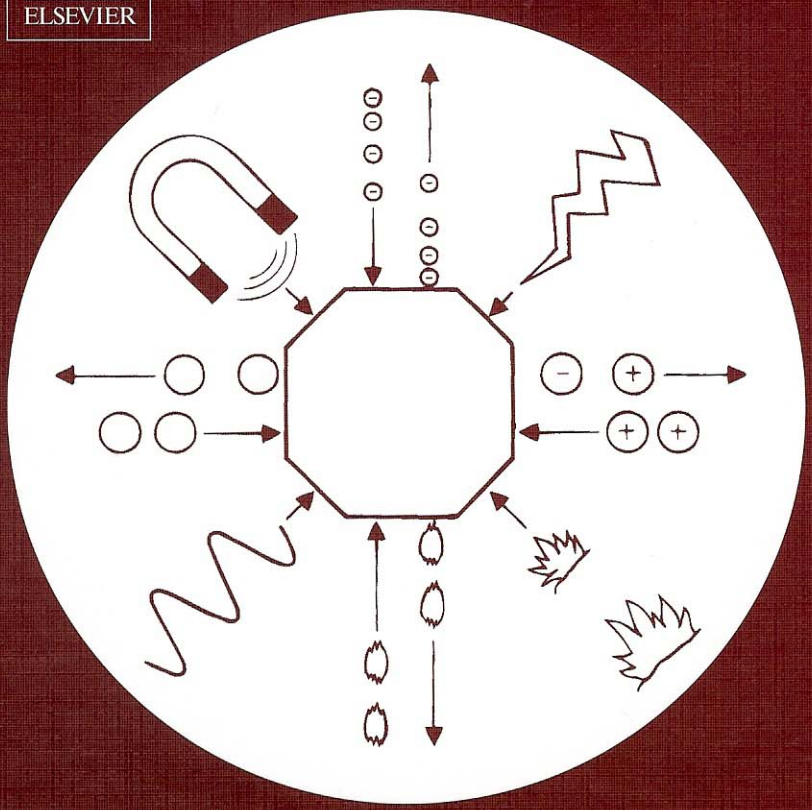
studies in surface science and catalysis



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RECENT PROGRESS IN MESOSTRUCTURED MATERIALS

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Recent Progress in Mesostructured Materials
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Nano-replication to mesoporous metal oxides using mesoporous silica as template

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Mesoporous materials constructed with different framework compositions such as iron oxides and manganese oxides, etc. have been successfully obtained by the impregnation with desired metal precursors into the bicontinuous cubic *Ia3d* mesoporous silica, crystallization to metal oxides at desired temperature and subsequent silica removal using NaOH aqueous solution.

1. Introduction

Since the discovery of mesoporous materials, ordered mesoporous silicas such as MCM-41, SBA-15 and KIT-6 have attracted much attention for various applications due to their tunable mesopore and the subsequent high surface area [1-3]. In addition, it is reported that mesoporous silicas can be used as a sacrificing template for the nano-replication to mesoporous materials constructed with different framework compositions [4]. Recently, preparation of ordered mesoporous materials metal oxides via nano-replication method using mesoporous silicas as a template has been reported [5-6]. These efforts enabled the preparation of mesoporous materials with various framework compositions, which are believed to have inherent properties as catalytic, optical and electronic materials. Moreover, these mesoporous metal oxides prepared by nano-replication method possess regular mesopore and high surface area. This can lead great advantages for applications such as catalysis or sensing due to its extremely high ratio of the number of surface atoms to the number of bulk atom.

In this work, we have used large mesoporous silica, KIT-6 as a template for the fabrication of mesoporous materials constructed with various metal oxides such as iron oxide and manganese oxide.

2. Experimental Section

The mesoporous silica KIT-6 has been prepared by the self-assembly method using the Pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$) and tetraethyl orthosilicate (TEOS). 30 g of P123 was dissolved in the mixture of 1085 g distilled water, 30 g of *n*-butanol and 59 g of HCl (35%). After stirring the solution for 1 hr, 64.5 g of TEOS is added to the homogeneous clear solution. This mixture is left under constant stirring at 35°C for 24 hrs. The precipitate was filtered, dried at 80 °C and finally calcined at 550°C.

For the synthesis of mesoporous metal oxides, 0.4 g of metal precursors ($FeCl_3 \cdot 6H_2O$, 98%, $Mn(NO_3)_3 \cdot xH_2O$, 98%, Aldrich) was dissolved in 1.0 g of distilled water. These solutions were incorporated into 1.0 g of mesoporous silica template using the impregnation method. The impregnated samples were dried in an oven at 80°C for 1 d and calcined at various temperature ranges, from 300 to 700°C. The silica template was removed from the composites of silica and metal oxide by treating three times using 1 – 2 M NaOH aqueous solution

3. Result and Discussion

X-ray diffraction (XRD) patterns in Fig. 1 show typical diffraction patterns of bicontinuous cubic Ia3d mesophases of mesoporous silica KIT-6, and replicated mesoporous metal oxides that were heated at 500°C before the removal of silica template. XRD results of mesoporous metal oxides show relatively weak peaks at low angle, which have similar d-spacing values with the mesoporous silica

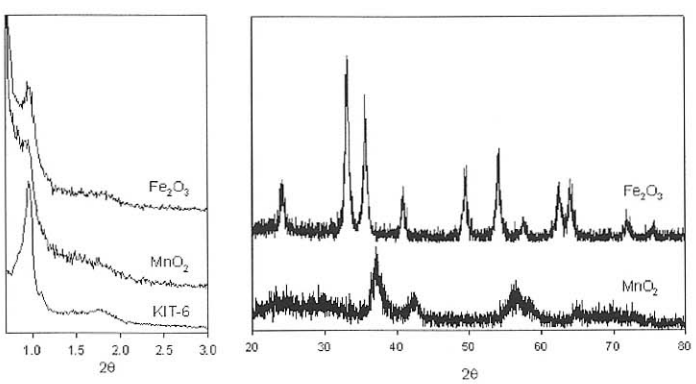

Fig. 1. XRD patterns of KIT-6 and mesoporous metal oxides replicated from the KIT-6.

template. The XRD peaks in the 2θ ranges of 0.7 – 3° can be indexed to 211, 220, and 332 which are typical characteristics of bicontinuous cubic Ia3d mesophase. Wide-angle XRD patterns on the right side of Fig. 1 clearly show crystalline framework structures for the replicated metal oxides. The line-widths

Table 1. Physical property of mesoporous silica and mesoporous metal oxides

Materials	Surface Area (m^2/g)	Pore Volume (cc/g)	Unit cell Parameter (nm)	Pore Size (nm)
KIT-6	700	0.91	22.5	8
Fe_2O_3	99	0.22	22.5	2.5
MnO_2	109	0.39	22.5	2.5

of XRD patterns are relatively broad similar with those of nanoparticles. The crystallite size of mesoporous metal oxides that calculated by Scherrer equation is estimated to be around 10 nm.

Table 1 show the physical properties such as surface area, pore size, unit cell parameter and pore volume of mesoporous silica, Fe_2O_3 and MnO_2. The mesoporous silica, KIT-6 with BET surface area of 700 m^2/g, total pore volume of 0.91 cc/g and BJH pore size of 8 nm, is replicated to mesoporous Fe_2O_3 and MnO_2. The replicated mesoporous Fe_2O_3 and MnO_2 materials (in Fig. 1) exhibit quite high BET surface area of 99 and 109 m^2/g, and total pore volume of 0.22 and 0.39 cc/g, respectively. BJH pore sizes of mesoporous Fe_2O_3 and MnO_2 are around 2.5 nm in diameter.

One more interesting thing is that the particle morphology of replicated mesoporous metal oxides is quite different with that of sacrificial silica template.

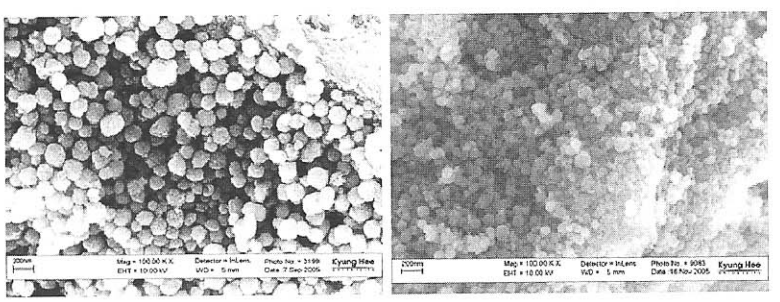

Fig. 2. FESEM images of iron oxide(left) and manganese oxide(right)

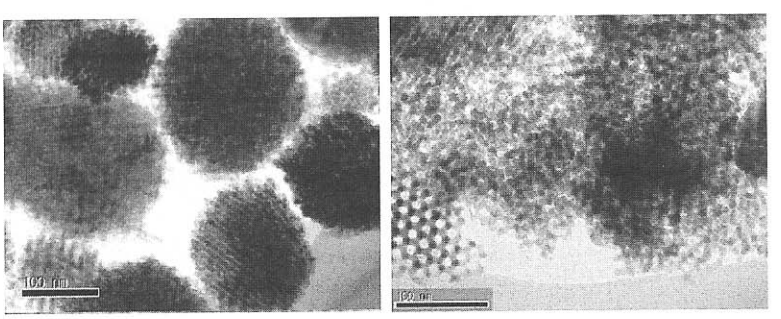

Fig. 3. HRTEM images of iron oxide(left) and manganese oxide(right)

Even though the particles of mesoporous silica template are very irregular and pretty big, the replicated mesoporous metal oxides have spherical morphology with very uniform particle size about 100 nm in diameter as shown in FESEM images in Fig. 2. HRTEM images of mesoporous metal oxides in Fig. 3 clearly reveal that the not only the mesoscopic order but also the atomic crystallinity of the replicated mesoporous metal oxides showing three dimensional network topology of metal oxide nano rods.

4. Conclusion

Ordered mesoporous silica is successfully converted to mesoporous materials with various framework composition by means of nano-replication technique. The mesostructural properties are maintained after the template removal and framework crystallinity can be controlled by annealing process before the removal of rigid and thermally stable mesoporous silica template. This nano-replication route would be able to used as a facile method for the preparation of mesoporous materials constructed with various crystalline frameworks, which would have intense potentials for the practical applications.

5. Acknowledgement

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