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Mesoporous niobosilicates serving as catalysts for synthesis of fragrances

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ABSTRACT

Niobium-containing siliceous-MSU-X mesoporous molecular sieves have been prepared according to an original pathway by the reaction between low-cost niobium species (ammonium trisoxalate complex of niobium (V)), silica precursor (tetraethyl orthosilicate), and biodegradable surfactant in strong acidic, acidic or almost neutral medium. The selective oxidation of several terpenes and terpenoids (geraniol, limonene, α-terpineol) using hydrogen peroxide as an oxidant agent over novel Nb-catalysts is studied in this work. A variety of (Nb)MSU-X and (Ru,Nb)MSU-X materials prepared under different conditions has been employed (supermicroporous/mesoporous molecular sieves) for this purpose. The structure–function relationships in these catalysts are reported.

1. Introduction

The fragrance chemistry is a fascinating blend of natural product, synthetic, analytical, and physical chemistry with a certain amount of creative fantasy for odors and molecular structures. Terpenes are natural and sustainable feedstocks for the fine fragrance industry, as they can be used as intermediates and components for flavors and fragrances [1–4]. Both heterogeneous and homogeneous catalysis play here an important role and have grown extensively over the last few decades [3]. The epoxidation of terpenes is an attractive chemical transformation as such epoxides are versatile building units [4–7]. Particularly, epoxidation products, e.g., limonene 1,2-monoepoxide, are promising monomers for the synthesis of a new biodegradable "polylimonene carbonate" from biorenewable resources [8]. However, even nowadays the most useful way to obtain epoxides is the reaction between a peracid and the desired olefin, which cannot be considered an environmental friendly process (due to the formation of the corresponding acid). It is generally accepted that catalysis is the most important technology for "Green Chemistry". However, heterogeneous catalysis offers an additional advantage in facilitating separation at the end of the reaction and increasing catalyst life-time [e.g., 7]. Thus, the development of environmentally friendly solid catalysts for the synthesis of fine chemicals, pharmaceuticals and fragrances is becoming an area of growing interest because the use of heterogeneous catalytic processes allows easier separation, recovery, and recycling of the catalysts from the reaction mixtures.

Heterogenization chemistry is an art that requires a careful choice of support to deliver a catalytic species or "reagent" to a "location" where it is meant to achieve an catalytic effect. The synthesis of mesoporous materials is mainly related with "building mesopores" [9]. Mesoporous molecular sieves are obtained from the organic inorganic assembly by using soft matter, that is, organic molecules or supramolecules (e.g., surfactants). Nonionic surfactants are available in a wide variety of different chemical structures. They are widely used in industry because of attractive characteristics like low price, nontoxicity, and biodegradability [10–13]. One of them is the MSU-X porous structure that represents a 3D interconnecting network of 'worm-like' channels. The open frameworks and tunable porosities endow mesoporous materials with accessibility to chemical reagents. Our previous work showed the ability of the p-nonyl phenyl polyoxyethylene-polyoxypropylene ether/water micellar system to act as a template for the synthesis of the mesoporous silica and niobosilicate of MSU-type [14]. Few years ago, we reported high catalytic activity of MCM-41 materials containing niobium in the cyclohexene epoxidation [15]. Thus, in this work, we describe the activity of the heterogeneously catalyzed epoxidation of some terpenes/terpenoids using heterogeneous catalysts, i.e., mesoporous materials containing niobium ((Nb)MSU-X) or niobium and ruthenium ((Ru,Nb)MSU-X).

2. Experimental

The (Nb)MSU-X and (Ru,Nb)MSU-X samples were prepared at room temperature 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 poly-

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oxyethylene (PO) group numbers, i.e., 7 or 14. Tetraethyl orthosilicate (TEOS, Fluka, 99.9%), ammonium trisoxalate complex of niobium (V) (CBMM, Brazil, >98.0%), and chloropentaaminoruthenium (III) chloride (Strem Chemicals Inc., >98%) were used as silicon, niobium, and ruthenium sources, respectively. The TEOS/surfactant, Si/Nb, and Si/Ru molar ratios were kept as 7, 32, and 32 in all the syntheses procedures, respectively. After mixing all the ingredients, the pH of the synthesis gel was adjusted to 0.1, 2 or 6. The synthesis system was stirred at a moderate speed for 20 h at room temperature (RT). The solids were then recovered by filtration, washed with distilled water, and air-dried at room temperature 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: (Nb)MSU-*y*-*z* or (Nb, Ru)MSU-*y*-*z*, where *y* is the amount of PO groups in the surfactant and *z*—rounded pH of the synthesis gel.

Various physicochemical techniques such as XRD, TEM, N_2 physisorption, XRF, H_2-TPR, FTIR and DR–UV–vis spectroscopies, were used to find the location of niobium and/or ruthenium ions in the MSU matrix and to determine the mesoporosity of the samples. In addition, the pH effect on the properties of these materials was studied too.

The oxidation of terpenes/terpenoids was carried out in glass batch reactor under vigorous stirring at 313 K. The reaction was initiated by adding 2 mmol H_2O_2 (34%, 0.17 cm^3) to a mixture containing 2 mmol of terpenes (namely geraniol (IFF), limonene (IFF), a mixture of limonene and α-terpineol (IFF)), 0.04 g catalyst, and 10 cm^3 of ethanol. Aliquots of reaction mixture were drawn each hour until 6 h of a reaction time and after 23 h (by syringe through a septum without opening the reactor), diluted 20-fold with ethanol and analyzed by GC (Varian 3800 instrument, VF-5 ms capillary column). Products were quantified using calibration curves obtained with standard samples. The GC mass balance typically made up ca. 95% based on the substrate charged. The difference can be attributed to the formation of oligomers, which were not GC determinable. The reaction products were further confirmed by GC–(EI)MS–MS. The analysis was performed by using a Varian GC3800 gas chromatograph coupled with a Varian 4000 ion trap mass spectrometer.

3. Results and discussion

The evolution of Si/Nb ratio in a function of pH for (Nb)MSU-X and (Ru,Nb)MSU-X materials prepared with p-nonyl phenyl polyoxyethylenepolyoxypropylene ether with different (PO) group number, i.e., 7 or 14 was checked. The Si/Nb and Si/Ru molar ratios of the calcined products were four times higher than those of the initial gel mixtures in a case of pH = 0.1 in the gel, indicating that not all niobium/ruthenium were incorporated to the final product. The Si/Nb and Si/Ru molar ratios decrease with an increase of the pH value. Due to the lack of space the detailed characterization data will not be presented.

The powder XRD patterns of the calcined (Nb)MSU-X and (Ru,Nb)MSU-X materials showed a single, somewhat broad, peak arising from the average pore–pore separation in the disordered worm-hole framework, characteristic of disordered MSU-type materials. For higher pH values the main XRD peak was shifted to smaller 2θ angles suggesting the unit cell expansion. In addition, the main peak position shifted to smaller 2θ values ($d_{1\,0\,0}$ value) upon increase in the number of PO groups in the template suggesting an increase in the distance of two nearest pore centers. No XRD peaks corresponding to the presence of the bulk Nb_2O_5 phase and/or RuO_2 crystallites were observed over a wide range of 2θ angles.

Almost all the N_2 isotherms for (Nb)- and (Ru,Nb)MSU-X samples were of type IV in the IUPAC classification. It should be noted that, with increasing pH value of the micellar solution from ~0.1 to 6.0, the 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. The N_2 isotherms for the samples prepared at pH = 0.1 can be classified as intermediate type I (characteristic of a microporous adsorbent) and IV isotherm, which is characteristic of supermicroporous compound, i.e., porous material with pores ranging between 1.5 and 2.0 nm. The (Nb)- and (Ru,Nb)MSU-X materials studied possess high surface area (~500–1000 $m^2\,g^{-1}$), large pore volume (up to 0.8 $cm^3\,g^{-1}$) and narrow pore size distribution (~2.5–5.2 nm pore width range) that are typical for mesoporous silicas (Table 1). There are no significant differences in most textural parameters if one compares (Nb)MSU-X with (Ru,Nb)MSU-X.

The diffuse-reflectance UV–vis and H_2-TPR measurements (not shown here) additionally confirmed that niobium and ruthenium were incorporated into the MSU-X framework.

To conclude, supermicroporous and/or mesoporous molecular sieves of the (Nb)- and (Ru,Nb)MSU-X type have been synthesized by neutral templating in strong acidic, acidic or almost neutral medium. The nanostructure of these materials can be monitored by the accurate control of the synthesis parameters.

Terpenic-type compounds often show valuable organoleptic properties and form the largest group of modern fragrance ingredients. Geraniol is an interesting substrate that can be epoxidized to epoxy- or diepoxygeraniol (Scheme 1). In Fig. 1 the data on the catalytic activity of the different calcined (Nb)MSU-X materials after 23 h of the reaction is shown. The results of this monoterpene oxidation showed that 6,7-epoxygeraniol is the main product, followed by 2,3-epoxygeraniol and 2,3:6,7-diepoxygeraniol. The catalytic epoxidation of geraniol gives for (Nb)MSU-X ~98% selectivity for the 6,7-epoxide. With the niobium systems

Table 1
The structural/textural data for (Nb)- and (Ru,Nb)MSU-X materials.

Catalysts	Si/Nb, Si/Ru	$d_{1\,0\,0}$	Surface area ($m^2\,g^{-1}$)	Pore vol. ($cm^3\,g^{-1}$)		Pore width (nm)	Wall thickness (nm)
				Total	Meso		
(Nb)MSU-7-0	162	3.9	860	0.38	0.24	2.2	1.7
(Nb)MSU-7-2	26	5.1	650	0.61	0.50	3.1	2.0
(Nb)MSU-7-6	13	6.8	470	0.71	0.58	4.0	2.8
(Nb)MSU-14-0	104	4.7	1020	0.47	0.35	2.6	2.3
(Nb)MSU-14-2	24	6.0	860	0.65	0.55	3.6	2.4
(Nb)MSU-14-6	12	7.6	640	0.79	0.69	5.2	2.4
(RuNb)MSU-7-0	91, 89	4.1	820	0.38	0.20	2.2	1.9
(RuNb)MSU-7-2	44, 45	4.9	605	0.46	0.29	2.6	2.3
(RuNb)MSU-7-6	15, 15	6.8	450	0.74	0.57	4.3	2.5
(RuNb)MSU-14-0	109, 82	4.3	960	0.50	0.37	2.5	1.8
(RuNb)MSU-14-2	19, 49	5.9	650	0.61	0.44	3.7	2.2
(RuNb)MSU-14-6	16, 28	7.1	270	0.75	0.64	4.2	2.8