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Microwave-assisted synthesis of nioboorganosilicates and microwave-accelerated catalytic activity of thereof

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ABSTRACT

A novel type of organic–inorganic hybrid mesoporous material, i.e., mesoporous silica with organic groups and niobium species as lattice fundamentals was prepared. This new material was synthesized by self-assembly of bridged silsesquioxane precursor containing ethane-bridging group that connects two silicon atoms to surpass an oxygen atom in the mesoporous framework. They had been synthesized by using nonionic template Pluronic P123 as a structure-directing agent under microwave irradiation. The properties of obtained materials were confirmed by X-ray diffraction (XRD), transmission electron microscopy (TEM), adsorption measurements, DTG/TG, DR-UV–vis, Raman and FTIR spectroscopies. The Nb-PMOs were tested in the oxidation reaction of cyclohexene to epoxide in the liquid phase using hydrogen peroxide as an oxidant. The reaction took place under conventional thermal heating and for comparison in the presence of microwaves. The microwave-assisted cyclohexene oxidation over nioboorganosilicates was completed within 1 h in comparison to 36–40 h for conventional method with comparable conversion and slightly higher selectivity to cyclohexene epoxide.

1. Introduction

Periodic mesoporous organosilicas (PMOs) with controlled texture and morphology are a new class of organic–inorganic mesostructured hybrid materials promising for applications in catalysis, adsorption, separation, biosorption, chromatography and sensors due to possibilities to tune their chemical and physical properties [1–3]. Self-assembly of bistrialkoxysilyl precursor: $(C_2H_5O)_3Si–R–Si(OC_2H_5)_3$, in which bonding between silicon and carbon is established with the assured stoichiometry, undergoes in the presence of ionic alkyl ammonium surfactants or block copolymers as structure directing agents. It provides to direct integration of organic groups into silica framework through covalent Si–C bonds. That kind of ordered organosilicas were first synthesized in 1999 by three independently working groups [4–6]. Since that time various organic groups have been incorporated into the silica matrix, from simple hydrocarbon groups (methane, ethane, ethene, acetylene), aromatic and its derivatives to heterocycles and sandwich-type compounds [1,3,7].

While the introduction of metals into organic–inorganic frameworks provides their potential application in catalytic transformations, the incorporation of the specific organic functionalities creates hydrophobic properties of the inner surface of nioboorganosilicate and shows promise in order to improve interactions at the water (oxidant)–organic interface. That is the main reason of the possible application of Nb-containing mesoporous organosilica in oxidation reactions that require weak acidic sites and low temperatures, for example in epoxidation reactions, especially using hydrogen peroxide as the oxygen donor according to the current environmentally friendly fine chemistry trends. An application of microwave irradiation for the epoxidation is a much faster method. Microwaves have been previously efficiently used for example in acceleration of organic syntheses [e.g., 8–11] as well as a way of hydrothermal syntheses of metal nanoparticles, zeolites, and mesoporous molecular sieves [e.g., 12–17], so there are applicable to a wide variety of processes. The main goal of this work was to evaluate the potential of microwave heating for the rapid synthesis of nioboorganosilicates and additionally for the liquid catalytic oxidation process.

2. Experimental

The ordered nioboorganosilicates have been synthesized by the simultaneous hydrolysis and condensation of bridged silsesquioxane precursors containing ethane-bridging group ($(C_2H_5O)_3Si–CH_2–CH_2–Si(OC_2H_5)_3$) in presence of nonionic template, Pluronic P123 ($(EO)_{20}(PO)_{70}(EO)_{20}$), employed as the structure directing agent. Block copolymer was obtained from BASF, while the source of

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organic groups, i.e., 1,2-bis(triethoxysilyl)ethane (BTEE) was kindly provided by ABCR GmbH & Co. As the source of niobium ammonium trisoxalate complex of niobium(V) was used. The Si/Nb molar ratios were 16, 32 and 64 and the TEOS/surfactant molar ratio was kept as 60 and in all the syntheses procedures, respectively.

In the conventional hydrothermal synthesis, the water solution of template Pluronic P123 was slowly added to the mixture of BTEE, ammonium trisoxalate complex of niobium(V) in HCl and H_2O, then was stirred for 24 h at 313 K. In the next step the slurry was hydrothermally treated at 373 K for 20 h in a polypropylene bottle. The formed white solids were filtered, washed with deionized water and ethanol, and dried under ambient conditions. The template was removed by solvent extraction (mixture of ethanol and HCl).

The synthesis of the niobium-substituted organosilicas using microwave irradiation was investigated systematically. The mixture of Pluronic P123, BTEE, ammonium trisoxalate complex of niobium(V) in HCl and H_2O prepared as described above was transferred into microwave reaction vessel (10 cm^3) and treated in the CEM microwave system under stirring at 373 K for 1 h. The temperature and pressure in the vessel had been controlled by program during the whole time reaction. The template was removed as reported earlier.

The samples will be denoted as Nb(*R*)PMO-E in the case of different Si/Nb molar ratios (*R*) for conventional and as Nb(*R*)PMO-E-M for microwave-assisted syntheses.

Various physicochemical studies (XRF—Philips MiniPal; DR-UV–vis—Varian Cary 300; FTIR—Varian Scimitar 800; X-ray diffraction (XRD)—Bruker AXS D8Advance; transition electron microscopy (TEM)—JEOL 2000 (80 kV); N_2 physisorption measurements at 77 K—Micromeritics 2010; and thermal decomposition measurements DTG/TG—Setaram) were used to check the mesoporosity and to find the location of niobium ions and organic groups in the Nb-PMOs.

All prepared materials were tested in the oxidation of cyclohexene with hydrogen peroxide using standard thermal method. To 0.04 g of a dried catalyst placed in the flask acetonitrile was added. Then cyclohexene (2 mmol) and 34 vol.% hydrogen peroxide (2 mmol) was added and the mixture was stirred for 40 h at 318 K. The probes for microwave-assisted method were prepared similarly as for standard method and were carried out at 318 K in acetonitrile in a glass tube in Discovery microwave system (CEM) for 4 h. The reaction mixtures were analyzed in both cases each 1 h with Varian CP-3800 chromatograph equipped with a VF-5MS capillary column and a flame ionization detector (FID).

3. Results and discussion

The possibility of the isomorphous substitution of silicon with niobium in mesoporous molecular sieves was checked by using X-ray fluorescence spectroscopy. The evolutions of Si/Nb ratio are presented in Table 1. The Si/Nb ratios of the extracted Nb-PMOs products are four times lower than assumed ratios and twice lower than for pure niobosilicate, which clearly shows that there is a competition between the introduction of organic groups and niobium species. The C:Si molar ratio of the extracted Nb-PMOs samples (based on the DTG/TG and elemental analyses) was close to 0.92: 1. Thus, the presences of a supplementary amount of carbon coming from residual Pluronic P123 (surfactant) was excluded, while a slight decrease of C amount is probably due to volatile hydrocarbons departure during the synthesis/extraction procedures.

Highly ordered mesoporous nioboorganosilicates with niobium species and ethane-bridging groups were obtained in acidic conditions in the presence of block copolymer by using standard, i.e., conventional hydrothermal method and in the presence of microwaves irradiation. It is well known that PMO materials prepared conventionally under strong acidic conditions with nonionic copolymers as surfactants usually exhibit poorly ordered mesostructured [18], whereas Nb-PMO-E prepared in this work by using hydrothermal treatment possessed high surface area (from 700 $m^2\,g^{-1}$ for Si/Nb ratio of 64 [19], through 800 for Si/Nb = 32 [this work] to 900 $m^2\,g^{-1}$ for Si/Nb ratio of 16 [this work]) and uniform mesopores of width ca. from 8 to 10 nm (for Si/Nb ratios from 64 to 16, respectively). Very similar textural data was obtained when the microwave-assisted synthesis was applied for the preparation of Nb-PMO-E samples. Thus, one can conclude that the microwave-assistance allowed to reduce the hydrothermal treatment time from 20 to 1 h while maintaining the mesoporous ordering.

The isotherms of all samples are type IV with an uptake in the relative pressure (p/p_0) range of 0.7–0.9 (Fig. 1). It is associated with capillary condensation in the mesopores, which shows that the mesopores possesses quite uniform size. The hysteresis loops are of type H1 and they are characteristic for mesoporous materials with large pores and uniform cylindrical channels [20]. At relative pressure range $p/p_0 > 0.9$ the adsorption increases, which is due to the existence of interparticle pores. Pore diameters were calculated using the Kruk–Jaroniec–Sayari alteration of the Barret–Joyner–Halenda method on the adsorption branch, and ranged from 8 to 11 nm (Table 1). On modifying organosilica with niobium species, the surface area (determined using the multi-point BET – Brunauer–Emmett–Teller – method with data points over the range 0.04–0.2p/p_0) of the new Nb-PMOs increased from 700 to 940 $m^2\,g^{-1}$, whereas the pore diameter decreased from 10.3 to 8.2 nm. The incorporation of niobium into the organosilicas framework also causes an increase in the mesopore volume and wall thickness (Table 1). The latter feature is connected with the higher external surface area due to the presence of very small amounts of extra framework niobium species (as confirmed by hydrogen temperature programmed reduction experiments). The

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

Material	Si/Nb	a_0 (nm)	Surface area ($m^2\,g^{-1}$)	Pore width (nm)	Pore volume ($cm^3\,g^{-1}$)			Wall thickness[a] (nm)
					Total	Meso	Micro	
Nb(64)PMO-E-M	243	13.6	720	10.6	1.05	0.93	0.06	3.0
Nb(32)PMO-E-M	123	12.8	840	9.4	1.09	0.99	0.08	3.4
Nb(16)PMO-E-M	81	12.0	940	8.2	1.19	1.08	0.10	3.8
Nb(64)PMO-E	241	13.6	720	10.6	1.05	0.93	0.03	3.0
Nb(32)PMO-E	123	13.0	820	9.8	1.12	0.92	0.08	3.2
Nb(16)PMO-E	80	12.0	940	8.5	1.19	0.93	0.12	3.5
PMO	–	13.2	700	10.3	0.89	0.68	0.09	2.9
Nb-SBA-15[b]	158	13.8	730	11.2	0.78	0.46	0.17	2.6

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

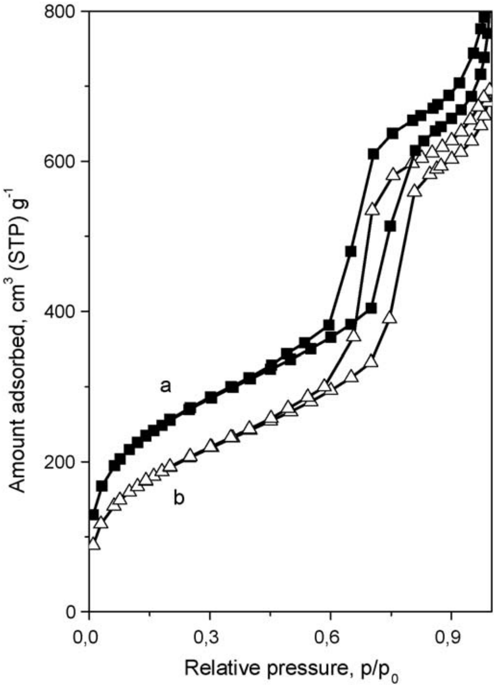

Fig. 1. Nitrogen adsorption–desorption isotherms at 77 K for Nb-PMO-E materials with Si/Nb ratio equal to 16 (a) and 64 (b).

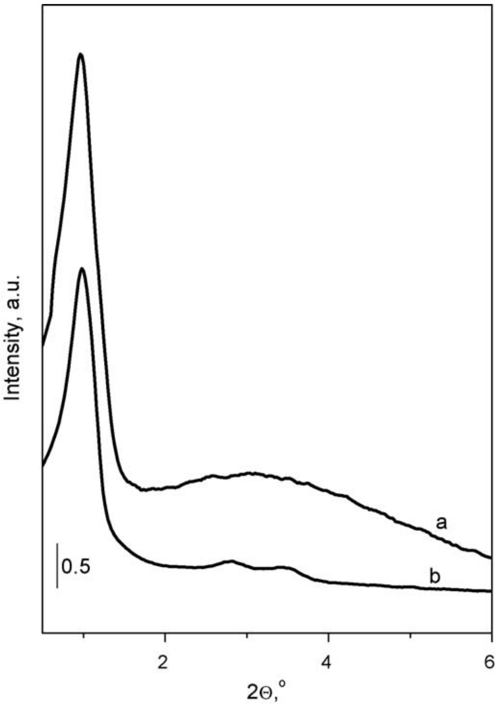

Fig. 2. XRD patterns for Nb-PMO-E samples prepared via hydrothermal (a) and under microwave-assisted syntheses (b).

role of Si/Nb ratio was also considered—the lower Si/Nb ratio (16) the higher surface area. The wall thickness and pore volume decrease with the decrease of Nb content (from Si/Nb = 16 to 64), while the pore diameter increases in the same order.

Similarly to the pure niobiosilica and organosilica counterparts, Nb-PMOs exhibited XRD patterns dominated by low-angle peaks (Fig. 2). For template containing niobiosilicates XRD data (not presented here) showed a mesostructural ordering of the samples, but higher order peaks were not present. The extracted Nb-PMO-E samples prepared via standard method exhibit a high intensity prominent peak at $2\theta < 1.6^\circ$ and a broad less resolved peak, which confirmed that the sample has hexagonal (P6mm symmetry group) pore channel ordering. The extraction procedure does not affect the structure of Nb-PMOs, as evidenced by the fact that the intensity of powder XRD does not decrease after the extraction procedure for Nb(64)PMO-E [19]. A higher (1 0 0) peak intensity and resolution of (1 1 0), (2 0 0) and (2 1 0) reflections for samples prepared via microwave-assisted method can be attributed to the long-range regularity of Nb-PMO rods because of the use of microwaves for heating (Fig. 2). The incorporation of Nb into the framework of PMOs is evidenced by a decrease in the unit cell parameter of Nb-PMO samples, suggesting a thicker framework in after niobium incorporation.

To confirm the hexagonal arrangement of mesopores the TEM images of the extracted samples have been made. The transmission electron microscopy (not shown here) confirmed the presence of 2D hexagonally organized mesopores with P6mm symmetry.

The FTIR and Raman data proved that the organic bridges are intact within the framework (presence of $\mathrm{CH_2{-}Si(OSi{\equiv})_3}$ groups). The FTIR spectra (Fig. 3A) of the template-removed Nb-PMOs show

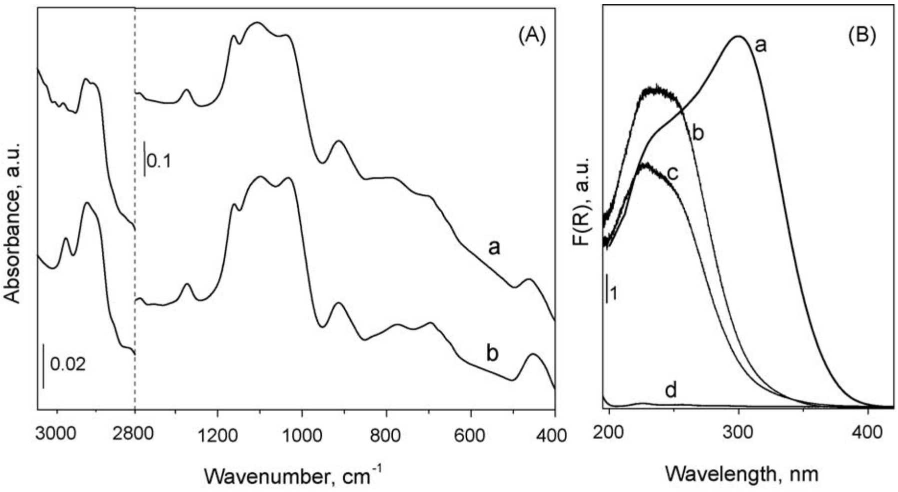

Fig. 3. The spectroscopic data, i.e. (A) FTIR and (B) DR-UV–vis spectra for various Nb-PMO-E materials: (A) Nb-PMO-E with Si/Nb ratio of 16 (a) and 64 (b), and (B) Nb-PMO-E with Si/Nb ratio of 16 (b), 32 (c) and for comparison pure siliceous PMO-E (d) and Nb_2O_5 (a).

bands at 2930 cm^{-1} (asymmetric C–H stretching vibration of $-CH_2-$ fragments), 2860 cm^{-1} (symmetric C–H stretching vibration of $-CH_2-$ fragments), 1170 cm^{-1} (Si–CH_2–CH_2–Si stretching mode), 1410 and 1270 cm^{-1} (CH_2 deformation vibrations), as well as 696 and 768 cm^{-1} (Si–C stretching modes), which are consistent with those observed in the literature for hydrocarbon-bridged PMO materials, showing their successful synthesis. Furthermore, the Raman data provided a strong evidence that the template was completely removed via extraction and the Si–C bond was formed during synthesis and was not altered during extraction stages. In addition, these data confirm the completion of the template removal via extraction.

After the identification of the mesophase structure and organic groups presence within the framework, the next step was to determine the environment (i.e., coordination) of Nb species in the organosilica matrix. A band at ~220 nm on the UV–vis patterns for Nb-PMOs clearly indicates a successful incorporation of Nb into the framework in comparison to band at ~300 nm, which is characteristic for niobium at extra-framework position (pattern of Nb_2O_5) (Fig. 3B). Furthermore, the band intensity increases with increasing amount of niobium in the niobiosilicate structure (decreasing value of Si/Nb ratio). Other characterization results also indicate the presence of niobium inside the silica walls (FTIR data), as well as a good dispersion of the niobium in the framework positions (e.g., hydrogen temperature programmed reduction profiles).

Since Nb-PMOs were expected to find application as a water-tolerant solid catalyst for reactions that require weak acidic sites and low temperatures, they were tested for various oxidation reactions with hydrogen peroxide as oxidant. It was shown that the novel Nb-containing organosilica materials are suitable for epoxidation of olefins. The results are shown in Fig. 4, which gives, for each catalyst, the conversion of cyclohexene and the selectivity to the desired product—cyclohexene epoxide. The new hydrophobic catalysts showed good performance (high epoxide selectivity). The microwave-assisted method over Nb-PMOs allows to end the reaction within 60 min with similar or even better results. Cyclohexene conversions after 40 h under conventional thermal heating varied from 12% to 22% for different nioboorgonosilicates, whereas after 1 h under microwave treatment were a slightly lower, up to 16% for Nb(16)PMO-E. Nevertheless, the selectivity to cyclohexene epoxide surprisingly was higher in presence of microwaves and reached up to 90%. In comparison to conversion results, where standard method gave a slightly higher conversions, the selectivity to epoxide is better for microwave-assisted method; i.e., microwaves assist the selectivity to epoxide. This feature can be explained by direct delivery of energy throughout the mass of the product not at surfaces [21] preventing the oxirane ring opening to diols. The most reactive catalyst appeared to be Nb(16)PMO-E catalyst with the Si/Nb ratio equal to 16, which showed 65% of selectivity to epoxide in standard thermal method and 85% in the presence of microwaves (Table 1). The reactivity in epoxidation of cyclohexene decreases with the increase of Si/Nb ratio in obtained catalyst. It is noteworthy that low amounts of water do not interfere with the reaction in the Nb-PMOs systems. It was also observed that the calcined Nb-PMOs samples (after thermal treatment at 823 K in order to remove organic-bridging groups) showed lower catalytic conversion than the surfactant-extracted Nb-PMOs samples, where the organic groups are intact in the frame wall positions. Also in this case the most reactive catalyst was nioboorganosilicate with Si/Nb ratio of 16.

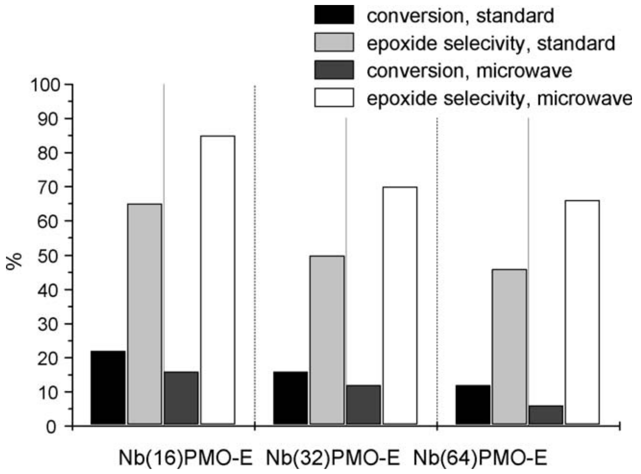

Fig. 4. Activity of nioboorganosilicates in oxidation of cyclohexene by hydrogen peroxide.

4. Conclusions

The ordered nanoporous ethane-bridged nioboorganosilicates have been synthesized by the simultaneous hydrolysis and condensation of bridged silsesquioxane precursors containing $-C_2H_4$-bridging groups in the presence of block copolymer P123 in acidic conditions using standard hydrothermal and microwave–assisted method. The presence of niobium and organic groups inside the framework and getting the hexagonally ordered structure of Nb-PMO-E were confirmed by various methods. The obtained materials were tested in reaction of epoxidation of cyclohexene using hydrogen peroxide as oxidant. The microwave-assisted cyclohexene oxidation over Nb-PMOs was completed within 60 min whereas the conventional oxidation took at least 36–40 h for completion. The epoxide yields obtained from microwave-assisted synthesis were slightly higher than from the conventional processes. In comparison with conventional heating, the microwave process is a very useful alternative for introducing of the oxirane ring because of the reduction of reaction time. This general and selective protocol is extremely fast and can be applicable to a wide variety of substrates.

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