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Rational design of NbMSU-X type nanoporous materials with desired textural properties

A. FELICZAK, I. NOWAK*

Faculty of Chemistry, Adam Mickiewicz University, ul. Grunwaldzka 6, 60-780 Poznań, Poland

The so-called rational design principle – synthesis of materials with predictable structures and textures – has been explored using appropriate organic molecular structure directing agent, i.e. *p*-nonyl phenyl polyoxyethylene (PEO) polyoxypropylene (PPO) ether and tetraethyl orthosilicate (source of silicone) as a linker agent connecting to metal nodes via oxygen to control pore size and functionality of open coordination lattices. To rationally design new nanoporous materials based on niobosilicate, a small library of NbMSU-X nanoporous materials has been collected and its composites have been investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and by nitrogen adsorption/desorption study. Design of structure directing agents and their composites with niobosilicates can lead to a rational synthesis of molecular sieves. We approach this strategy by using different pH and surfactant chain length.

Key words: *NbMSU-X synthesis; porous worm-like structure; characterization*

1. Introduction

Framework materials, three-dimensional (3D) solid-state assemblies, represent one of the most fascinating areas of current materials science. The significance of such constructions lays in their functional properties and applications as porous hosts for guest molecular species and as materials with interesting magnetic, electronic, optical and/or catalytic properties. A key topic of interest within the area of framework materials contains rational design and synthesis of such species allowing targeting properties of materials such as pore size, surface area, morphology, etc.

Nonionic alkyl poly(ethylene oxide) compounds are an important family of surfactants widely used as emulsifying, defoaming/antifoaming, coating, solubilizing, cleaning, lubricating and wetting agents. Pinnavaia et al. [1–3] used them to synthesize mesoporous silica and alumina in neutral aqueous solutions. The pore architecture of

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*Corresponding author, e-mail: nowakiza@amu.edu.pl

the MSU-X molecular sieve materials is described as 3D interconnecting networks of worm-like channels. Although this class of mesoporous molecular sieves shows ‘poor ordering’, potential advantages of so-called MSU-X synthesis are lower surfactant toxicity and cost, high biodegradability, effortlessness for removal and regeneration [4]. Among various mesoporous molecular sieves, MSU-X materials possess regular pore diameters and wall thicknesses similar to MCM-41-type materials but generally they do not exhibit a long-range periodicity. On the other hand, a more disordered structure could have an immense impact on the catalytic activity and thus the incorporation of niobium into MSU-X framework is in the frame of our interest, as NbMCM-41 appeared to be highly active in the reaction of epoxidation [5]. Recently, these imperfectly ordered mesoporous materials were claimed to be more active in diffusion-limited reactions due to a faster effective diffusion in comparison to MCM-41 and SBA-15 materials [6]. Various strategies of synthesis for MSU-X materials have been applied since the first report [1–4]. Usually, alkyl-polyoxyethylene (PEO), alkyl aryl-PEO, polyoxypropylene(PPO)-PEO block copolymers or Tween-type nonionic ethoxylated sorbitan esters are used as the structure directing agents under neutral or acidic conditions.

Here, we report the formation of mesoporous silicas using low-cost commercially available nonionic surfactants, namely *p*-nonyl phenyl polyethylene polypropylene ether. The aim of this work was to find the synthesis conditions that would lead to the formation of materials with various textural properties, which after incorporation of niobium, would gain catalytic activity for the liquid phase oxidation of substrates with various sizes.

2. Experimental

The NbMSU-X samples were prepared at room temperature (RT) by using two different nonionic surfactants Rokafenol N8P7 and N8P14: *p*-nonyl phenyl polyoxyethylene(PEO) polyoxypropylene(PPO) ethers of general formula: 2-[(4-nonylphenoxy)(ethoxy)$_8$(propoxy)$_y$]ethanol: with different polyoxyethylene (PO) group numbers, i.e., 7 or 14. Tetraethyl orthosilicate (TEOS, Fluka) and ammonium trisoxalate complex of niobium(V) were used as silicon and niobium sources, correspondingly. The TEOS/surfactant and Si/Nb molar ratios were kept as 7 and 32 in all syntheses, respectively. After mixing all the ingredients, pH of the synthesis gel was adjusted to 0.1, 2 or 6. The synthesis system was stirred at moderate speed for 20 h at RT. The solids were then recovered by filtration, washed with distilled water, and air-dried at RT overnight. The template was then removed by calcination in air at 873 K for 4 h. The samples used in this work will be denoted as follows: NbMSU-X-*y*-*z*, where *y* is the amount of PO groups in the surfactant and *z* – rounded pH of the synthesis gel.

Various physicochemical studies, viz., X-ray diffraction (XRD), transition electron microscopy (TEM), N_2 physisorption, X-ray fluorescence spectroscopy (XRF),

H_2-temperature programmed reduction (H_2-TPR) were used to find the location of niobium ions in the MSU matrix and to check the mesoporosity of the samples with an emphasis on verification how the pH may affect the property of the NbMSU-X materials. XRD patterns were measured with a TUR-62 diffractometer (CuK$_\alpha$ radiation, 40 kV) 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 at the relative pressure (p/p_0) from 0.05 to 0.2. Pore sizes were obtained from the N_2 adsorption branch, by the Barret –Joyner–Halenda (BJH) method with the corrected Kelvin equation, i.e. the KJS–BJH method at the maximum of pore size distribution [7]. Moreover, the α_s-plot analysis [8] 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 images were obtained using a JEOL-2000 transmission electronic microscope with an accelerating voltage of 80 kV. The metal content in the calcined NbMSU-X samples was determined by X-ray fluorescence spectroscopy (MiniPal, Philips) using calibration curves. The H_2-TPR of the samples was carried out using 10 vol. % H_2 in Ar as reducing agent (flow rate 10 $cm^3 \cdot min^{-1}$). The sample (0.1 g) was filled in a quartz tube, treated in a flow of helium at 623 K for 1 h and cooled down to room temperature. Then it was heated at the rate of 10 $K \cdot min^{-1}$ to 1373 K under the reducing mixture. Hydrogen consumption was measured by a thermal conductivity detector in the Micromeritics AutoChemII apparatus.

3. Results and discussion

The possibility of the isomorphous substitution of silicon with niobium in MSU-X mesoporous molecular sieves is dependent on the conditions of synthesis. The evolutions of Si/Nb ratio as a function of pH for NbMSU-X materials prepared with *p*-nonyl

Table 1. Structural and textural properties for NbMSU-X materials

Material	Si/Nb ratio	*d* [nm]	Surface area [$m^2 \cdot g^{-1}$]	Pore volume [$cm^3 \cdot g^{-1}$]				Pore width [nm]	t^a [nm]
				Total	Meso1st	Text.	Micro		
NbMSU-X-7-0	162	3.9	860	0.38	0.24	0.09	0.05	2.2	1.7
NbMSU-X-7-2	26	5.1	650	0.61	0.50	0.10	0.01	3.1	2.0
NbMSU-X-7-6	13	6.8	470	0.71	0.58	0.13	0.00	4.0	2.8
NbMSU-X-14-0	104	4.9	1020	0.47	0.35	0.08	0.04	2.6	2.3
NbMSU-X-14-2	24	6.0	860	0.65	0.55	0.10	0.01	3.6	2.4
NbMSU-X-14-6	12	7.6	640	0.80	0.69	0.11	0.00	5.2	2.4

[a] *t* – wall thickness calculated as the difference between *d* and a pore width.

phenyl polyoxyethylene polyoxypropylene ether with different (PO) group numbers, (7 or 14) are presented in Table 1. The Si/Nb ratios of the calcined products were four times higher than those of the initial gel mixtures at pH = 0.1 in the gel, indicating that not all niobium was incorporated to the final product. The Si/Nb ratio decreases with the increase of pH. At pH=6, the Si/Nb ratios are equal to 13, suggesting that a part of Si from the reactant mixture was not incorporated in the final product.

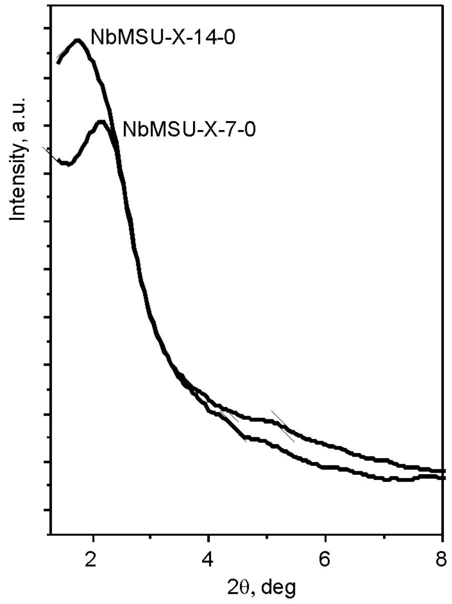

Fig. 1. XRD patterns for the NbMSU-X samples prepared at pH = 0.1

The powder XRD patterns of calcined NbMSU-X materials (representative low-angle diffraction patterns are shown in Fig. 1) showed single, rather broad peaks arising from the average pore–pore separation in the disordered worm-hole framework, characteristic of MSU-type materials. The mesoporous niobosilicates exhibit a single peak at low 2θ values in the X-ray diffraction patterns corresponding to a large *d* spacing whose intensity, position and width depend on the synthesis conditions. The basal distance (*d*) changed from 3.9 for pH = 0 to 6 for pH = 6 showing a gradual increase of the average pore-to-pore separation. The positions of the main diffraction line are correlated with the size of the surfactant. They moved to a lower 2Θ value upon increase of the PO group number (e.g., the *d* spacing increases from 3.9 to 4.9 for samples prepared at pH = 0.1 with the use of N8P7 and N8P14 types surfactants, respectively (Table 1)) thus suggesting the growth of the distance between two nearest pore centres. Additionally, X-ray diffraction data at high angles (2θ in the range of 10–60°) do not show any peaks of niobium(V) oxide phase.

The existence of the worm-like channel array was further confirmed by the transmission electron microscopy. Figure 2 shows the TEM micrograph of one representative of the NbMSU-X family. The disks of light contrast correspond to pores, while the dark networks represent silica walls. One can clearly see that this sample presents a worm-like structure which has commonly been observed for MSU-type materials. Both XRD patterns and TEM micrographs suggest that NbMSU-X samples belong to the MSU-type materials.

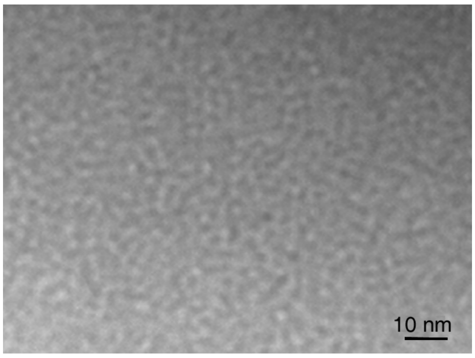

Fig. 2. Transmission electron micrograph for NbMSU-X-14-0

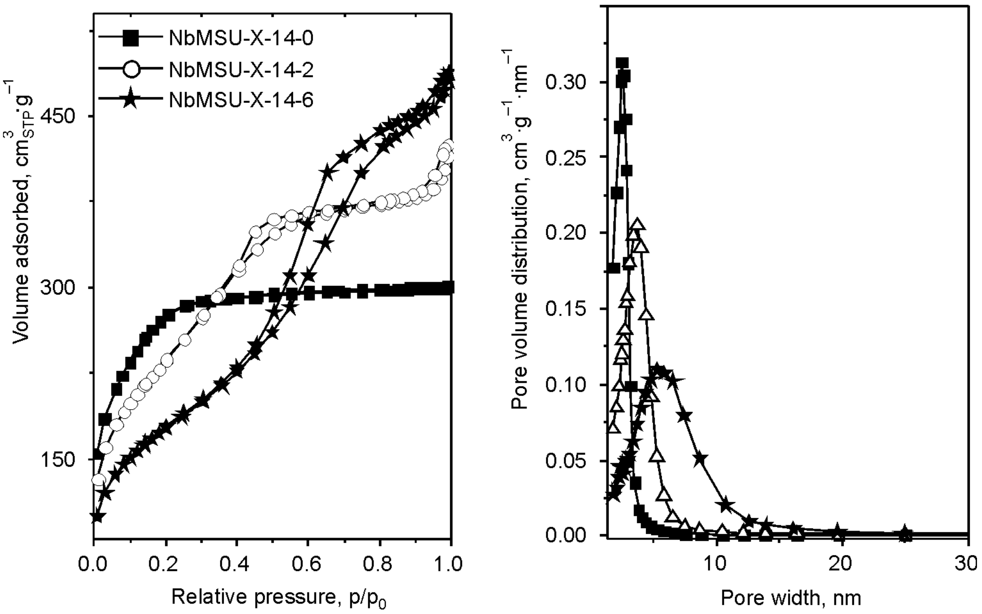

Fig. 3. Nitrogen adsorption-desorption isotherms at 77 K (left) and pore size distributions (right) for the NbMSU-X-14-z materials

Almost all N_2 isotherms for NbMSU-X samples (Fig. 3 shows nitrogen adsorption isotherms for a series of NbMSU-X-14-*z*) were of type IV, indicating that all materials belong to the mesoporous family. It should be noted that, with increasing pH value of the micellar solution from ~0.1 to 6.0, a sharp increase in the adsorbed volume (due to capillary condensation) shifts towards higher relative pressures. At pH = 6, the adsorbed volume still increases instead of reaching a plateau at high relative pressures. This explains the appearance of secondary porosity (compare textural pore volume in

Table 1). The N_2 isotherms for the NbMSU-X-14-0 (Fig. 3) and NbMSU-X-7-0 (not shown here) can be classified as intermediate Type I (characteristic of a microporous adsorbent) and IV isotherm in the IUPAC classification, which is characteristic of supermicroporous compounds, i.e., porous material with pores ranging between 1.5 and 2.0 nm [9, 10].

Narrow pore size distributions (PSDs) for mesoporous materials were characteristic of NbMSU-X prepared at pH = 0.1. The FWHM (full width at a half maximum) of about 1 nm measured for the pore size distribution curve (Fig. 3, right side) indicates that the NbMSU-X sample prepared via nonionic templating at very low pH has well-defined uniform pore dimensions. This behaviour is similar to that observed for mesoporous silicas prepared using ionic alkyl ammonium surfactants. The PSD became broader as the initial pH value increased and their maximum shifted from values below 2.6 nm for pH = 0.1 to 5.2 nm for pH = 6. It is worthy to stress that the NbMSU-X materials showed narrower PSD than the corresponding pure siliceous materials. The average pore widths estimated from the TEM images agree well with the results obtained from nitrogen adsorption data.

Table 1 summarizes all the textural characteristics of the niobium-containing MSU materials. The NbMSU-X samples hold the classical advantages of high surface area (~500–1000 $m^2\cdot g^{-1}$), large porosity (total pore volume up to 0.8 $cm^3\cdot g^{-1}$) and uniform pore size (pore width range: 2.4–5 nm) as typical mesoporous silicas. The evolutions of specific surface area vs. pH of micellar solution (Table 1) show that its value decreases between pH = 0.1 and 6. Despite incorporating large amount of niobium, the textural properties of NbMSU-X are better or similar to those of pure siliceous MSU-X (not shown here). The BET surface area for all niobium-containing materials studied was higher than that for corresponding pure siliceous materials. The total pore volume of Nb-containing materials was between 0.4 and 0.8 $cm^3\cdot g^{-1}$ with the highest value for pH = 6 and also higher than for siliceous ones. The existence of micropores in NbMSU-X is obvious from Table 1. The pore width increases with increasing number of PO groups. Notably, the pore-wall thickness, as obtained from the difference between the pore–pore correlation distance and pore width, increases from 1.6 to 3.0 nm with increasing acid concentration and was higher for NbMSU-X than for MSU-X. Such an effect was more pronounced for samples made with the assistance of N8P7 surfactant. Apparently, these results of the analysis of N_2 adsorption were consistent with the XRD and TEM observations.

H_2-TPR profiles of the series of materials prepared at pH = 0.1 are presented in Fig. 4. The materials show a main reduction peak starting at 1200 K assigned to the stepwise reduction of framework niobium [11]. The same profiles were also observed for samples prepared at higher pH values. The TPR studies indicate that for all materials, a strong interaction of niobium with the siliceous framework is evidenced and the reduction of framework niobium is difficult and observed at temperatures higher than 1200 K. Also the DR UV-Vis spectra (not shown here) of the NbMSU-X materials displayed similar features, consisting of the main absorption band at 220 nm that can be mainly ascribed to

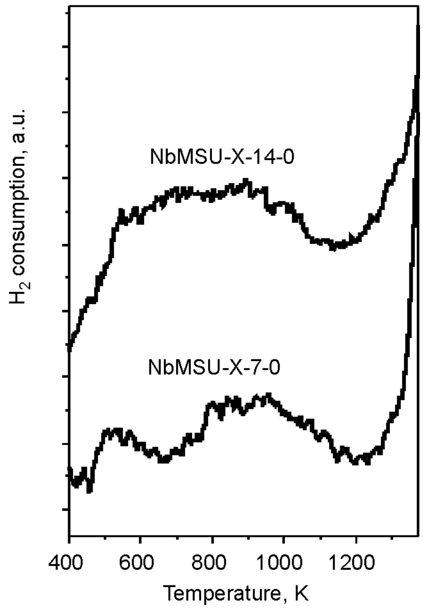

Fig. 4. H_2-TPR profiles for the NbMSU-X materials at pH = 0.1

Nb^{5+} in tetrahedral coordination [12]. No bands typical of five and six-coordinated Nb species (~250 nm) in small niobia nanodomains species [12] or of bulk niobia were observed in the spectra. Based on H_2-TPR and UV-Vis studies it is believed that niobium was incorporated into the framework of all samples studied.

4. Conclusions

The template properties have quite pronounced effect on the structural characteristics of mesoporous NbMSU-X molecular sieves prepared by using nonionic surfactant templates under acidic conditions. The ability of the *p*-nonyl phenyl polyoxyethylene polyoxypropylene ether/water micellar system to act as a template for the synthesis of mesoporous niobium-containing MSU-type materials was proved. As a result, supermicroporous and/or mesoporous molecular sieves of the NbMSU-X type have been synthesized by templating in strong acidic, acidic or almost neutral medium. Thus, the nanostructure of these materials can be monitored by the accurate control of the parameters of synthesis. Due to the simplicity of preparation and adjustable textural parameters, Nb-MSU-X materials can be expected to provide potentially high catalytic activity for a number of catalytic processes.

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