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Synthesis of 2D-hexagonally ordered mesoporous niobium and tantalum mixed oxide

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A well ordered 2D-hexagonal mesoporous niobium and tantalum (Nb : Ta = 1 : 1) mixed oxide (denoted mesoporous NbTa oxide) was successfully prepared. Pore size, pore volume and wall thickness of the mesoporous NbTa oxide were found to be strongly affected by the amounts of water and metal sources in a starting ethanol solution involving non-ionic surfactant P123. X-Ray diffraction, N_2 sorption, and transmission electron microscopy analyses revealed that a hexagonally ordered mesoporous NbTa oxide could be synthesized by appropriate control of the preparation conditions.

1 Introduction

Silica-based mesoporous materials such as MCM-41,[1] FSM-16,[2] and SBA-15,[3] *etc.*, have been well investigated, and their preparation methods and applications have already been covered by several excellent reviews.[4–7] On the other hand, less work has been directed towards non-silica-based mesoporous materials although they have great potential in a wide range of applications.[8] The synthesis of the most of non-silica-based mesoporous materials often suffers from difficulty in controlling the rates of hydrolysis, condensation and subsequent mesostructure assembly in the presence of excess water.[9] Furthermore, phase transitions accompanied by thermal destruction of the structural integrity occur upon the thermal removal of the templates for the creation of porous materials.[10] Also, considering applications as inorganic materials, the poor mechanical and thermal stabilities due to the amorphous walls of many synthesized mesoporous non-silica-based mesoporous oxide materials remain a problem. Once these problems are overcome, the amount of research and the attention to the non-silica oxides would increase, especially with respect to applications. In practice, few highly ordered non-silica-based mesoporous oxides have been reported.[10] The reports on the synthesis of ordered non-silica-based mesoporous oxides synthesized by the use of metal chlorides and non-ionic surfactants through so-called N^0I^0 interaction are limited to those of Yang *et al.*[9,10] The mesostructure of the ordered mesoporous titanium, zirconium, niobium and tantalum oxides were stable after the removal of the templates by calcination at 673 K in air. The synthesis of mesoporous non-silica based mesoporous oxides with crystallized frameworks is regarded as an important technique, which enables wide application. We recently succeeded in the synthesis of crystallized mesoporous $(Nb,Ta)_2O_5$.[11] The crystallized $(Nb,Ta)_2O_5$ (NbTa-TIT-1) exhibited excellent mechanical strength and hydrothermal stability. Moreover, the mesoporosity was confirmed not to originate from the agglomeration or aggregation of smaller crystallites, but each single-crystal particle possesses mesopores.[11] In the case of pure mesoporous Nb or Ta oxides, polycrystalline wall structures were formed, where mesopores originated from interparticle voids.[11] However, the original mesoporous structure before crystallization was disordered, and the crystallized particles also consisted of wormhole-like mesopores. This synthesis was carried out with ethanol as solvent in the absence of water, although the presence of water is essential for hydrolysis and subsequent condensation in the sol–gel process. It is considered that the amount of water might greatly affect the rate of gelation and micelle formation of the template. Also, the amount of metal source would be a significantly important factor, considering its relations to wall thickness and Cl^- amount, pH, and so on. Therefore, it is essential to study the influence of the amounts of water and metal sources for obtaining highly ordered mesoporous materials. In this communication, we report that a mesoporous niobium and tantalum mixed oxide (denoted mesoporous NbTa oxide) with a 2D-hexagonal ordered structure can be synthesized in narrow range of water and metal sources contents.

2 Experimental

2.1 Preparation of mesoporous niobium and tantalum mixed oxide

Mesoporous NbTa oxide was prepared following the similar method to that reported by Yang *et al.* as follows.[10] 1 g of the triblock copolymer $(HO(CH_2CH_2O)_{20}(CH_2CH(OH)CH_2O)_{70}(CH_2CH_2O)_{20}H$, P123, BASF) was dissolved in 10 g of ethanol by stirring for 10 min. To this solution, 0.003–0.010 mol of a mixture of $NbCl_5$ and $TaCl_5$ (Nb : Ta = 1 : 1, Kojundo Chemical Lab Co., Ltd) was added with vigorous stirring for 20 min. Water (trace–0.333 mol) was added to the solution with further stirring for 10 min. A trace amount of water from air was involved. The resulting sol was gelled in a Petri dish at 313 K in air for 3 d. The aged gel samples were then calcined at 723 K for 5 h in air for the removal of the surfactant.

2.2 Characterization

X-Ray diffraction (XRD) patterns were obtained using a Rigaku RINT 2100 diffractometer with CuKα radiation. N_2 sorption isotherms were recorded using a Coulter SA3100 system. The sorption data were analyzed by the Barrett–Joyner–Halenda (BJH) method.[10] Transmission electron microcopy (TEM) images and electron diffraction patterns were obtained on a JEOL JEM2010F (200 kV).

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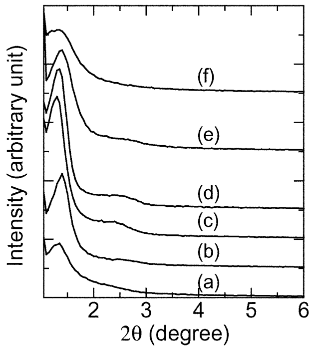

Fig. 1 Low-angle X-ray diffraction patterns of mesoporous NbTa oxide samples prepared by calcination at 723 K for 5 h with added water: (a) trace, (b) 0.018 mol, (c) 0.063 mol, (d) 0.096 mol, (e) 0.165 mol and (f) 0.333 mol.

3 Results and discussion

3.1 Effect of adding water

The amount of added water was varied from a trace to 0.333 mol for a constant metal source content of 0.007 mol. The structure of the walls of mesoporous NbTa oxide samples was confirmed to be amorphous by the absence of any peaks in the $2\theta = 10$–60 degree range in the XRD patterns. Fig. 1 shows the low-angle XRD patterns of the prepared $(Nb,Ta)_2O_5$ samples after calcinations at 723 K for 5 h. The first diffraction peak, tentatively indexed as the (100) reflection,[11] appeared at $d(100) = 63$–68 Å. The intensity of the first peak and second broad shoulder changed with the amount of water added, and relatively high intensity was obtained by the addition of 0.018–0.096 mol of water. The change in the low-angle XRD peaks indicates that the mesoporous structure is influenced by the amount of water added in the synthesis of mesoporous NbTa oxide.

Fig. 2 shows N_2 adsorption isotherms of several NbTa oxide samples. The NbTa oxide samples exhibited type-IV isotherms according to the IUPAC classification,[12] which is typical for mesoporous materials. A relatively large increase in the N_2 uptake into the mesopores at $P/P_0 = 0.4$–0.6 was observed for samples prepared by the addition of relatively small amounts of water in this synthesis. Additional evidence for the mesoporous structure of NbTa oxide samples is provided by the TEM images. All TEM images observed for NbTa oxide samples synthesized with various amounts of water (corresponding to Figs. 1 and 2) revealed a wormhole mesoporous structure (not shown). This result may be consistent with the unclear second broad shoulder seen in the XRD measurements.

Table 1 is a comparison of BET surface area, pore volume, pore size and wall thickness, obtained by XRD and N_2 sorption measurements. BET surface area increased with the addition of water, but did not greatly differ in the range from 159 to 173 $m^2\ g^{-1}$. However, pore size of NbTa oxide samples varied significantly even though they were synthesized using the same surfactant; increasing from 40 to 49 Å with the addition of water from trace to 0.063 mol, and decreasing from 49 to 38 Å with further addition. The pore volume also increased and then decreased with increasing water content.

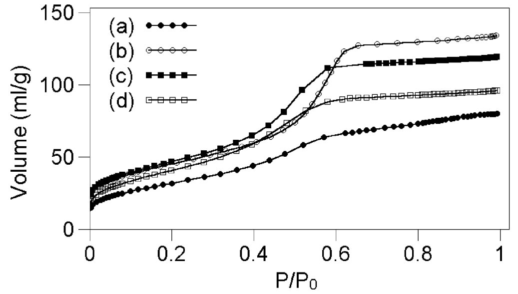

Fig. 2 N_2 adsorption isotherms of mesoporous NbTa oxide samples prepared with various amounts of water: (a) trace, (b) 0.063 mol, (c) 0.165 mol and (d) 0.333 mol. Metal sources were fixed at 0.007 mol.

Table 1 BET surface area, pore size, pore volume, *d*(100) and wall thickness[a] value of NbTa oxide samples prepared by the addition of various amount of water and 0.007 mol of metal sources

Water/ mol	BET surface area/$m^2\ g^{-1}$	Mesopore volume/ ml g^{-1}	Mesopore size/Å	*d*(100) value/ Å	Wall thickness/ Å
Trace	118	0.14	40	65	25
0.018	159	0.24	42	65	23
0.063	161	0.29	49	68	19
0.096	162	0.26	43	65	22
0.165	173	0.24	41	63	22
0.333	162	0.18	38	66	28

[a] Wall thickness was calculated from simple subtraction of pore size from *d*(100) value.[13]

In the case of the non-ordered mesoporous structure, the wall thickness is estimated by simple subtraction of pore size from the *d*(100) value.[13] The walls of mesoporous NbTa oxide samples prepared by the addition of a relatively small amount of water are thin in comparison with those prepared by adding relatively large or trace amounts of water. As shown in these results, the amount of water in this synthesis influenced the resultant mesoporous structure, and increasing water content results in differences in the XRD and N_2 sorption measurements. Water is expected to affect hydrolysis and condensation, and it is considered that the mesoporosity and stability of the mesoporous structure of this mesoporous NbTa oxide can be improved with the addition of an appropriate amount of water.

3.2 Effect of amount of metal sources

Next, we examined NbTa oxide samples synthesized with various amounts of metal sources in the range of 0.003–0.010 mol and constant water addition of 0.063 mol in 10 ml of ethanol. The XRD patterns of mesoporous NbTa oxide samples are shown in Fig. 3. The secondary broad shoulder in XRD was readily discernible for samples prepared with lower amounts of metal sources (0.010 to 0.005 mol). This secondary broad shoulder implies the formation of an ordered mesoporous structure. In the case of 0.003 and 0.004 mol of metal sources, the mesoporous periodicity is considered to be poor because only a broad peak was confirmed in the low angle region. The adsorption isotherms for the samples synthesized with various amounts of metal sources are shown in Fig. 4. The N_2 uptake in the range of $P/P_0 = 0.5$–0.7 gradually increased with decreasing amount of metal sources from 0.010 to 0.005 mol.

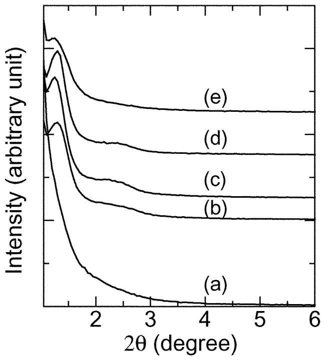

Fig. 3 Low-angle X-ray diffraction patterns of NbTa oxide samples prepared with 0.063 mol of water and various amounts of metal sources: (a) 0.003 mol, (b) 0.005 mol, (c) 0.006 mol, (d) 0.007 mol, (e) 0.010 mol.

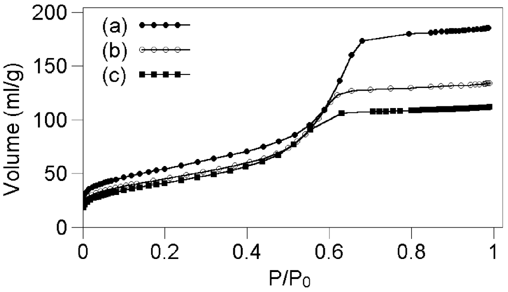

Fig. 4 N_2 adsorption isotherms of the NbTa oxide samples prepared with 0.063 mol of water and various amounts of metal sources: (a) 0.005 mol, (b) 0.007 mol, (c) 0.010 mol.

Table 2 is a summary of the BET surface area, pore size, pore volume and wall thickness obtained by XRD and N_2 sorption measurements for mesoporous NbTa oxide samples prepared with various amounts of metal sources. BET surface area decreased gradually from 194 to 150 $m^2\ g^{-1}$ with increasing metal source content, and pore size and pore volume increased from 44 to 58 Å and from 0.21 to 0.38 ml g^{-1}, respectively. The wall thickness increased from 16 to 27 Å with increasing metal source content. Similar to the results in section 3-1, better mesoporosity was obtained with relatively thin walls. In the case of 0.005 mol of metal sources, a TEM image with hexagonally ordered mesoporous structure was observed (not shown).

These results conclusively indicate that the mesoporosity of NbTa oxide is considerably affected by the amount of metal sources, as well as the amount of water added. It is considered that the wall thickness, governed by the distance between micelle rods in the gel sample, is one of the most important factors affecting the formation of highly ordered mesoporous structures. The stronger interaction between micelle rods over short distances, leading to thin walls, would be preferable for the formation of ordered mesoporous structures.

3.3 Optimization of preparation conditions for highly ordered mesoporous structures

From sections 3-1 and 3-2, the amounts of added water and metal sources have been found to influence the properties of synthesized mesoporous NbTa oxide. In particular, it tends to be that better ordered mesoporous structures are obtained with thin wall thicknesses. We therefore optimized the amount of water so as to produce a well ordered mesoporous structure for a metal content of 0.005–0.006 mol. As shown in Fig. 5, the TEM images of the NbTa oxide sample synthesized under the optimized conditions (addition of 0.018 mol of water to a mixture containing 0.0055 mol of metal sources) reveal 2D-hexagonally ordered mesoporous structures, viewed (a) perpendicular to the channel axis and (b) along the channel axis.[14] The 2D-hexagonally ordered mesoporous structure was further confirmed from hexagonally ordered spots in the electron diffraction patterns (inset of a and b). The mesoporous NbTa oxide sample observed by TEM (Fig. 5) was analyzed by XRD and N_2 adsorption isotherm. Both are shown in Fig. 6. The

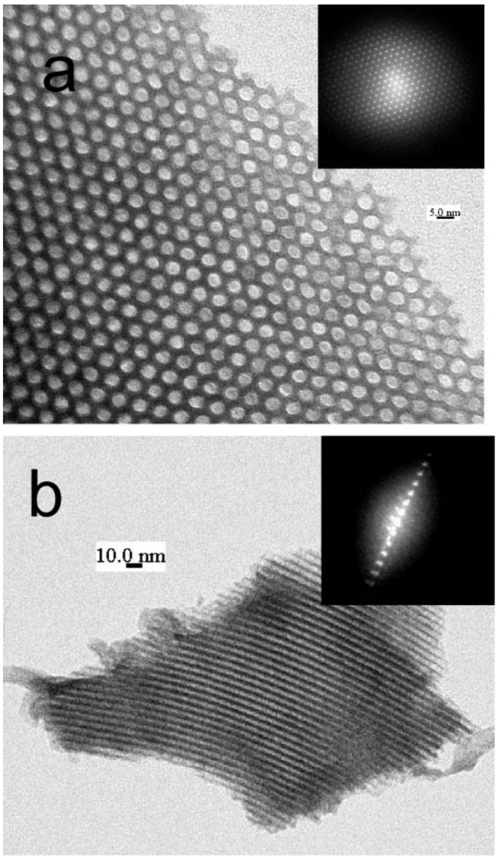

Fig. 5 Representative TEM images and electron diffraction patterns (inset) of prepared under optimized conditions: 0.018 mol water and 0.0055 mol of metal sources: (a) perpendicular to channel axis and (b) parallel to channel axis.

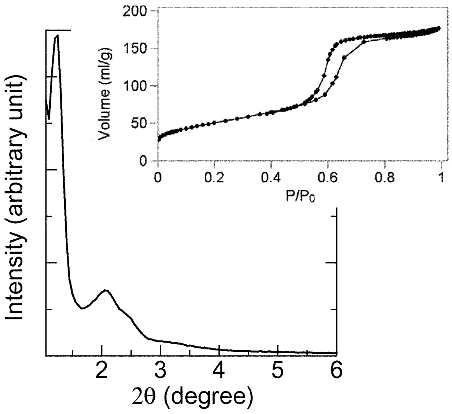

Fig. 6 Low-angle XRD and N_2 sorption isotherm (inset) for NbTa oxide sample prepared under the conditions of 0.018 mol of water and 0.0055 mol of metal sources.

Table 2 BET surface area, pore size, pore volume, *d*(100) and wall thickness[a] value of NbTa oxide samples prepared by the addition of 0.063 mol water and various amount of metal sources

Metal source/mol	BET surface area/$m^2\ g^{-1}$	Mesopore volume/ml g^{-1}	Mesopore size/Å	*d*(100) value/Å	Wall thickness/Å
0.005	194	0.38	58	74	16
0.006	178	0.29	52	68	16
0.007	161	0.29	49	68	19
0.008	158	0.25	44	65	21
0.009	149	0.23	43	65	22
0.010	150	0.21	44	71	27

[a] Wall thickness was calculated from simple subtraction of pore size from *d*(100) value.[13]

Table 3 Representative BET surface area, pore size, pore volume, wall thickness[a] and (d(100), d(110)) value of hexagonally ordered mesoporous NbTa oxide sample prepared under the optimized condition of addition of water (0.018 mol) and 0.0055 mol of metal sources

BET surface area/$m^2\ g^{-1}$	Mesopore volume/ml g^{-1}	Mesopore size/Å	d(100) value/Å	d(110) value/Å	Wall thickness/Å
184	0.34	56	74	44	29

[a] Wall thickness was calculated from $(2d(100)/1.732) - $ (mesopore size).

low-angle XRD pattern is consistent with a hexagonally ordered mesoporous structure, and the N_2 adsorption isotherm (inset) supports the proposal that the mesoporous NbTa oxide sample consists of uniform mesopores. The broad XRD peaks at 1–2 degrees may be attributed to diffuse scattering derived from slightly different wall shapes, particle sizes, pore size distributions, the existence of various ordered structural domains in a particle, and so on. However, the relationship between (100) and (110) reflections corresponded to a 2D-hexagonal structure. The physical properties of the hexagonally ordered mesoporous NbTa oxide sample are summarized in Table 3. It is noted that the wall thickness estimated by assuming a hexagonal structure (Table 3) agrees closely with the value directly observed in the TEM image.

Considering the observed effect of the amount of water in this synthesis, the rate of gelation, or rate of hydrolysis and condensation, is important for obtaining highly ordered mesoporous structures.[10] The mesoporosity of the present structure can be improved by using lower amounts of metal sources, except for the cases of 0.003 and 0.004 mol. This indicates that higher concentrations in a sol solution interrupt the interaction of co-existing micelle templates for the formation of a hexagonally ordered mesoporous structure.

Fig. 7 shows the relationship between mesoporous structure formed and preparation conditions (water and metal source contents) for synthesized mesoporous NbTa oxides in this study. Filled circles (●) represent 2D-hexagonally ordered mesoporous structures. Open triangles (Δ) correspond to mesoporous structures with low ordered periodicity. Crosses (×) symbolize disordered mesoporous structures, judged from weak or absent peaks in low angle XRD patterns and TEM images. In conclusion, it found that 2D-hexagonally ordered mesoporous NbTa oxide can be synthesized under the conditions of an extremely narrow range of the amounts of water and metal sources, as shown in Fig. 7.

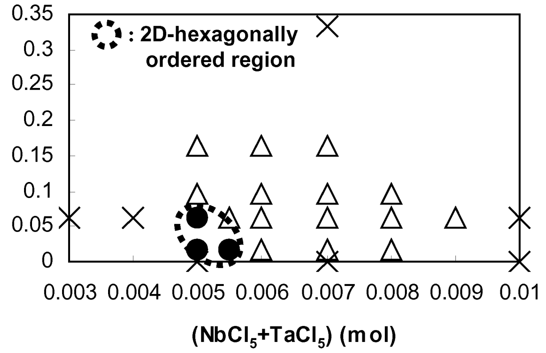

Fig. 7 Relationship between mesoporous structure formed and preparation conditions (water and metal source contents) for NbTa oxide samples evaluated by XRD and TEM ((●) 2D-hexagonally ordered mesoporous structure, (△) low ordered mesoporous structure, (×) disordered mesoporous structure).

4 Conclusions

The properties of mesoporous NbTa oxide, such as pore size, pore volume and wall thickness, were found to be strongly affected by the amounts of water and metal sources in a sol solution involving a non-ionic structure-directing agent (P123). The stoichiometric relationship between the amount of water added and metal sources in the present synthesis is complicated by many factors, such as concentration of surfactant, Cl^- amount, pH, rate of gelation, and so on. The amount of water and metal sources can be used to control the hydrolysis, condensation and interaction between co-existing micelle templates. As a result, NbTa oxide with a 2D-hexagonally ordered mesoporous structure was successfully synthesized by appropriate control of water added and metal source contents. The next step in this study is to attempt the crystallization of mesoporous NbTa oxide, examining the preservation of the original ordered mesoporous structure.

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References

1 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.

2 S. Inagaki, Y. Fukushima and K. Kuroda, *J. Chem. Soc, Chem. Commun.*, 1993, 680.

3 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.

4 U. Ciesla and F. Schüth, *Microporous Mesoporous Mater.*, 1999, **27**, 131.

5 Y. J. Ying, C. P. Mehnert and S. M. Wong, *Angew. Chem., Int. Ed.*, 1999, **38**, 56.

6 A. Corma, *Chem. Rev.*, 1997, **97**, 2373.

7 M. Linden, S. Schacht, F. Schüth, A. Steel and K. K. Unger, *J. Porous Mater.*, 1998, **5**, 177.

8 F. Schüth, *Chem. Mater*, 2001, **13**, 3184.

9 P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Nature*, 1998, **396**, 152.

10 P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Chem. Mater.*, 1999, **11**, 2813.

11 B. Lee, D. Lu, J. N. Kondo and K. Domen, *Chem. Commun.*, 2001, 2118.

12 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academic Press, New York, 1982.

13 S. Kim, R. Pauly and T. J. Pinnavaia, *Chem. Commun.*, 2000, 835.

14 M. Yada, M. Machida and T. Kijima, *Chem. Commun.*, 1996, 769.