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Novel nanoporous organic-inorganic hybrid materials containing niobium

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A synthetic protocol with the versatility to make high-quality periodic mesoporous organosilicas containing niobium and bridging carbon functional groups has been presented. This flexibility is discussed in terms of organic precursor structures. Niobium-containing silica-bridged periodic mesoporous organosilicas (Nb-PMOs) were synthesized by self-assembly of the nonionic surfactant P123, $EO_{20}PO_{70}EO_{20}$, and trimethoxysilyl functionalized organic compounds, namely silica precursors containing two different organic bridging groups ($(C_2H_5O)_3Si{-}R{-}Si(OC_2H_5)_3$, R – ethylene or octylene) under acidic conditions. The obtained bifunctionalized Nb-PMOs have been characterized by X-ray diffraction, transmission electron microscopy, and nitrogen physical sorption. Experiments show that the Nb-PMOs exhibit hexagonal mesoscopic structures. Increasing the amount of the organic chain length functionality in the precursors results in significant worsening of the mesostructural ordering of the product. It is shown that the organic monomer can act as a template in making nanoporous silica materials.

Key words: *Nb-PMOs; inorganic/organic hybrid; bimodal mesopores distribution*

1. Introduction

Since the advent of high surface area mesoporous molecular sieves (e.g., MCM-41 type silica materials) via a surfactant-templated synthesis route by Mobil in 1992 [1], organic modification schemes imparting various functionalities to the inorganic silica surface have received much attention. By using a bistrialkoxysilyl precursor in which bonding between silicon and carbon is established with the assured stoichiometry, periodic ordered mesoporous organosilicas (PMOs) in which organic groups were directly integrated into the silica framework, were synthesized in 1999 by three independently working groups [2–4]. These new materials have been expected to lead to advanced materials due to the possibility of controlling the kind of functional groups in the bridged organosilane precursors $(R'O)_3{-}Si{-}R{-}Si{-}(OR')_3$ (e.g., [5]). To date, PMOs with simple bridging groups derived from methane, ethane, ethylene, acetylene,

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phenyl and its derivatives, thiophene, and ferrocene have been developed (e.g., review paper [6]). The pore diameters of the PMOs prepared by structure-directing agents with ionic alkyl ammonium surfactants (with chain lengths from C12 to C20) were restricted to the range between 2 nm and 5 nm. This limitation was finally overcome by using nonionic triblock copolymers such as P123 ($EO_{20}PO_{70}EO_{20}$) used previously as a structure directing agent in the synthesis of large-pore mesoporous SBA-15 pure silica phase. This kind of material with a hexagonal *p6mm* type structure is a representative of 2D mesostructure and possesses wall thicknesses between 3.1 nm and 6.4 nm with pore sizes in the range of 4.6–30 nm [7].

The PMOs materials have gained a general expectation that their efficient uses can be dimensionally expanded to a number of versatile applications as catalysts. Hence, intellectual efforts have been devoted to extend their unique properties in the area of heterogeneous catalysis, by the substitution of active metal sites in the wall positions so that they can be used as catalysts for various hydrophobic reactions, e.g. epoxidation processes, in order to improve the contact at the water (oxidant)–organic (cyclohexene) interface. Since the Nb-containing silicas were found to be active in oxidation processes, in this work we synthesized and optimized the synthesis condition of a new Nb-PMOs catalyst that is expected to find applications as a water-tolerant solid acid catalyst for the reactions requiring weak acidic sites and low temperatures.

2. Experimental

The nanostructured hybrid nioboorganosilicates have been synthesized by the hydrolysis and condensation of bridged silsesquioxane precursors containing two different organic bridging groups ($(C_2H_5O)_3Si–R–Si(OC_2H_5)_3$, R – ethylene or octylene. The triblock copolymer Pluronic P123 ($(EO)_{20}(PO)_{70}(EO)_{20}$) was obtained from BASF, while 1,2-bis(triethoxysilyl)ethane (BTEE) and 1,2-bis(triethoxysilyl)octane (BTEO) were kindly provided by ABCR GmbH & Co. In a typical synthesis, the P123–H_2O solution was slowly added to the BTEE (or BTEO)–Nb source–H_2O–HCl mixture that was stirred for 24 h at 313 K. Ammonium trisoxalate complex of niobium(V) was used as a source of niobium, furthermore the TEOS/surfactant and the Si/Nb molar ratios were kept as 60 and 64 in all the syntheses, respectively. The slurry was then transferred into a polypropylene bottle and hydrothermally treated at 373 K for 20 h. White solids were recovered by filtration, washed with deionized water and ethanol, and dried under ambient conditions. For all as-synthesized materials, the surfactant molecules (occluded inside the pores of the hybrid material) were removed by solvent extraction (mixture of ethanol and HCl). The samples will be denoted as Nb-PMO-E in the case of using BTEE and Nb-PMO-O for BTEO, respectively, as the bistrialkoxysilyl precursors. The materials were then calcined at 773 K for 4 h to remove ethane or octane fragments chemically bonded in the framework. For comparison, an Nb-SBA-15 sample with Si/Nb ratio of 64 was also prepared and the details of the synthesis procedures have been reported elsewhere [8].

Various physicochemical studies (viz., X-ray diffraction (XRD), transition electron microscopy (TEM), N_2 physisorption) and XRF spectroscopy were used to check the mesoporosity and to find the location of niobium ions in the NbPMO.

X-Ray diffraction patterns were recorded with a TUR-62 diffractometer using CuK_α radiation and operating voltage of 40 kV. The samples were disc shaped pressed powders. The diffractograms were recorded at room temperature in two 2Θ ranges: 1.2–10° and 4–60° with the step size of 0.02° or 0.05°, respectively. Adsorption/desorption experiments using N_2 were carried out at 77 K on a Micromeritics ASAP 2010. Before each measurement, the samples were first outgassed at 573 K for 3 h in vacuum. The N_2 isotherms were used to determine the specific surface areas using the standard BET equation in the relative pressure (p/p_0) from 0.05 to 0.2 and the cross-sectional area of nitrogen molecule of 0.162 nm^2. Pore sizes were obtained from the N_2 adsorption branch, using the Barret–Joyner–Halenda (BJH) method with the corrected Kelvin equation, i.e. KJS–BJH method at the maximum of pore size distribution [9]. Moreover, the α_s-plot analysis [10] was performed for all obtained samples for the evaluation of the micropore volume. The single-point total pore volume was obtained from the amount adsorbed at $p/p_0 = 0.98$. Transmission electron microscopy (TEM) images were obtained using a JEOL-2000 transmission electronic microscope with an accelerating voltage of 80 kV. The samples were dispersed in ethanol under ultrasonic conditions and deposited on a copper grid before examination. The metal content in the calcined samples was determined by X-ray fluorescence spectroscopy (XRF, MiniPal, Philips) using calibration curves prepared from mixtures of mesoporous pure silica and Nb_2O_5.

3. Results and discussion

Highly ordered mesoporous nioboorganosilicates with large pores were synthesized under acidic conditions using a nonionic surfactant as a supramolecular structure directing agent. The mesostructural ordering of the as-synthesized and extracted Nb-PMOs was confirmed by powder XRD. Similarly to pure niobosilicate analogues, Nb-PMOs without extraction exhibit XRD patterns dominated by low-angle peaks, typically with a prominent peak with a d spacing of ca. 13 nm (Fig. 1, line a). The XRD pattern indicates a significant level of mesostructural ordering [12]; however, there is a lack of higher order peaks. This is a known feature of XRD patterns of template-containing mesophases. The XRD pattern of the extracted nioboorganosilicate Nb-PMO-E exhibits a high intensity prominent (100) peak along with (110) and (200) peaks, therefore confirming that the mesophase has a hexagonal (*P*6*mm* symmetry group) pore channel ordering. The material obtained from the silica source containing longer bridging carbon chain (Nb-PMO-O; not shown here) showed characteristic peaks at a low angle; they were, however, less resolved. Similarly to pure niobosilicate counterparts, Nb-PMOs exhibit XRD patterns dominated by low-angle peaks, typically with a prominent peak at $2\theta < 1.6^\circ$. After calcination, a decrease in d_{100} peak intensity, long-range ordering and lattice contraction is observed (Fig. 1, line c), showing the cross-linking of the framework silanols and/or the lack of ordering between the structures of adjacent pores. In addition to the structural ordering, XRF analysis showed that the hydrophobic nature of surfactant also plays a vital role in the amount of metal incorporation (Table 1). Even though there is no stoichiometric incorporation of niobium under the present synthesis conditions, it is likely that a large part of the metal remains in the gel solution.

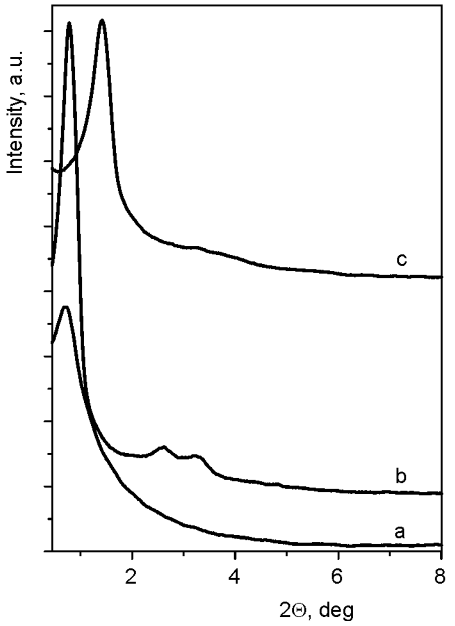

Fig. 1. XRD patterns for the Nb-PMO-E samples: a) as-synthesized; b) after extraction with HCl/EtOH mixture; c) after extraction and calcination at 773 K for 4 h

Table 1. Textural and structural properties of Nb-PMOs materials and their niobosilicate analogues

Material	Si/Nb	a_0[a] [nm]	Surface area [$m^2 \cdot g^{-1}$]	Pore width [nm]	Pore volume [$cm^3 \cdot g^{-1}$]			Wall thickness [nm]
					Total	Meso	Micro	
Nb-PMO-E	248	13.6	720	10.6	1.05	0.93	0.06	3.0
Nb-PMO-O	238	9.5	230	~6.0	0.51	0.37	0.05	3.5
Nb-SBA-15[b]	158	10.6	730	8.6	0.78	0.46	0.17	2.0

[a] a_0 – wall thickness ($a_0 = 2d_{100} \times 3^{-1/2}$, d – pore width).
[b] Synthesized with TEOS as a Si source.

To further elucidate the mesoporous characteristics of the obtained samples, their detailed pore structures were studied by the TEM technique. The TEM images of the extracted sample Nb-PMO-E observed from different orientations are shown in Fig. 2. They confirmed the 2D hexagonal pore structure with *P*6*mm* symmetry. For octane-functionalized nioboorganosilicate two dimensional channels has been undoubtedly seen, however some areas with a lower order are also noticeable (not shown here).

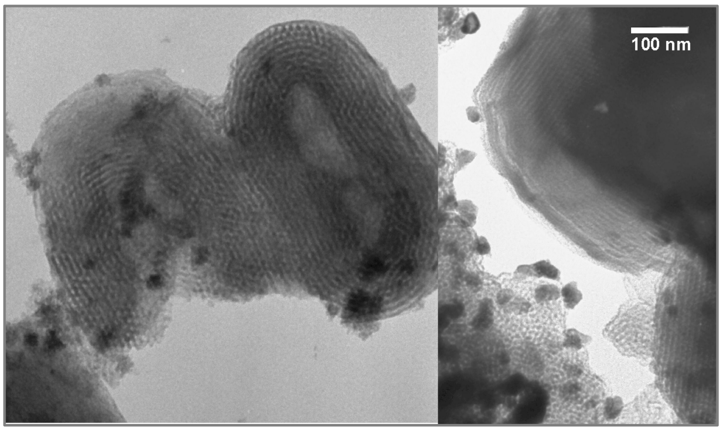

Fig. 2. Transmission electron micrographs for Nb-PMO-E

Surface areas, pore sizes, and pore volumes of the Nb-PMO materials are given in Table 1. The synthesis yielded Nb-PMO-E materials with the pore size of 10.6 nm and the specific surface area of 700 $m^2 \cdot g^{-1}$. The isotherm of PMO-E sample is of type IV with a pronounced uptake in the relative pressure (p/p_0) range of 0.7–0.9 due to capillary condensation in the mesopores, indicating the presence of relatively uniform mesopores (Fig. 3).

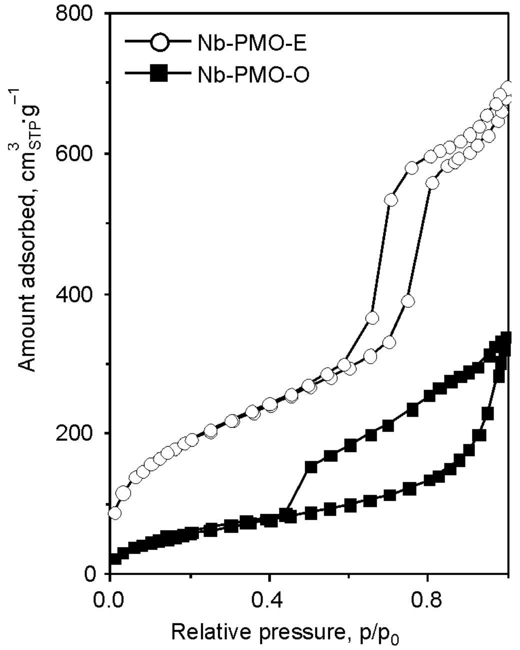

Fig. 3. Nitrogen adsorption-desorption isotherms at 77 K for Nb-PMOs materials

It is known that the inflection position depends on the width of the mesopores and that the sharpness usually indicates the uniformity of the mesopores, due to capillary condensation of N_2 within the mesopores. H1-type hysteresis loop displayed at a high relative pressure is characteristic of large-pore mesoporous materials with uniform cylindrical channels [7]. A visible increase in the adsorption at $p/p_0 > 0.9$ associated with the hysteresis for Nb-PMOs could be attributed to the existence of interparticle pores. The isotherm of the Nb-PMO-O sample is between type I and IV and thus can be regarded as supermicroporous (pores ranging between 1.5 and 2.0 nm [14]) which is further evidenced by a small contribution of typical mesopores (pore width ~6.0 nm) in the pore size distribution (Fig. 4). A decrease in the micropore volume is observed after introduction of silica source with bridging organic groups into the synthesis gel. This is also accompanied by a decrease in the primary mesopore volumes for longer organic chain in bridging positions, while an increase is visible for ethane group (Table 1). The wall thickness increases upon incorporation of organic groups. It is clearly visible from Table 1 that the sample prepared with the PO number equal to 7 possesses a lower wall thickness than the sample with $y = 14$. Moreover, the calcined samples lost the sharpness in the capillary condensation step, suggesting a partial collapse of the mesostructure, as observed from the XRD measurements (figure not shown) and a decrease of ~10–20% in the surface area in comparison to the extracted materials.

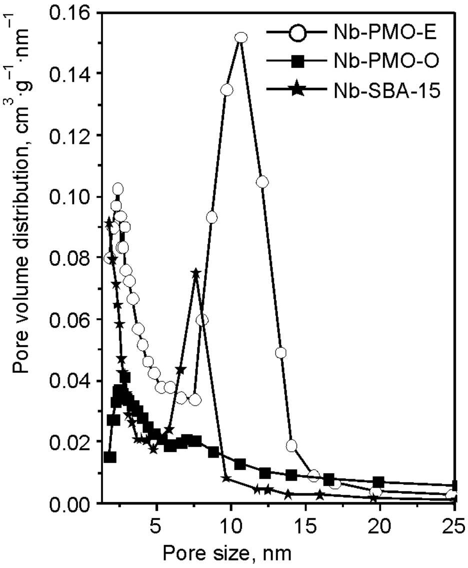

Fig. 4. Pore size distributions for the Nb-PMOs materials and their niobosilicate analogue

The pore size distribution (PSD) curves of the Nb-PMO-E and Nb-PMO-O are shown in Fig. 4. The KJS-BJH pore size distributions describe obvious existence of the bimodal pore structure, including some super micropores with widths lower than 2 nm and primary mesopores above 6 nm. It can be seen that Nb-PMO-E has a broader pore size distribution, however with increased intensity compared to the pure Nb-SBA-15, indicating a lower degree of mesoorder obtained for the functionalized Nb-PMOs. As can also be seen, the pore size distribution for Nb-PMO-O material reveals only a very small mesopore volume in the typical mesoporous range (besides the supermicropores with pore widths lower than 2 nm). This feature is due to the nature of different sizes and molecular configurations of employed organic bistrialkoxysilyl precursors which causes different pore size distribution curves and ultimately different degrees of pore blockage/wall thickness.

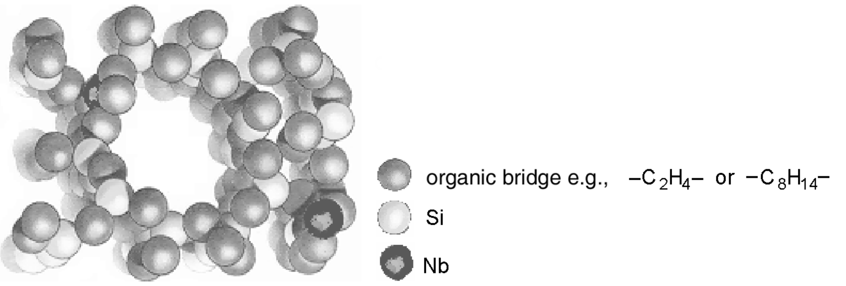

Fig. 5. General idea of the structure of Nb-PMOs materials synthesized from bissilylated organic bridging units and niobium species. Oxygen atoms have not been shown to make the picture clearer

FTIR and Raman data (not shown here) proved that the organic bridges are intact within the framework. Furthermore, these data provided evidence that the template was completely removed via extraction and there was no Si–C bonds cleaved during synthesis and extraction stages. The band at 225 nm on the UV-Vis patterns for Nb-PMOs (not shown here) clearly indicated a successful incorporation of Nb into the framework. Thus the framework clearly consists of both, organic groups and niobium species counterparts as shown in Fig. 5.

4. Conclusions

The nanostructured bridged nioboorganosilicates have been synthesized by the acid catalyzed hydrolysis and condensation of bridged silsesquioxane precursors containing two different organic bridging groups ($(C_2H_5O)_3Si–R–Si(OC_2H_5)_3$, R – ethylene or octylene) in the presence of nonionic template P123. The retention of niobium in the organosilica framework was ensured by a slow template removal. A successful synthesis of Nb-PMOs was confirmed by powder XRD (high periodicity), N_2 adsorption (surface area above 700 $m^2 \cdot g^{-1}$ and pore sizes with the maximum at about 8–11 nm), diffuse reflectance UV-vis spectroscopy (characteristic absorption band for Nb in the framework), and FTIR and Raman spectroscopies (presence of $CH_2–Si(OSi\equiv)_3$ groups).

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