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# Highly Stable Mesoporous Metal Oxides Using Nano-Propping Hybrid Gemini Surfactants

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Mesoporous materials, obtained by the favorable self-assembly between organic templates and inorganic precursors, have opened many new possibilities for applications in catalysis, separation, and nanoscience due to their large, controllable pore sizes, high surface areas, and easy functionalization.[1,2] The nature of organic templates is one of the most important factors for designing and synthesizing mesoporous materials.[3] In general, surfactants with cationic, anionic, and neutral charges and amphiphilic block copolymers have been utilized as organic templating agents.[2] Most research in this field has been focused on silica as a framework constituent. However, mesoporous materials derived from transition metal oxides instead of the silica frameworks are expected to be quite useful for several applications. There have been several reports concerning the synthesis of mesoporous metal oxides, such as titanium, vanadium, zirconium, tungsten, niobium, and tantalum oxides via surfactant templated,[4] ligand-assisted,[5] polymer templated,[6] and nanoreplicated pathways.[7,8] However, the synthesis of mesoporous metal oxides has been less successful as compared to those of silica materials. One difficulty lies in a facile crystallization of most metal oxides, accompanied by structural collapse, during the mesostructure formations and the removal of organic templates.

Here, we describe a new type of Gemini surfactant containing a siloxane moiety, which can yield highly stable mesoporous metal oxides after the removal of the surfactant via the nano-propping pathway. Figure 1 shows the structure of the surfactant and the schematic diagram for the nano-propping pathway. In the surfactant, we can control the length of the hydrophobic tail ($n$), the length of the siloxane moiety ($m$), and the length of the spacer between the positively charged headgroup and the siloxane moiety ($k$). The Gemini surfactants containing the siloxane moiety are denoted as $C_{n-k}Si_m$. A typical synthesis procedure of $C_{18-3}Si_3$ surfactant is provided in the Supporting Information.

Mesoporous metal oxides were prepared as follows: the $C_{n-k}Si_m$ surfactant and distilled water were initially mixed to obtain a homogeneous solution. An aqueous solution of metal oxide precursors such as zirconium sulfate, vanadyl sulfate, and titanium sulfate was added to the surfactant solution under vigorous magnetic stirring. The molar composition of the synthetic mixture was 1 metal precursors:0.05−0.5 $C_{n-k}Si_m$:100 $H_2O$. The mixture was aged with stirring for 1 h at room temperature and subsequently heated to 373 K in an oven under static conditions for 24 h. The precipitates were filtered, washed with distilled water, and dried at 373 K. The product was calcined at 823 K in air flow.

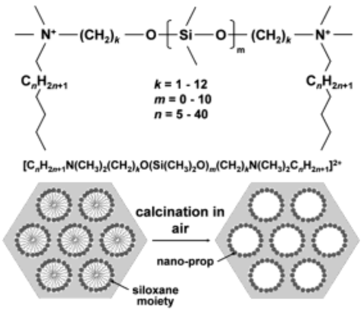

***Figure 1.*** Structure of the Gemini surfactant and a schematic diagram for the nano-propping pathway.

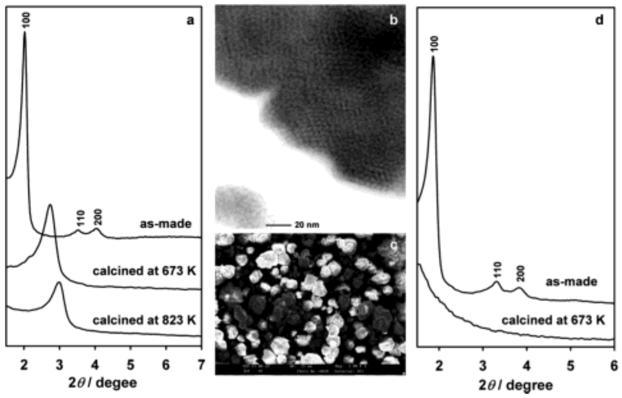

***Figure 2.*** (a) XRD patterns for the mesoporous zirconium oxide obtained from $C_{18-3}Si_3$ before and after calcination, and the corresponding (b) TEM image and (c) SEM image of the material after calcination at 823 K, and (d) XRD patterns for the mesoporous zirconium oxide obtained from normal Gemini surfactant without the siloxane moiety.

Figure 2a shows X-ray diffraction (XRD) patterns of the mesoporous zirconium oxide obtained by using $C_{18-3}Si_3$ surfactant as a template. As shown in Figure 2a, the zirconium oxide exhibits the XRD patterns with a very intense diffraction peak and two weak peaks before calcination, which are characteristic of the 2-D hexagonal (*P*6*mm*) structure.[1−3] It is quite noteworthy that the mesoporous zirconium oxide exhibits ordered structure even after the calcination at 823 K. Figure 2b shows the transmission electron microscopic (TEM) image of the mesoporous zirconium oxide after calcination. In the TEM image, the mesopores are packed in a hexagonal way, implying that the material has a highly ordered 2-D hexagonal structure. The scanning electron microscopic image in Figure 2c shows that the morphology of the material is quite uniform. Generally, the structure constructed with zirconium oxide is often collapsed or transferred to a poorly ordered structure by the thermal damage of structural integrity. For comparison,

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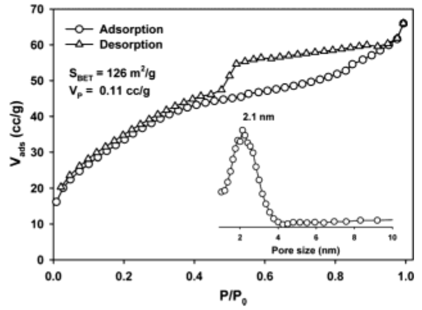

***Figure 3.*** Nitrogen adsorption−desorption isothems of the mesoporous zirconia in Figure 2a and the corresponding pore size distribution curve obtained from the adsoption branch (inset).

zirconium oxide mesostructure has been obtained by the same synthetic procedure using a Gemini surfactant ($C_{16}H_{33}N(CH_3)_2$-$(CH_2)_6N(CH_3)_2C_{16}H_{33}Br_2$)[9] without the siloxane moiety as a template. The material thus obtained shows the highly ordered 2-D hexagonal structure as shown in Figure 2d before calcination. However, the ordered structure is completely collapsed upon calcination at 673 K. A widely used organic template for the synthesis of mesoporous materials, cetyltrimethylammonium bromide,[1,2] also results in the formation of ordered mesoporous zirconium oxide before calcination and the complete structural deconstruction after calcination (not shown). These results indicate that the siloxane moiety introduced in the Gemini surfactants in the present work acts as a stabilizer for the zirconium oxide framework during the calcination.

The self-assembly of cationic zirconium species, which are present in the reaction mixture, with the surfactants is known to be mediated by sulfate anions because the zirconium species are protonated under this condition.[10] The sulfate anion may be an excellent mediator between cationic metal precursors and cationic surfactants due to its large size and divalent charge. Consequently, metal sulfates generally yield highly ordered mesoporous materials in the presence of cationic surfactants. However, the presence of sulfate groups in the inorganic framework prevents full condensation, and this leads to the major framework disruption because of the sulfate removal upon calcination. The siloxane species in the present surfactant molecules seem to play a nano-propping role, to maintain the mesostructure during the calcination, as shown in Figure 1. Elemental analysis of the calcined zirconium oxide indicates that a small amount of silica species exists within the framework ($Si/Zr = 0.09$) after calcination. Stabilization of the mesostructured metal oxide by the silica species is similar to the effects of phosphate or chromate which can improve the stability of the materials so that the materials retain the mesoporosity after calcination.[11] We also found that the lattice contraction of the materials after the calcination at 823 K is dependent on the number of siloxane groups within the Gemini surfactant. $C_{18-3}Si_2$, $C_{18-3}Si_3$, and $C_{18-3}Si_4$ surfactants give 30%, 24%, and 20% of the lattice contractions, respectively, which also indirectly confirms the nano-propping role of the siloxane moieties.

Figure 3 shows the nitrogen adsorption and desorption isotherms for the mesoporous zirconium oxide obtained after calcination at 823 K. A small stepwise increase appears in the adsorption isotherm around $P/P_0 = 0.2$, indicating capillary condensation in the mesopores. No hysteresis loop is obtained in this region; however, there is a hysteresis that appears at $P/P_0 = 0.5$, which is presumably due to the interparticular spacing between agglomerated particles (see Figure 2c). A BJH pore size curve obtained from the adsorption branch of the isotherm indicates that the material has well-defined mesopores centered at 2.1 nm.

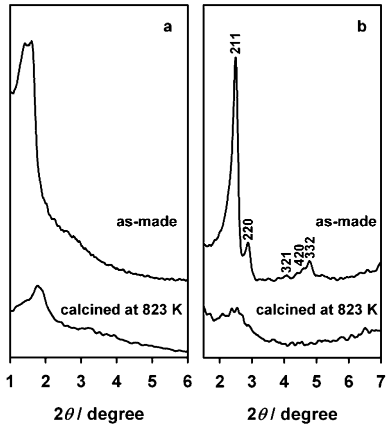

***Figure 4.*** XRD patterns for the mesostructured (a) titanium oxide and (b) vanadium oxide before and after calcination, obtained from the $C_{18-3}S_3$ surfactant.

The mesoporous materials based on titanium and vanadium oxides can also be synthesized using the present Gemini surfactants and also demonstrate high thermal stability as shown in Figure 4. In the case of mesoporous titanium oxide, the mesostructure thus obtained is somewhat disordered. We are currently optimizing the synthetic conditions to obtain the highly ordered materials. Figure 4b indicates that the vanadium oxide mesostructure has a well-defined bicontinuous cubic symmetry (*Ia*3*d*), similar to the MCM-48 structures.[1] However, the mesostructure almost disappears upon calcination, which is believed to be due to the weak thermal stability of the framework.

In conclusion, Gemini surfactants containing a siloxane moiety have been designed and successfully synthesized in the present study and are utilized as templates for mesoporous metal oxides such as zirconia, titania, and vanadia. The siloxane moiety is believed to play an important nano-propping role during the surfactant removal by direct calcination, yielding thermally stable mesoporous metal oxides. It is believed that the synthesis strategy described here can be applied to the synthesis of robust nanostructured materials such as nanoparticles and nanorods in addition to mesoporous materials.

**Acknowledgment.** This work was supported by the Korea Research Foundation Grant (KRF-2003-015-C00319). K.C. also acknowledges the financial support from the National Research Laboratory Program (Grant M1-0104-00-0191).

**Supporting Information Available:** Detailed synthesis conditions for the $C_{18-3}Si_3$ surfactant (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0390348