

Niobium-induced synthesis of SBA-15 type nioboorganosilicates - oxidation catalyst

Izabela Nowak* and Katarzyna Walczak

Adam Mickiewicz University, Faculty of Chemistry, Poznan, PL-60-780 (Poland)

*nowakiza@amu.edu.pl

Introduction

Periodic mesoporous organosilicates (PMOs) represent a new class of organic-inorganic hybrid materials suitable for a broad range of applications. Unlike in organic functionalized mesoporous silica phases obtained via grafting or co-condensation procedures, the organic groups in PMOs are direct parts of the 3D framework structure, thus giving rise to enormous possibilities to tune their chemical and physical properties in designated ways by varying the structure of the precursors [1]. The introduction of specific functionalities into the walls of mesostructured silicas has received a massive attention in order to improve the contact at the water (oxidant)-organic(cyclohexene) interface. We previously have found that Nb-containing mesoporous silica with isolated and tetrahedrally coordinated Nb-oxide species, when activated in acetonitrile with hydrogen peroxide (H_2O_2), catalyzes highly selective epoxidation of olefins [2]. In the present work, we have employed Nb-containing mesoporous organosilicates (NbPMOs) with $(-CH_2-)_n$ bridge synthesized by a surfactant templating method as the oxidation catalyst.

Materials and Methods

The nanostructured 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 (donated by ABCR). A triblock copolymer Pluronic P123 $((EO)_{20}(PO)_{70}(EO)_{20})$ (obtained from BASF) was employed as the structure-director. For all as-synthesized materials, the surfactant molecules were removed by solvent extraction (mixture of ethanol and HCl). The samples will be denoted as Nb(R)-PMO-E in the case of using ethylene and Nb(R)-PMO-O for octylene bridged organosilane, respectively, where R = Si/Nb ratio. The materials were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), adsorption measurements, DTG/TG, DR-UV-Vis, FTIR and Raman spectroscopies. They were tested in the liquid phase oxidation of cyclohexene at 318 K and hydroxylation of phenol at 333 K with H_2O_2 .

Results and Discussion

Highly ordered mesoporous nioboorganosilicates with large pores were synthesized for the first time under acidic conditions using nonionic surfactant as supramolecular structure directing agent. This synthesis afforded Nb-PMO materials with pore sizes between ~2.3-10.6 nm and specific surface areas in the range of 320-940 $m^2 g^{-1}$. Surface areas, pore sizes and pore volumes of the PMO materials are tabulated in Table 1. It is worthy to add that the use of large organosilanes (e.g., octylene bridged) as the exclusive silicon source under PMO synthetic conditions has led generally to amorphous materials, while in our case the highly porous materials were obtained (NbPMO-O vs. PMO-O in Table 1). Similarly to the pure niobosilica counterparts, Nb-PMOs exhibited XRD patterns dominated by low-angle peaks, typically with

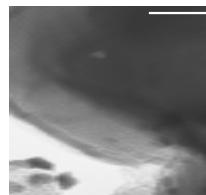


Figure 1. TEM image for Nb(16)PMO-E

a prominent peak at $2\theta < 1.6^\circ$. The transmission electron microscopy further confirmed the hexagonal arrangement of mesopores (Fig. 1). The FTIR and Raman data proved that the organic bridges are intact within the framework ((presence of $CH_2-Si(OSi\equiv)_3$ groups). Furthermore, these data provided evidence that the template was completely removed via extraction and there was no Si-C bond cleaved during synthesis and extraction stages. A band at ~220 nm on the UV-Vis patterns for Nb-PMOs clearly indicated a successful incorporation of Nb into the framework. The Nb-PMOs synthetic protocols offered opportunities for the preparation of hybrid inorganic-organic materials with cylindrical shape of particles.

As the Nb-containing mesoporous materials are expected to find applications as a water-tolerant solid catalyst for those reactions requiring weak acidic sites and low temperatures, we have tested the catalysts in the oxidation reactions. The activity in cyclohexene oxidation was found to be higher for Nb-PMO-O than for Nb-PMO-E materials. The new hydrophobic catalysts showed better performance (almost twice increase in epoxide selectivity) when compared to the niobosilica catalyst (i.e., Nb(64)SBA-15; Table 1). The catalytic potential of Nb-PMO is connected with the increased hydrophobicity. The increase in the carbon chain length of the organic molecule was a contributing factor for the increased hydrophobicity and thus a better selectivity (e.g., ~90% epoxide selectivity). It was moreover found that depending on the Nb content, the obtained materials showed significant differences in regards to their catalytic performance (low Si/Nb molar ratio, least active catalysts). Phenol conversion in water by NbPMOs prepared was ca. 15% (please note that the highest conversion at phenol: H_2O_2 = 3:1 is 33%) with the catechol/hydroquinone ratio of ~0.7.

Table 1. Textural data and catalytic performances of Nb-PMO samples

Catalyst	Surface area, $m^2 g^{-1}$	Pore width, nm	Mesopore vol., $cm^3 g^{-1}$	C_6H_{10} conv., %	Selectivity, %		
					Epoxide	Diol	Others ^a
Nb(16)-PMO-E	940	8.5	1.04	22	60	39	1
Nb(32)-PMO-E	820	9.8	1.00	18	47	52	1
Nb(64)-PMO-E	720	10.6	0.99	13	45	52	3
PMO-O	20	2.8	0.04	6	23	66	1
Nb(16)-PMO-O	400	2.4	0.54	79	88	10	2
Nb(32)-PMO-O	350	2.7	0.44	59	86	14	0
Nb(64)-PMO-O	320	2.8	0.37	48	88	11	1
Nb(64)SBA-15 ^b	900	10.3	0.96	49	48	48	4

^acyclohex-2-en-1-one; cyclohex-2-en-1-ol. ^b synthesized with TEOS as a Si source

Significance

The presence of niobium species neighboring with organic bridges in Nb-PMOs offers new prospects for application of these materials in catalysis. These nioboorganosilicates showed excellent catalytic activity and selectivity for direct oxidation of cyclohexene to epoxide and hydroxylation of phenol under mild liquid phase conditions.

References

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