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Three-Dimensionally Ordered Mesoporous Niobium Oxide

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Recently, several mesoporous metal oxides have been reported, which were synthesized by neutral templating[1] and ligand-assisted templating methods.[2] Despite successful development on mesoporous silica, mesoporous transition metal oxides have been less explored. Metal oxides for mesoporous materials are often more susceptible to hydrolysis, redox reactions, or phase transitions accompanied by thermal damage of the structural integrity, while silica and aluminosilicates are typically stable materials.[3]

Highly ordered mesoporous materials have been reported to be prepared with titanium,[1,4] vanadium,[5] zirconium[1], tungsten[1], niobium[1,2] and tantalum oxides,[1,6] while the most of mesoporous metal oxides show nonordered pores originated from the void among the particles.[7] Differently from the structural variety of the mesoporous silica which has two-dimensional (2D) (*P*6*mm*) and three-dimensional (3D) ($P6_3/mmc$) hexagonal,[9,10] cubic (*Pmm*, *Iad*, *Imm*),[9] lamellar (La)[9] and wormhole-like structures,[11] few structural selectivities have been known in mesoporous transition metal oxides.[12] Even in the case of hexagonally ordered structures, XRD patterns indicate poorer regularity than mesoporous silica; specific second and third peaks of the hexagonal structure were broad or difficult to identify.[1]

In the case of mesoporous silica, a neutral templating route (N^0I^0) leads to wormhole-like mesoporous structures, where N^0 and I^0 are denoted as neutral template and inorganic precursor, respectively.[11] Cation or anion additions in the neutral templating route was developed that is known as $(N^0M^{n+})I^0$ or $(N^0X^-)I^0$ synthetic route, where M^{n+} and X^- are denoted as cations and anions.[13,14] In these synthetic routes, wormhole-like mesoporous structure proceeded to long-range ordered mesostructures by the electrostatic effects between neutral template and ions. The ion effect is considered to be utilized in the syntheses of mesoporous transition metal oxide systems. Without ion addition, mesoporous metal oxides prepared through the N^0I^0 route resulted in 3D channels of wormhole-like structure.[15] By elaborate ion addition, the wormhole-like structure is considered to be changeable to highly ordered 3D mesoporous structures.

Mesoporous niobium oxide is expected to be applicable in electronic and magnetic devices,[16] biotechnology,[17] and nanotechnology.[18] However, the 2D channel system limits the further coating or incorporation applications by means of their porous orientation. An ordered mesoporous system extended to 3D structure is, therefore, strongly demanded.

Here, we report a mesoporous niobium oxide with a highly ordered 3D mesoporous structure prepared via the N^0I^0 route with an addition of a trace amount of cations.

Mesoporous niobium oxide was prepared by neutral templating route. Triblock copolymer P-85 ($HO(CH_2CH_2O)_{26}(CH_2CH(CH_3)O)_{39}(CH_2CH_2O)_{26}H$) and niobium pentachloride were employed as the template and inorganic source, respectively. Typical synthesis was proceeded in the molar ratio, 35 Nb:1 P-85:835 propanol:0.25 cation:280 H_2O.

For instance, 0.007 mol of $NbCl_5$ was added to the template solution where 2.2×10^{-4} mol P-85 is dissolved in 10 g of propanol. After vigorous stirring for 5 min, ca. 1.0 mL of 0.05 M NaCl solution was added and stirred for 30−40 min more. Final sol solution was then aged at 40 °C for one week to obtain gel product. To obtain the homogeneous aging conditions, sol solution was applied onto glass plates. Template was removed by calcination at 450 °C for 5 h in air.

Figure 1 shows X-ray diffraction (XRD) patterns of mesoporous niobium oxides prepared with and without cation addition. Mesoporous niobium oxide synthesized without cation addition shows a main peak at 1.3°, which indicates d_{100} (6.8 nm) of mesoporous structure (Figure 1a). Because there is a shoulder peak at around 2−2.5°, a long-range ordered mesostructure is expected because a strong first peak and a weak second peak are generally found in ordered mesostructures.[1] Although the XRD pattern was suggestive of hexagonally ordered or at least highly ordered mesoporous structure, the transmission electron microscopy (TEM) observation revealed mainly wormhole-like mesoporous structure. Therefore, it is considered that a small amount of ordered mesoporous particles are included in the mesoporous niobium oxide sample.

By the addition of a small amount of cations, mesoporous structure was dramatically improved. In Figure 1b, mesoporous niobium oxide with 5×10^{-5} mol Ca^{2+} addition indicates the specific peaks of 3D hexagonal structure. From the XRD pattern, mesoporous niobium oxide can be indexed in the space group $P6_3/mmc$. The cell parameter ratio of c/a was 1.62, whereas the ideal c/a ratio of hexagonal close-packed phase is 1.633.

TEM investigation verifies 3D hexagonal structure. In Figure 2, three electron diffraction patterns taken from different zone axes indicate a $P6_3/mmc$ structure, which is similar to SBA-2,[10] 3D hexagonal mesoporous silica. Ordered pores found at different zone axes strongly evidence a three-dimensionally ordered mesoporous structure of the sample.

The optimized preparation condition lay on extremely narrow range of the amounts of cations and niobium precursor. Highly ordered mesoporous structure was found at 0.007 mol of $NbCl_5$ in 10 g of template solution, which was produced by varying $NbCl_5$ amount from 0.005 to 0.01 mol on 10 g of template solution. Concentration of cation solution was fit on 0.05 M, while lower or higher concentration gave poorer ordering of mesoporous structure. The timing of the addition of cations also affected the regularity of pores. Slower or faster addition of cations produced a poorly

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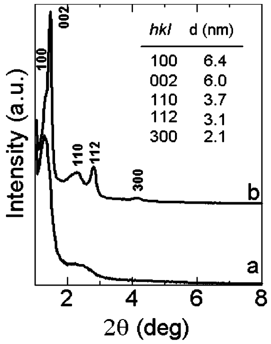

Figure 1. XRD pattern of mesoporous niobium oxide without (a) and with cation addition (b). Ca^{2+} was employed as the cation source.

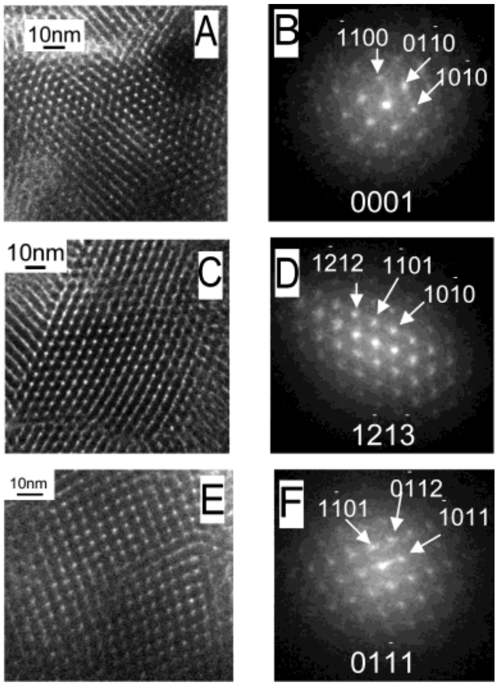

Figure 2. TEM image of mesoporous niobium oxide with cation addition. Lattice image of mesoporous structure (A) and its electron diffraction (ED) (B) patterns viewed along the [0001] zone axis. Lattice image (C) and its ED pattern along the [11] zone axis (D). Lattice image (E) and its ED pattern along the [011] zone axis (F).

ordered mesoporous structure, because the hydrolysis step was extremely fast. (The pH was changed from less than 1 at 0th minute to more than 7 at 30th minute of reaction time.)

Either Li$^+$, Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, or Ba^{2+} was added as the cation source. Withe the exception of K$^+$, which showed poorer mesoporosity, cation-added samples showed a strong main peak at around 1−2° and other second and third peaks at around 2−4°. It is indicative that the obtained mesoporous structures are identical with that from Na$^+$-added sample of 3D hexagonal mesoporous structure.

N$_2$ gas adsorption−desorption isotherms and Barrett−Joyner−Halenda (BJH) analysis[7] of pore size distribution are shown in Figure 3. The isotherm curve indicates stepwise adsorption and desorption, which is indicative of 3D intersection of porous structure.[7,13] Pore size distribution estimated from the adsorption curve shows ca. 5 nm of mesopores (Figure 3, inset). From the pore size distribution and XRD results, pore size and wall thickness were estimated to be ca. 5 and 2 nm, respectively. The Brunauer−Emmett−Teller (BET) surface area was estimated as 210−220 m^2/g.

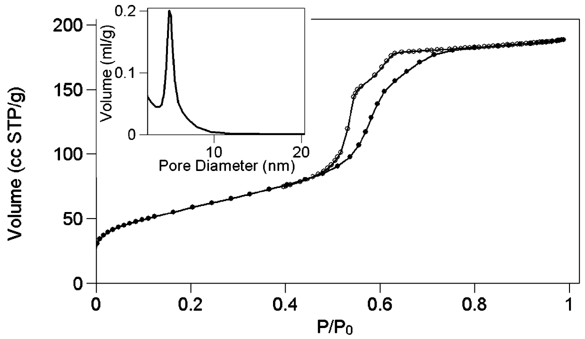

Figure 3. N$_2$-gas adsorption−desorption isotherm of mesoporous niobium oxide with cation addition and pore size distribution (inset). Filled and blank dots indicate adsorption and desorption curves, respectively. Pore size distribution was calculated by BJH equation in adsorption branch.

In conclusion, 3D hexagonal mesoporous niobium oxide was successfully prepared by a neutral templating route. By addition of cations under precisely controlled conditions, wormhole-like mesoporous structure was dramatically changed to highly ordered 3D hexagonal structure. This result is suggestive of a structural control effect of cations in a neutral templating route for the synthesis of mesoporous transition metal oxides.

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Supporting Information Available: Figure S1 and Table S1 (PDF). This material is available free charge via the Internet at http://pubs.acs.org

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