Preparation of Ordered Supermicroporous Niobium Oxide

Byongjin Lee,[†] Daling Lu,[††] Junko N. Kondo,[†] and Kazunari Domen*[†,††]
[†]*Chemical Resources Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8503*
[††]*CREST, Japan Science and Technology, 2-1-13 Higashiueno, Taito-ku, Tokyo 110-0015*

(Received August 2, 2002; CL-020647)

Ordered supermicroporous (1.0–2.0 nm) niobium oxide was prepared by sol-gel method using neutral templating route, where the template was removed by water washing after 2-step aging.

Recently various mesoporous transition metal oxides have been prepared using neutral block copolymer templating route.[1,2] However, few results have been reported about the materials possessing regular pores in the 1.0 to 2.0 nm range (supermicropores). The supermicroporous (1.0–2.0 nm) materials, is commercially important for heavy fraction crude-oil processing, fine chemical processing and pharmaceutical precursor synthesis.[3]

In the case of mesoporous silica, the neutral templates could be removed by solvent extraction, while calcination or acid treatment is usually applied for template removal.[4,5] Among them, calcination has been known as the most general way to remove the template. Ethanol extraction for the preparation of mesoporous silica, HMS, resulted in larger pore size than the calcined sample, which is a good example of pore size control by template removal method.[4] It implies that pore size could be controlled by template removal method in the neutral templating route.

To the best of our knowledge, there has been no report on the use of water extraction treatment for template removal. Template removal by washing with water is regarded as a possible candidate for the alternative of the typical methods for the template removal, i.e. calcination or acid treatment, which is considered to be the less expensive and environment-friendly synthetic route. Moreover, pore size is considered to appear differently for the water-washed sample from that prepared by calcination since heating procedure might affect the structure of the metal oxide walls. In this study, therefore, niobium oxide is investigated for the preparation of supermicroporous materials by the neutral templating route.

10 wt% solution of triblock copolymer, poly(alkylene oxide), $HO(CH_2CH_2O)_{26}(CH_2CH(CH_3)O)_{39}(CH_2CH_2O)_{26}H$ (Pluronic P-85, Adeka Co.) was prepared in propanol solvent. 0.007 mol of $NbCl_5$, metal precursor, was added in 10 g of template solution and then stirred for 40 minutes. During the reaction ca. 1 mL of water or NaCl solution was introduced to promote hydrolysis and structural regularity.[6,7] Finally, sol solution was aged at 40 °C in air for one week to obtain template-containing niobium oxide or hydroxide gel.

The obtained gel was divided to some parts, and one was washed with 0.5–1.0 L of distilled water to remove the template. Other gel samples were aged in the 2nd step from 60 to 140 °C for 1–2 days and then washed with the same amount of distilled water. Washed samples were dried in the air for one night. For comparison, another gel sample was calcined at 450 °C for 5 hours to remove the template.

Since the triblock copolymers are micellized in the temperature region of 20–40 °C,[8] as-synthesized porous niobium oxides were aged at 40 °C. Aging above 40 °C is evaded for the initial aging in the present study, because macroscopic phase separation occurs at about 65–75 °C.[8] Template removal was confirmed by element analysis of carbon and chloride contents. Contents of carbon and chloride were estimated to be less than 0.1% after template removal, while about 24 and 6% of carbon and chloride were detected before template removal. Since the neutral template forms weak hydrogen bond with inorganic precursor, it was completely removed by simple water washing.

Figure 1 shows N_2 gas adsorption-desorption isotherms of porous niobium oxide samples. In the sample calcined at 450 °C after aging at 40 °C, formation of mesoporous niobium oxide is confirmed by N_2 uptake at 0.5–0.6 P/P_0. (Figure 1, curve a) Type IV isotherm curve is indicative of mesoporous structure. BJH analysis in adsorption isotherm indicates 5 nm of pore size and 0.42 mL/g of pore volume. (Figure 1, inset, curve a) Triangular hysteresis loop by adsorption-desorption curve implies ink-bottle type or wormhole-like mesoporous nature.[2]

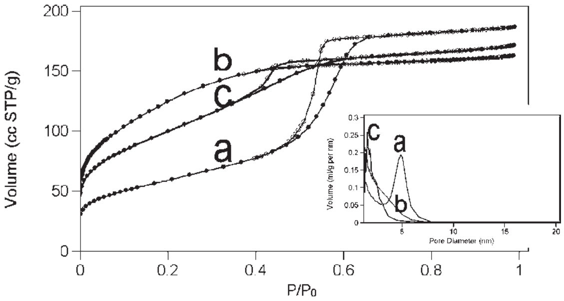

Figure 1. N_2 gas adsorption-desorption and BJH pore size distribution (inset) of porous niobium oxides: template-removed by calcinations (a), and water washing after 1st step aging (b) and after 2nd step aging (c). Filled and blank circles indicate adsorption and desorption isotherms,

On the other hand, water-washed sample after 40 °C aging shows wider microporous nature (Figure 1, curve b). N_2 uptake occurs at lower relative pressure range ($<0.03\ P/P_0$), and gradual increase in the amount of N_2 adsorption from 0.1 to 0.4 P/P_0 range is observed. This isotherm curve is indicative of widely distributed pore size from microporous to mesoporous range. Mesoporous and microporous volumes were estimated as 0.14 (2–50 nm range) and 0.18 ml/g (0.3–2 nm range) by BJH and HK equations, respectively. BET surface area was estimated to be 444 m^2/g, which was considerably higher than the calcined sample (211 m^2/g). Pore size distribution calculated by BJH equation indicates widely distributed pore size below 5 nm (Figure 1, inset, curve b).

Copyright © 2002 The Chemical Society of Japan

Since the widely distributed wider microporous structure was found from the water-washed niobium oxide, 2-step aging was employed to stabilize the niobium oxide network in wall structure. Curve c in Figure 1 indicates niobium oxide sample template-removed by water washing after 2nd step aging at 100 °C. The isotherm curve is very similar with the supermicroporous zirconia prepared by ionic template route, which has ca. 2 nm of pore size.[9] Hysteresis loop is clearly observed, which implies the improved porous regularity. A peak in the pore size distribution (Figure 1, inset, curve c) is more apparent than 1st step-aged sample. Pore size of ca. 1.7 nm indicates supermicroporous nature. The BET surface area and pore volume were estimated to be 363 m^2/g and 0.41 ml/g respectively.

The XRD results indicated a sharp peak at around 1.5 degree in water-washed sample after 2nd step aging, where the *d* value was 5.0–6.0 nm. From the result of N_2 gas adsorption-desorption and XRD, it was concluded that the water-washed sample has 2 nm pore size and 3–4 nm wall thickness.

The TEM image reveals the porous structure of niobium oxide after template removal (Figure 2). In Figure 2A, the calcined sample shows wormhole-like mesoporous nature with 4–5 nm pore size and 2 nm wall thickness.

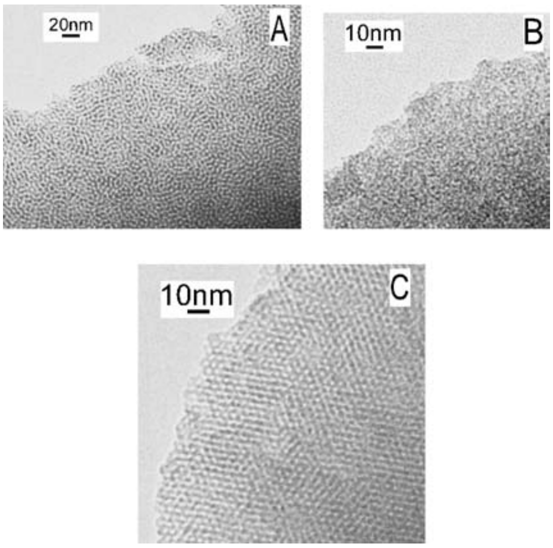

Figure 2. TEM images of porous niobium oxide: template-removed by calcinations (A), and water washing after 1st step aging (B) and after 2nd step aging (C).

In the case of water-washed sample after 1st step aging, wormhole-like microporous structure is observed. (Figure 2B) From the TEM image the pore size and wall thickness are estimated to be ca. 1–2 nm and ca. 2 nm, respectively, indicating microporous nature. Widely distributed pore size and irregural pore structure are indicative of the structural degredation of water-washed sample after 1st step aging. It is considered that the unstable inorganic network is degraded by water washing after the complete removal of the template. This is probably due to the insufficient condensation of the inorganic phase.

In Figure 2C, TEM images of the sample aged in 2nd step are shown. The 2nd step aging results in ordered supermicroporous structure. Pore size and wall thickness measured from TEM are 1.5–2.0 nm and 3–4 nm, respectively. The niobium oxide wall is stabilized by 2nd step aging, so that the ordered wall structure is remained after washing for template removal.

The supermicroporous structure obtained by washing procedure was unchangeable under higher temperature treating. The pore size was unchanged after heating at 500 °C, which was confirmed by TEM observation. Above 580 °C, the supermicroporous structure was collapsed with crystallization of niobium oxide.

It is considered that in the case of niobium oxide the ordered porous nature is easily changeable by the method for template removal; either by calcination or by water washing wormhole-like porous structure was finally obtained. The 2nd step aging is, therefore, considered as an essential factor to fabricate the ordered microporous structure.

In conclusion, water washing turned out to be an appropriate removing method of neutral template. Moreover, 2-step aging resulted in ordered supermicroporous structure of niobium oxide. In conclusion, a new phenomenon was found: the smaller supermicropore was obtained by water washing while mesoporous structure was produced by calcination. Detailed study will be reported elsewhere.

The authors gratefully acknowledge the assistance of Adeka Co. who provided neutral block copolymer, P-85. This work was supported by the Core Research for Evolutional Science and Technology (CREST) program of the Japan Science and Technology (JST) Corporation.

References

1 P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka, and G. D. Stucky, *Chem. Mater.*, **11**, 2813 (1999).
2 B. Lee, D. Lu, J. N. Kondo, and K. Domen, *Chem. Mater.*, **14**, 867 (2002).
3 S. A. Bagshaw and A. R. Hayman, *Adv. Mater.*, **13**, 1001 (2001).
4 P. T. Tanev and T. J. Pinnavaia, *Science*, **267**, 865 (1995).
5 P. T. Tanev and T. J. Pinnavaia, *Supramol. Sci.*, **5**, 399 (1998).
6 T. Katou, D. Lu, J. N. Kondo, and K. Domen, *J. Mater. Chem.*, **12**, 1480 (2002).
7 B. Lee, D. Lu, J. N. Kondo, and K. Domen, *J. Am. Chem. Soc.*, accepted.
8 G. Fleischer, *J. Phys. Chem.*, **97**, 517 (1993).
9 J. L. Blin, R. Flamant, and B. L. Su, *Int. J. Inorg. Mater.*, **3**, 959 (2001).