

# “Hard” vs. “soft” template synthesis of mesoporous Nb<sub>2</sub>O<sub>5</sub> catalysts for oxidation reactions

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## Introduction

The discovery of M41S silicate materials opened a new era in the synthesis of ordered mesoporous materials and inspired the research for structurally similar phases with non-silicate compositions. Until recently, the processes used to synthesize mesoporous metal oxides afforded amorphous wall structures. Achieving a crystalline pore-wall structure has been an important issue in attempts to extend applications of mesoporous materials to heterogeneous catalysis. Numerous methods have been reported on the synthesis of nanoporous oxides [1]. “Soft” and “hard” templates are commonly employed for the preparation of oxide nanostructures [2]. Among transition metal oxides, Nb<sub>2</sub>O<sub>5</sub> is of great interest because of its photocatalytic properties. Here, ordered mesoporous silicas, SBA-15 and FDU-1, are used as hard templates [3], while for the first time alkyl polyethylene glycol ethers are employed as soft templates for the synthesis of thermally stable mesoporous Nb oxides.

## Materials and Methods

“Hard” *Template Synthesis*. SBA-15 and FDU-1 (designated later as T in the symbol) were synthesized using BASF<sup>®</sup> P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) and Dow Chemical<sup>®</sup> B50-6600 (EO<sub>39</sub>BO<sub>47</sub>EO<sub>39</sub>) triblock copolymers, respectively, HCl solution and tetraethyl orthosilicate (TEOS). Niobium in the form of ammonium tris(oxalate) complex ((NH<sub>4</sub>)<sub>3</sub>[NbO(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>]) was introduced into the mesopores by wetness impregnation method. The resulting samples were subjected to a programmed thermal decomposition up to 973 K. The product was impregnated for two consecutive steps. After each step of impregnation, the solid was recovered by filtration, washed, dried, and calcined as above. The silica template was removed from the final composite by treating several times with dilute sodium hydroxide (NaOH) solution. The nano-crystalline niobia will be denoted as NbH/T. “Soft” *Template Synthesis*. Alkyl polyethylene glycol ethers made from saturated linear alcohols: C<sub>16-18</sub>EO<sub>11</sub> (Lutensol<sup>®</sup> AT11, designated later as T in the symbol) and iso-C<sub>13</sub>EO<sub>10</sub> (Lutensol<sup>®</sup> TO10, C<sub>13</sub>H<sub>27</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>11</sub>OH) were used as structure directing agents. In a typical synthesis, a 0.17 mmol of template was dissolved in 10 cm<sup>3</sup> of ethanol. Then, a 0.0055 mol of niobium salt was added to this solution under vigorous stirring for 30 min, followed by addition of 0.018 mol of distilled water. The resulting sol solution was stirred for another 30 min and next was gelled at 313 K in air for 3 days. The first-step calcination was performed at 673 K for 20 h followed by the calcination at 973 K to obtain the final product. The nononiobia obtained using this method will be denoted as NbS/T.

The samples were studied by X-ray diffraction (XRD), transmission and scanning electron microscopies (TEM and SEM), N<sub>2</sub> sorption measurements, temperature programmed reduction (H<sub>2</sub>-TPR), and thermogravimetry (TG/DTA) and X-ray fluorescence spectroscopy (XRF).

## Results and Discussion

After calcination at 973 K all the nanoporous niobia samples exhibited only one peak in the small-angle XRD pattern. Moreover, the presence of high angle reflections in the XRD pattern of all the calcined Nb oxides demonstrated the crystalline nature (pseudo hexagonal niobia for NbS/T and pseudohexagonal and orthorhombic with the domination of the latter for NbH/T) of inorganic walls in the resulting mesoporous oxides. Nitrogen adsorption/desorption isotherms were type IV, which is typical for mesoporous materials. The surface area (SA) varied from ~10 to 60 m<sup>2</sup> g<sup>-1</sup> (Table 1). Depending on the different factors (silica or alkyl polyethylene glycol ethers types), the TPR profiles showed one, two or three peaks over a wide temperature range: the first one at 923 K, then an intermediate at 1150 K and finally ~1323 K, arising from the reduction of different Nb species, i.e., different clusters' sizes.

**Table 1. Textural data and catalytic performances of nononiobia samples**

Material	Surface area, m <sup>2</sup> g <sup>-1</sup>	Total pore vol. cm <sup>3</sup> g <sup>-1</sup>	Cyclohexene conv., %	Selectivity, %		
				Diol	Epoxide	Others
NbH/FDU-1	51	0.20	29.0	55.0	45.0	0
NbH/SBA-15	10	0.05	2.9	23.0	40.0	37.0
NbS/AT11	19	0.03	29.9	89.2	3.4	7.4
NbS/TO10	29	0.07	29.0	88.0	4.0	8.0
Nb <sub>2</sub> O <sub>5</sub> amorph.	3	0.01	0.7	94.0	5.2	0.8

Reaction conditions: reaction temperature 318 K, reaction time 40 h, cyclohexene/H<sub>2</sub>O<sub>2</sub> (molar ratio) = 1, solvent: acetonitrile;

The catalytic activity and selectivities in the oxidation of cyclohexene over various nanoporous niobia are shown in Table 1. Cyclohexene was oxidized to produce diol as a main product, together with cyclohexene oxide, cyclohex-2-en-1-one and cyclohex-2-en-1-ol as by-products. The cyclohexene conversion was accompanied by the corresponding increase in the diol selectivity, which reached the maximum level after ca. 1000 min in each case. The efficiencies of the oxidants (H<sub>2</sub>O<sub>2</sub>) were very high over all catalysts tested in this study (not shown here). The highest yield of diol was observed for the samples prepared via “soft” template method. Phenol conversion in water at 333 K by nanoporous niobia prepared with a use of different templates was ca. 20% (please note that the highest conversion at phenol:H<sub>2</sub>O<sub>2</sub> = 3:1 is 33%) with the catechol/hydroquinone ratio of 1. Catechol, hydroquinone and black tarry material were formed in liquid phase, while no benzoquinone was detected. It is evident that conversion was caused by surface modification because amorphous niobia was completely inactive in the phenol hydroxylation.

## Significance

The catalytic test results clearly indicate the advantages of nanoporous niobia for the catalytic oxidation of bulky molecules.

## References

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