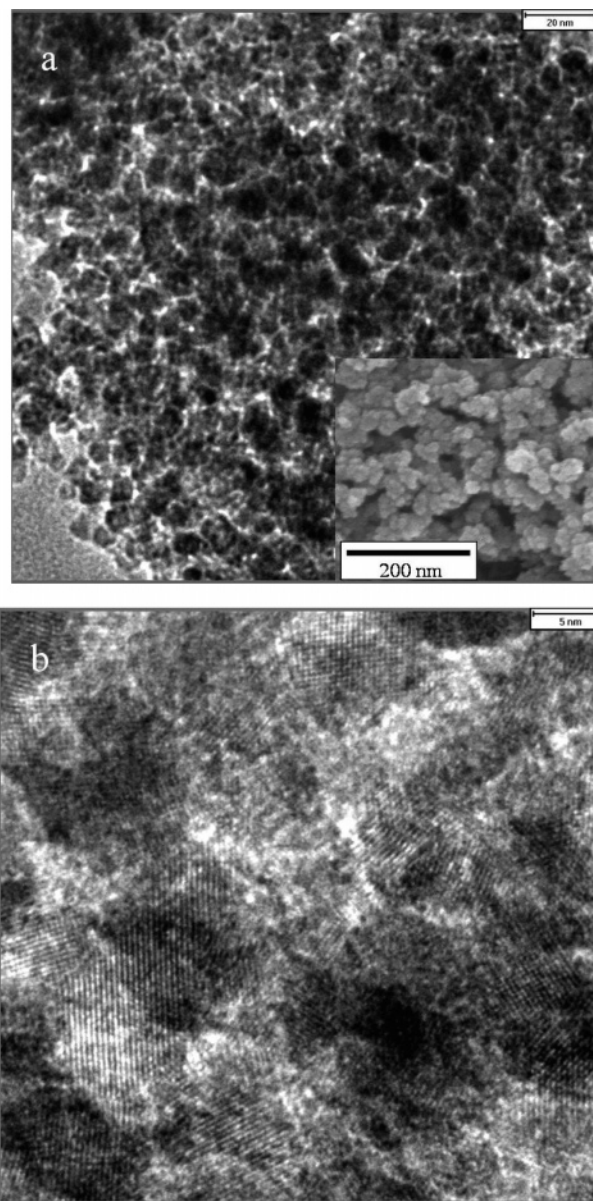


Figure 5. TEM images of the KRICT-MT calcined at 500 °C: (a) low magnification (the scale bar is 20 nm); (b) high magnification (the scale bar is 5 nm). The inset of part (a) is a SEM image of the KRICT-MT calcined at 500 °C (the scale bar is 200 nm).

the primary mesopores is composed of anatase nanocrystals below 10 nm. The three-dimensionally interconnected mesostructure of the KRICT-MT is expected to give high catalytic activity.

To investigate the catalytic activity of the KRICT-MT as a catalyst support, we fabricated the Pt(1 wt %)/KRICT-MT by impregnating the KRICT-MT with tetraammineplatinum(II) hydroxide precursor by means of the incipient wetness method and carried out the water–gas shift (WGS) reaction. For comparison, we also prepared the Pt(1 wt %)/Degussa P25 via the incipient wetness method. The Pt dispersions of the Pt/KRICT-MT and the Pt/Degussa P25 catalysts were 23% and 22%, which were determined by chemisorption using CO as a probe gas. Figure 6 presents CO conversions of the Pt/KRICT-MT and the Pt/Degussa P25 catalyst for the WGS reaction. Compared to the Pt/Degussa P25, the Pt/KRICT-MT showed a remarkable increase in the CO conversion at the low reaction temper-

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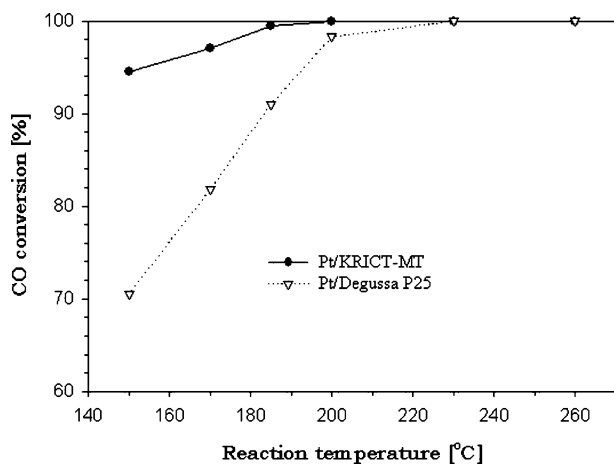


Figure 6. CO conversions of the Pt/KRICT-MT and the Pt/Degussa P25 catalyst with 1 wt % of Pt for water–gas shift reaction.

ature. Although the two catalysts had similar Pt dispersions, the catalytic activity of the Pt/KRICT-MT was much higher than that of the Pt/Degussa P25. The remarkably high catalytic activity of the Pt/KRICT-MT is attributed to the three-dimensionally interconnected mesopores and the bimodal mesostructure. The well-connected mesostructure

allowed the reactant molecules to more readily access the active sites.³¹ In addition, the large secondary mesopores reduced the limitation on the transport of reactants to the primary mesopores.

Conclusions

The mesoporous titania, designated KRICT-MT, was successfully synthesized via replication of the CA-templated mesoporous silica with the thermally stable silica-nanosphere framework. The KRICT-MT showed the extremely high thermal stability and bimodal mesostructure, which is three-dimensionally interconnected. The anatase–rutile phase transformation of the KRICT-MT was not observed up to 900 °C. The high pore properties and bimodal mesostructure were maintained up to 900 °C, which is attributed to the thermally stable anatase-nanocrystal framework. Moreover, the KRICT-MT was employed as a catalyst support for water–gas shift reaction. The catalytic activity of the Pt-impregnated KRICT-MT for the water–gas shift reaction was much higher than that of the Pt-impregnated Degussa P25. The remarkably high catalytic activity of the Pt/KRICT-MT was derived from the three-dimensionally interconnected mesopores and the bimodal mesostructure.

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