DOI: 10.1002/ejic.200600529

Niobium Oxide Mesophases Obtained by Self-Assembly of an Aqueous Soluble Niobium Complex Precursor and Organic Templates

Marcos A. Bizeto[a] and Vera R. L. Constantino*[a]

Keywords: Niobium / Mesophases / Organic–inorganic hybrid composites / Template synthesis / Sol–gel synthesis

In this paper the use of triammonium trioxalato(oxido)-niobate {$(NH_4)_3[NbO(C_2O_4)_3]$} as an inorganic precursor to assemble organized hybrid niobium oxide mesophases using *n*-octylamine (OCT) and cetyltrimethylammonium (CTA) bromide as structure-directing agents is described for the first time. The niobium complex is water-soluble and its hydrolysis at controlled pH and in the presence of organic templates leads to the formation of hybrid mesophases. A lamellar mesophase is produced by a neutral route based on the interaction of hydrolyzed units with the octylamine micelles. On the other hand, a hexagonal (*p*6*m*) mesophase is obtained when hydrolyzed species interact with CTA micelles through a charge-matching route (ionic route). This is the first time that such an ionic route has been described for the production of organized niobium oxide hybrids.

Introduction

Organic–inorganic hybrid materials obtained by soft chemistry routes are the basis for the production of hierarchical inorganic structures that are of great interest in scientific and industrial areas. The molding of an inorganic structure around templates constituted of micellar aggregates produces organized mesophases that are precursors of periodic porous materials. Upon template removal, the mesophase can be transformed into an inorganic structure full of voids with regular shapes and sizes that are useful for applications in some industrial and technological fields, such as catalysis, separations, sensing, and others.[1] The approach to tailor-made porous structures started with Mobil corporation researchers, who created a family of mesoporous silicas called M41S.[2] These materials are obtained by controlling the hydrolysis of an inorganic precursor, generally silicon alkoxides such as tetraethylorthosilicate, around surfactant micelles. Since the discovery of mesoporous silicas, much effort has been devoted to the development of new mesoporous systems based on non-silicate materials. A great deal of work has concentrated on the synthesis of transition metal mesoporous oxides due to the possibility of these metal centers participating in chemical reactions. However, these materials are difficult to synthesize due to their tendency to crystallize and undergo chemical reactions that lead to mesostructure collapse.[3] The critical step of the process is the mesostructure formation as it is necessary to provide experimental conditions where the interaction between the inorganic species and organic template is established at the interface and is strong enough to promote the self-assembly of the moieties. There are different ways for these interactions to occur. The simplest one happens when the inorganic and organic moieties have opposite charges under the synthesis condition,[4] known as the "ionic route". The interaction can also take place by H-bonding or dipolar forces − the "neutral route".[5] A third possibility is exclusive for some transition metals where interaction can occur by coordination of a structure-directing agent to the metal center, leading to the so-called "ligand-assisted crystal templating".[6] One of the first successful examples of a stable mesoporous structure based on a transition metal oxide was mesoporous niobium oxide.[6] Ordered porous niobium oxide phases have been obtained by synthetic procedures where inorganic precursors, such as niobium alkoxides or chlorides, are used together with neutral structure-directing agents based on alkylamines or nonionic surfactant micelles.[6,7] Mesoporous niobium oxides present interesting properties that can be used in many technological applications. The confinement of species into their pores, such as fullerides,[8] metallocenes,[9] or biomolecules,[10] produces materials with interesting electronic, magnetic, catalytic, and sensing properties. Taking these properties into account, the development of simple synthetic routes employing cheap and easy to handle reactants is an important issue to be resolved. The inorganic precursors normally used for this purpose are expensive, not easy to synthesize, and require controlled humidity conditions to be manipulated.

The niobium compound $(NH_4)_3[NbO(C_2O_4)_3]\cdot 3H_2O$ (Figure 1) has some interesting chemical properties that are useful not only for the assembly of mesoporous solid pre-

---

[a] Instituto de Química, Universidade de São Paulo,
C. P. 26077, CEP 05513-970, São Paulo – SP, Brazil
Fax: +55-11-3815-5579
E-mail: vrlconst@iq.usp.br

cursors (mesophases) but also in sol–gel-like soft-chemical routes. First of all triammonium trioxalato(oxido)niobate is water-soluble and stable in acid solution. Secondly, the niobium oxalate moiety has a negative charge and labile water molecules in the niobium coordination sphere when the aqueous equilibrium with the two oxalato ligands is considered.[11] These properties make this compound suitable for self-assembly with organic species by coordination and electrostatic interactions. The third and most important point is that triammonium trioxalato(oxido)niobate can be synthesized directly from niobium oxide by simple chemical procedures,[12,13] which means that the starting material can be easily recycled. Considering the possible interaction modes of trioxalato(oxido)niobate with organic moieties, in this paper we describe the use of a cationic surfactant and a long carbon chain amine as structure-directing agents for the generation of niobium oxide mesophases that might be further converted into mesoporous phases by template removal. A previous attempt at using a water-soluble niobium precursor derived from niobium pentoxide was not successful in a similar process.[6b]

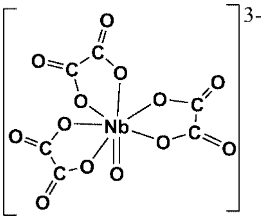

Figure 1. Chemical structure of $[NbO(C_2O_4)_3]^{3-}$.

Results and Discussion

Triammonium trioxalato(oxido)niobate is soluble in water and is in equilibrium[11] with dioxalate species in solution, according to the chemical equation below.

$$[NbO(C_2O_4)_3]^{3-} + 2\,H_2O \rightleftharpoons [NbO(C_2O_4)_2(H_2O)_2]^{-} + C_2O_4^{2-}$$

Both species in equilibrium have a heptacoordinate niobium atom.[14] The initial pH of an aqueous solution of the compound is very acid due to partial hydrolysis of the compound. Upon increasing the pH to near 4 with a hydroxide solution, the niobium oxalate hydrolysis reaction is favored and leads to the formation of a hydrated amorphous niobium oxide bulk phase.[11] Figure 2 shows the typical sodium hydroxide titration curve of an aqueous triammonium trioxalato(oxido)niobate solution. According to this curve, trioxalato(oxido)niobate hydrolysis occurs in the pH range 4.2–5.8. Thus, it is possible to modulate the interaction of the oxide phase with structure-directing agents by controlling the hydrolysis process by adjusting the amount of base added.

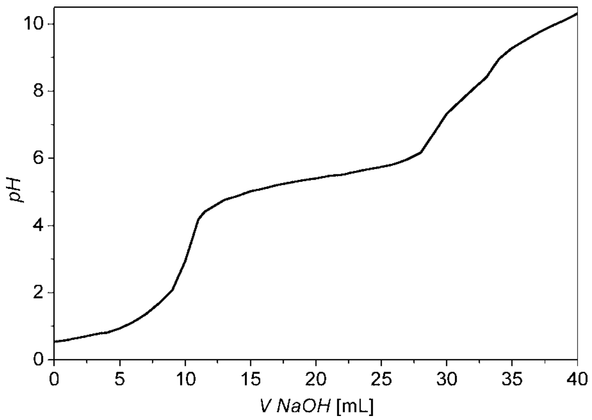

Figure 2. Titration curve of an aqueous solution of triammonium trioxalato(oxido)niobate (0.2 M) with a 3 M NaOH solution.

The crystal structure of triammonium trioxalato(oxido)-niobate belongs to the triclinic crystal system with the niobium atom heptacoordinate in a pentagonal-bipyramidal arrangement.[13] The high crystallinity of the solid can be seen in the powder XRD pattern shown in Figure 3. The solid isolated at a pH of around 5.5 is amorphous (Figure 3), while the solid isolated at higher pH (excess of base) is crystalline with a diffraction pattern very different from the pristine material (Figure 3). It is possible to produce an organized mesophase characterized by an amorphous inorganic framework with a regular repetition of voids filled with template micelles by performing the hydrolysis in the presence of a structure-directing agent. This synthetic approach was tested using cetyltrimethylammonium (CTA) bromide and *n*-octylamine (OCT) as structure-directing agents.

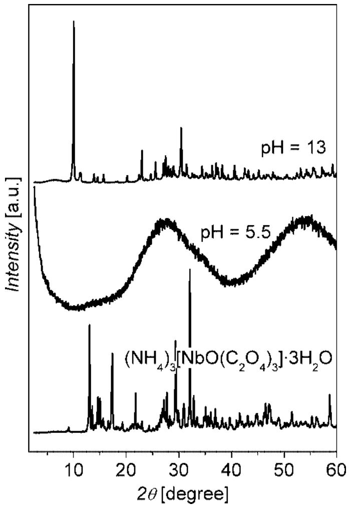

Figure 3. XRD patterns of triammonium trioxalato(oxido)niobate and its hydrolysis products isolated at different pH values.

CTA is a common template used in the synthesis of mesoporous silica, such as MCM-41, by a charge-matching ionic route. However, for niobium oxide hybrid mesostructures, only neutral routes with non-ionic surfactants have been performed until now. As can be seen in Figure 4, hydrolysis of the trioxalato(oxido)niobate in the presence of the CTA template produces a hexagonally packed mesostructure. The XRD pattern of this phase shows reflection peaks at low angles related to the long-range order of the assembled hybrid material (Figure 4). Two types of hexagonal phases are known for silica-based systems: 2D hexagonal *p6m* (MCM-41) and 3D $P6_3/mmc$ (SBA).[15] The diffraction peak distances in Figure 4 are in a ratio close to 1:3, which can be attributed to a *p6m* hexagonal phase. The diffraction pattern also indicates that the assembled hybrid structure is not highly ordered. Hexagonal phases with regular parallel channels filled with the template provide intense diffraction patterns with many peak orders.[16] In the case of the synthesized CTA/niobium oxide phase, however, only two diffraction peaks are observed in the low-angle region, which suggests a non-fully parallel channel architecture. According to the diffraction data, the most organized mesophases are generated when an Nb/CTA molar ratio of 1:1 is used. The d_{100} distance related to the first-order peak of the hexagonal mesophases has a mean value of 42.5 Å, while the mean d_{110} value is 23.3 Å.

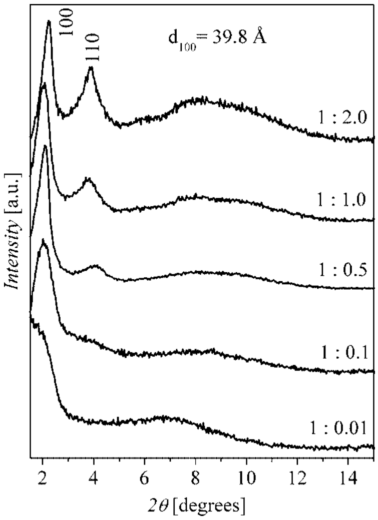

Figure 4. XRD patterns of the as-synthesized niobium oxide mesophase with CTA template at different Nb/CTA molar ratios.

The partial disorder of the porous architecture was confirmed by TEM (Figure 5). In the micrograph shown in Figure 5a, it is possible to observe that pores (elongation aligned parallel to the observer's view) are irregularly distributed along the material, like a wormhole pattern. In Figure 5b, the pores' elongation is parallel to the grid plane and some domains with well-ordered porous organization can be observed.

In the neutral-route synthesis the CTA template was replaced by *n*-octylamine (OCT), which resulted in a mesophase with a lamellar arrangement for Nb/OCT molar ratios above 1:0.5 (Figure 6). As can be seen from the XRD patterns in Figure 6, the distances of the diffraction peaks have a ratio of 1:2:3, which corresponds to a lamellar mesophase ($d_{001} \approx 24.5$, $d_{002} \approx 12.1$, and $d_{003} \approx 8.2$ Å). The TEM micrographs (Figure 7) also reveal a well-organized lamellar mesophase.

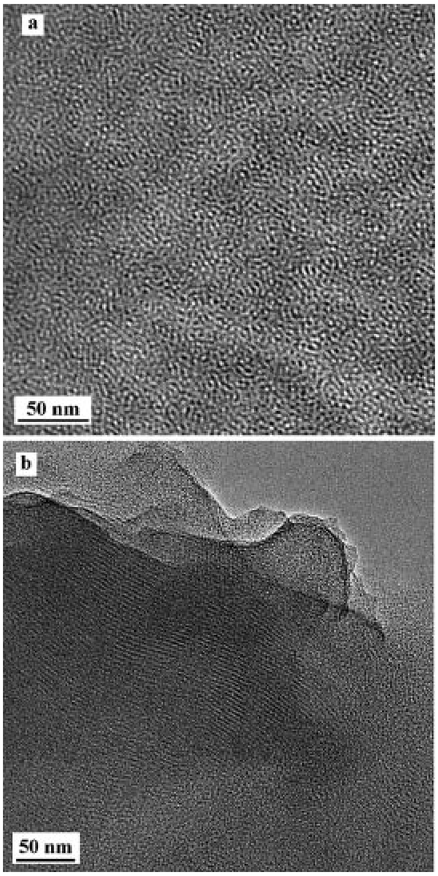

Figure 5. TEM images of the as-synthesized niobium oxide mesostructure (Nb/CTA molar ratio of 1:1): (a) porous elongation parallel to the view; (b) porous elongation perpendicular to the view.

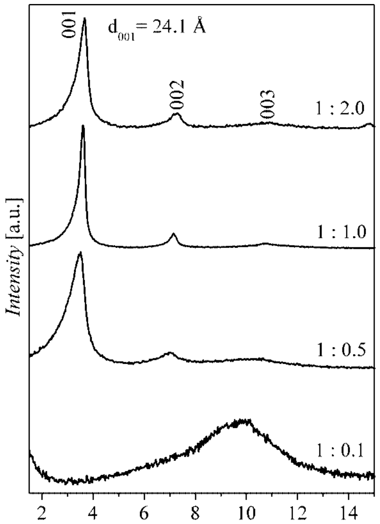

Figure 6. XRD patterns of the as-synthesized niobium oxide mesophase with *n*-octylamine as template at different Nb/OCT molar ratios.

To generate a mesoporous niobium oxide it is necessary to remove the template from the material to produce empty voids with regular shape and size along the mesostructure.

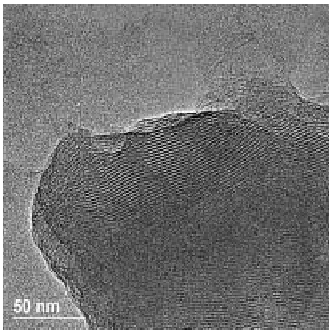

Figure 7. TEM image of the as-synthesized niobium oxide mesostructure (Nb/OCT molar ratio of 1:1).

This procedure is not possible in lamellar mesophases since the mesoporous phase is not stable after template removal due to the absence of species that keep the inorganic slabs apart. The collapse of lamellar mesostructures has already been observed in niobium oxide[6b] and silica MCM-50[17] phases.

The first attempt at CTA removal was made by solvent extraction, but due to the strong interaction between inorganic and organic moieties in the charge-matching mechanism of mesophase formation this solvent-template extraction was not an efficient process. Therefore, calcination of the hexagonal mesophase was performed based on thermogravimetric data obtained in air. According to thermogravimetric analysis (not shown), the complete removal of CTA occurs above 600 °C. The thermal stability of the generated mesoporous phase is closely related to the Tammann temperature of the respective oxide structure, which for Nb_2O_5 is 892 K (ca. 620 °C).[18] In the vicinity of the Tammann temperature the mobility of the atoms in the oxide structure increases significantly, thereby favoring the mesostructure collapse. Thus, the temperature requirement for complete template elimination is close to the Tammann temperature of niobium oxide, which makes calcination an unsuitable process for template removal in this case. In fact, when the mesophase calcination was performed at 600 °C we observed mesostructure collapse and production of an orthorhombic crystalline niobium oxide phase. The amorphous niobium oxide phase turns into a crystalline T-phase[12b] at around 500–600 °C, and this process could be the reason for the mesostructure collapse since the bridging Nb–O–Nb bond angles might change with crystallization. Other methods described in the literature[6b] for template removal by calcination also promoted the mesostructure collapse. In the charge-matching mechanism of mesophase formation, removal of the template leaves behind an unbalanced charge in the inorganic framework that contributes to the structure instability.[5] Considering this feature, the CTA removal was performed by combining a process of solvent extraction and ion exchange by using a mixture of ethanol and HCl, but also without success. Template extraction from the hexagonal mesophase was only possible when the ethanol/HCl solution was replaced by an ethanol solution of a large organic cationic species such as tetrabutylammonium (TBA) hydroxide. The organic cation provides the structural charge neutralization but, due to its large size, the porous voids are still occluded, thereby producing a material with low porosity, as confirmed by the desorption/adsorption isotherm experiments (not shown). Further calcination of the TBA-exchanged phase also promoted the mesostructure collapse.

In light of these results, an investigation of the causes of the low thermal stability of the hexagonal mesostructure was performed using vibrational Raman spectroscopy to determine the condensation degree of the inorganic framework. Intense bands between 900 and 1000 cm^{-1} are attributed to terminal Nb=O stretching modes, with the respective bending modes in the region 200–400 cm^{-1}.[11,19] The range between 500 and 700 cm^{-1} is dominated by Nb–O–Nb stretching modes of corner- or edge-shared octahedral NbO_6 units.[11,19] The presence of bands in this region indicates the condensation degree of the octahedral units that constitute the mesophase inorganic framework. Figure 8 shows the Raman spectra recorded for the mesophases. For comparison purposes, we have included the spectrum of HNb_2O_5, which is a thermodynamically stable niobium oxide crystalline phase.[12] Figure 8a presents the spectral region dominated by Nb–O vibrations. Thus, comparing the Raman spectra of the mesophases with that of HNb_2O_5 (Figure 8a) it is possible to determine a low condensation degree of the inorganic framework in mesophases due to the absence of strong bands in the region 500–700 cm^{-1}.

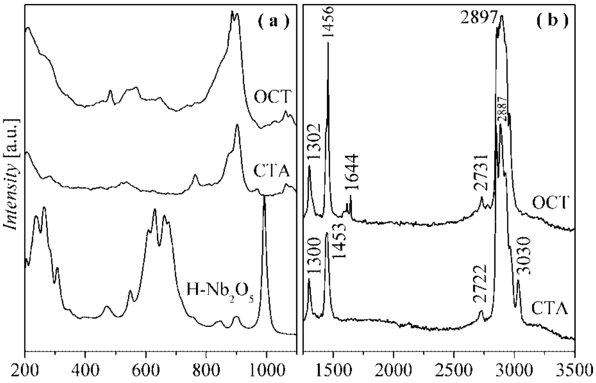

Figure 8. Raman spectra of niobium oxide mesophases (Nb/template molar ratio of 1:1) compared to HNb_2O_5: (a) region dominated by Nb–O vibrations; (b) vibrational region of organic templates.

The spectral region dominated by vibrational bands related to the organic moieties (1200–3500 cm^{-1}) is shown in Figure 8b, where it is possible to observe intense vibrational bands around 2900 cm^{-1} attributed to the ν(C–H) vibrational modes of the template's carbon chains. Figure 8b also shows vibrational bands in the region 1200–1500 cm^{-1} attributed to the oxalate ν_a(C=O), ν_s(C–O) and δ(O–C=O) modes,[20] thus indicating that the hydrolysis process of the inorganic precursor is not complete. This could be one of the factors that affect the mesostructure stability. So, modifications of experimental procedures are necessary to achieve a better condensation of skeletal inorganic units and also to ensure complete trioxalato(oxido)niobate hydrolysis.

Some information about the local structure of poorly crystalline solids can be obtained by X-ray absorption techniques. Figure 9 shows the X-ray absorption near-niobium *K*-edge (XANES) spectra of the *n*-octylamine niobium oxide mesophase, the starting triammonium trioxalato(oxido)niobate, and the crystalline HNb_2O_5 phase. The absorption edge outline is mainly related to the element oxidation state but some local structural information can be obtained by simple comparison with XANES spectra of compounds whose structures are already known. The intensity of the pre-edge peak at the low-energy side of the spectra is related to the coordination site distortions around Nb.[21] This pre-edge peak is low in intensity for an octahedral geometry.[22] Some authors assume that it is related to the presence of Nb=O bonds and its absence is related to the presence of tetrahedral NbO_4 units.[23] Extended niobium oxides are mainly constituted of joined distorted NbO_5 and NbO_6 octahedral units. As determined by Raman spectroscopy, the synthesized niobium mesophases have bands in the region attributed to Nb=O bonds. The beyond-edge peaks shown in Figure 9 indicate that niobium in the Nb_2O_5 mesophase has neighboring atoms in an arrangement similar to niobium in HNb_2O_5, which is expected by the hydrolysis of trioxalato(oxido)niobate and condensation of the generated hexacoordinate niobium octahedral centers. As previously mentioned, the starting triammonium trioxalato(oxido)niobate has heptacoordinate niobium centers in a pentagonal-bipyramidal arrangement.[13]

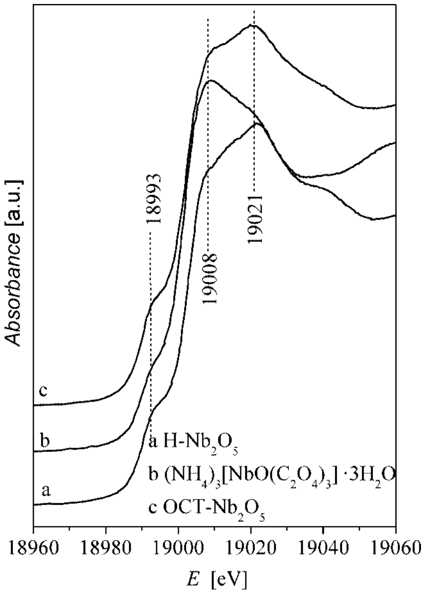

Figure 9. Niobium *K*-edge XANES spectra of (a) HNb_2O_5, (b) triammonium trioxalato(oxido)niobate, and (c) the OCT/Nb_2O_5 mesophase (Nb/OCT molar ratio of 1:1).

Other ways to achieve a better consolidation of the inorganic framework are under investigation. One of the synthetic changes tried comprises the use of a nonionic surfactant based on copolymers such as Brij56 (Aldrich). According to the literature,[5] nonionic routes produce mesostructures with thicker walls with a better thermal stability and easy template removal. When using Brij56 as structure-directing agent and triammonium trioxalato(oxido)niobate as inorganic precursor (Nb/Brij56 molar ratio of 1:0.5), the interaction at the interface of the inorganic and organic domains is very weak and no organized mesophase is produced, as shown in Figure 10 and also confirmed by X-ray diffractometry (not shown). The as-synthesized mesophase is even less stable than the mesophases described above since it crystallizes under the electron beam while registering the micrograph (TEM micrograph with higher magnification not shown). Maybe an organized mesophase with Brij56 as template can be obtained under experimental conditions (solvent/template/Nb molar ratios, pH, and temperature) distinct to those reported here.

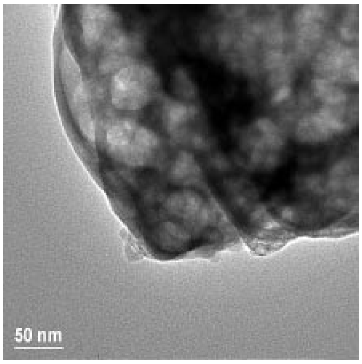

Figure 10. TEM image of the as-synthesized niobium oxide mesostructure using Brij56 as template (Nb/Brij56 molar ratio of 1:0.5).

Other synthetic modifications are still under investigation, such as the use of hydrothermal conditions, slow addition of the hydroxide to pH = 5.5, with constant monitoring of the pH, the use of other sources of base, such NH_4OH and tetraethylammonium hydroxide, and templates, pre-hydrolysis of the trioxalato(oxido)niobate before mixing with the template, and thermal treatment of the mesophase under an inert gas before template removal. All the products generated by these synthetic modifications are now being characterized.

Conclusions

In conclusion, this paper shows that it is possible to use triammonium trioxalato(oxido)niobate as an inorganic precursor to synthesize niobium oxide mesostructures by means of a neutral or an ionic route. The advantage of using this niobium compound instead of metal alkoxides or chloride precursors is related to its low cost, stability in water, easy manipulation, and possibility of recycling. Triammonium trioxalato(oxido)niobate can interact with neutral and cationic templates to produce organized mesophases under controlled pH conditions. To obtain mesoporous niobium oxides from the synthesized mesophases, further studies are necessary to define experimental conditions that promote a better condensation and consolidation of the skeletal inorganic units, since attempts at template removal by calcination or solvent extraction lead to the collapse of the mesostructure.

Experimental Section

In a typical synthesis, 12.0 g of triammonium trioxalato(oxido)-niobate, $(NH_4)_3[NbO(C_2O_4)_3]\cdot 3H_2O$ (CBMM; Companhia Brasileira de Metalurgia e Mineração) was dissolved in 200 mL of deionized water. The template [CTAB (Aldrich) or OCT (Merck)] was dissolved in 100 mL of a 3 M aqueous NaOH solution. The Nb/template molar ratios were varied from 1:0.1 to 1:2 to determine the influence of this parameter on mesophase formation. The solution of niobium complex was poured into the template solution (NaOH/Nb molar ratio of 4:1) and constantly stirred at room temperature for 48 h and at 80 °C for another 24 h to promote the decomposition of any remaining oxalate anion. After this period, the solid was filtered off, washed with water, and dried at 120 °C for 5 h. The obtained solids were characterized by X-ray diffractometry (XRD), transmission electron microscopy (TEM), Raman spectroscopy, and XANES. The standard HNb_2O_5 was obtained by treating a sample of Nb_2O_5 at 1200 °C for 2 h and its structure was confirmed by X-ray diffractometry.

X-ray diffraction patterns of the powdered samples were recorded with a Rigaku diffractometer model Miniflex using Cu-K_a radiation (1.541 Å, 30 kV and 15 mA), a step of 0.03°, and Ni filter. TEM images were recorded with a 300 kV JEM-3010 ARP microscope (1.7 Å point resolution) at the LME/LNLS (Laboratory of Electron Microscopy of the Brazilian Synchrotron Light National Laboratory, Campinas, Brazil). Samples were prepared by dispersing solids in ethanol in an ultrasonic bath followed by deposition on a carbon-coated Cu microgrid. Raman spectra were recorded with a Renishaw Raman Microscope model 3000, fitted with an Olympus metallurgical microscope (BH2-UMA) and a CCD camera (Wright, 600 × 400 pixels), with laser excitation line at 632.8 nm of an He-Ne laser (Spectra Physics, model 127). The XANES measurements at room temperature were performed at the XAFS beam line of Brazilian Synchrotron Light Laboratory (ring energy of 1.37 GeV and a beam current of about 175 mA). The monochromator was an Si(220) crystal and the recorded energy steps were 0.5 eV for the 18980–19060 eV XANES region in fluorescence mode. All energy values in the Nb *K*-edge spectra were calibrated against niobium metal.

Acknowledgments

The authors acknowledge the Brazilian agencies FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) and CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) for financial support and fellowships. We are thankful to LNLS for recording the HRTEM images and XANES spectra (projects TEM-2173 and D04B-XAFS1 4337/05). We are also grateful to the Companhia Brasileira de Metalurgia e Mineração (CBMM) for the triammonium trioxalato(oxido)niobate sample and the Laboratório de Espectroscopia Molecular (IQ-USP) for recording the Raman spectra.

---

[1] a) M. A. Davis, *Nature* **2002**, *417*, 813–821; b) F. Fajula, A. Galarneau, F. D. Renzo, *Microporous Mesoporous Mater.* **2005**, *82*, 227–239; c) C. Sanchez, B. Julián, P. Belleville, M. Popall, *J. Mater. Chem.* **2005**, *15*, 3559–3592.

[2] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartulli, J. S. Beck, *Nature* **1992**, *359*, 710–712.

[3] G. J. de A. A. Soler-Illia, C. Sanchez, B. Lebeau, J. Patarin, *Chem. Rev.* **2002**, *102*, 4093–4138.

[4] Q. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, R. Leon, P. M. Petroff, F. Schüth, G. D. Stucky, *Nature* **1994**, *368*, 317–321.

[5] P. T. Tanev, M. Chibwe, T. J. Pinnavaia, *Nature* **1994**, *368*, 321–323.

[6] a) D. M. Antonelli, J. Y. Ying, *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 426–430; b) D. M. Antonelli, A. Nakahira, J. Y. Ying, *Inorg. Chem.* **1996**, *35*, 3126–3136; c) S. Tao, J. Y. Ying, *Nature* **1997**, *389*, 704–706.

[7] B. Lee, D. Lu, J. N. Kondo, K. Domen, *J. Am. Chem. Soc.* **2002**, *124*, 11256–11257.

[8] a) B. Ye, M. Trudeau, D. Antonelli, *Adv. Mater.* **2001**, *13*, 29–33; b) B. Ye, M. Trudeau, D. Antonelli, *Chem. Mater.* **2001**, *13*, 2730–2741; c) B. Ye, M. Trudeau, D. Antonelli, *Chem. Mater.* **2002**, *14*, 2774–2781.

[9] a) S. Murray, M. Trudeau, D. Antonelli, *Adv. Mater.* **2000**, *12*, 1339–1341; b) S. Murray, M. Trudeau, D. Antonelli, *Inorg. Chem.* **2000**, *39*, 5901–5908; c) M. Vettraino, B. Ye, M. Trudeau, D. Antonelli, *J. Mater. Chem.* **2001**, *11*, 1755–1759; d) X. He, M. Trudeau, D. Antonelli, *J. Mater. Chem.* **2003**, *13*, 75–79.

[10] a) L. Washmon-Kriel, V. L. Jimenez, K. J. Balkus Jr, *J. Mol. Catal. B: Enzym.* **2000**, *10*, 453–469; b) X. Xu, B. Tian, J. Kong, S. Zhang, B. Liu, D. Zhao, *Adv. Mater.* **2003**, *15*, 1932–1936; c) X. Xu, B. Tian, S. Zhang, J. Kong, D. Zhao, B. Liu, *Anal. Chim. Acta* **2004**, *519*, 31–38.

[11] J. M. Jehng, I. E. Wachs, *ACS Symp. Ser.* **1990**, *437*, 232–242.

[12] a) F. Fairbrother, J. B. Taylor, *J. Chem. Soc.* **1956**, 4946–4954; b) F. Fairbrother, *The Chemistry of Niobium and Tantalum*, Elsevier, Amsterdam, **1967**.

[13] G. Mathern, R. Weiss, *Acta Crystallogr., Sect. B* **1971**, *27*, 1610–1618.

[14] B. K. Prodic, R. Liminga, S. Scavnicar, *Acta Crystallogr., Sect. B* **1973**, *29*, 864–869.

[15] Q. Huo, D. I. Margolese, G. D. Stucky, *Chem. Mater.* **1996**, *8*, 1147–1160.

[16] C. Y. Chen, S. Q. Xiao, M. E. Davis, *Microporous Mater.* **1995**, *4*, 1–20.

[17] J. C. Vartuli, K. D. Schmitt, C. T. Kresge, W. J. Roth, M. E. Leonowicz, S. B. McCullen, S. D. Hellring, J. S. Beck, J. L. Schlenker, D. H. Olson, E. H. Sheppardt, *Chem. Mater.* **1994**, *6*, 2317–2326.

[18] M. A. Carreon, V. V. Guliants, *Eur. J. Inorg. Chem.* **2005**, 27–43.

[19] J. M. Jehng, I. E. Wachs, *Chem. Mater.* **1991**, *3*, 100–107.

[20] R. L. Frost, *Anal. Chim. Acta* **2004**, *517*, 207–214.

[21] T. Tanaka, T. Yoshida, H. Yoshida, H. Aritani, T. Funabiki, S. Yoshida, J. M. Jehng, I. E. Wachs, *Catal. Today* **1996**, *28*, 71–78.

[22] M. S. P. Francisco, R. Landers, Y. Gushikem, *J. Solid State Chem.* **2004**, *177*, 2432–2439.

[23] T. Ushikubo, Y. Koike, K. Wada, L. Xie, D. Wang, X. Guo, *Catal. Today* **1996**, *28*, 59–69.

Received: June 6, 2006