Catalysis Today 142 (2009) 288–292

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Mesoporous niobosilicates serving as catalysts for synthesis of fragrances

Agnieszka Feliczak-Guzik, Izabela Nowak *

Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, PL-60-780 Poznan, Poland

ARTICLE INFO

Article history:
Available online 24 January 2009

Keywords:
(Nb)MSU-X
Terpenes and terpenoids oxidation
Selective oxidation
Ru addition

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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* Corresponding author. Tel.: +48 61 8291207; fax: +48 61 8291207.
E-mail address: nowakiza@amu.edu.pl (I. Nowak).

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doi:10.1016/j.cattod.2008.11.027

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.

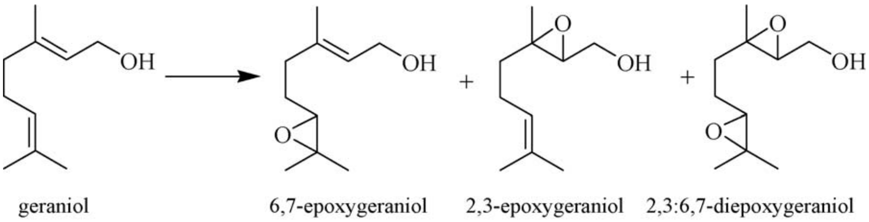
The diffuse-reflectance UV–vis and H_2-TPR measurements (not shown here) additionally confirmed that niobium and ruthenium were incorporated into the MSU-X framework.

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



Scheme 1. Geraniol oxidation pathway.

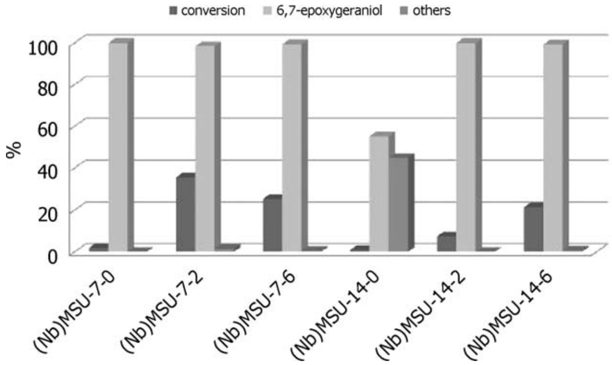


Fig. 1. Geraniol conversion and selectivity to monoepoxide over (Nb)MSU-X catalysts after 23 h of reaction time.

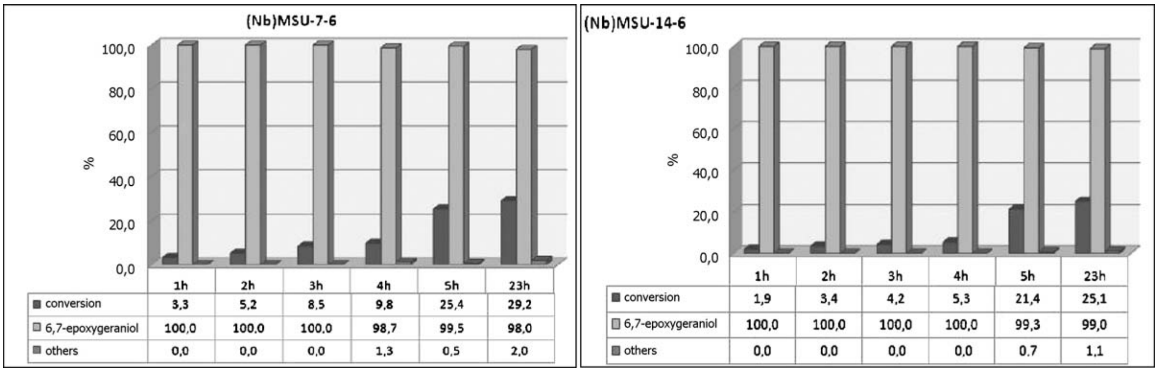
the epoxidation takes place exclusively at the more nucleophilic double bond (C6–C7). This is a typical behavior of an oxy species, which reacts faster with more electron-rich olefins. It is well known that the selectivity for epoxides could be understood through electronic structure calculations, which showed that the most nucleophilic group of each terpene is predominantly epoxidized [16].

The catalytic performance of (Nb)MSU-X samples as a function of the reaction time was studied (examples in Fig. 2). The catalytic activity was found to increase rapidly with the reaction time up to 5 h and then to slow down. The selectivity to monoepoxide almost does not change with time, although a small decline with time was observed.

The presence of ruthenium along with niobium in MSU-X materials was found to have negative effect as (Ru,Nb)MSU-X samples were less active (almost twice decrease in the activity) compared to Nb-containing samples (data not presented here). (Nb)MSU-X's higher conversion that can be related to the suitable hydrophilicity, acidity, and textural properties of the surface for the oxidative transformations is currently intensively studied. Moreover, one have to stress that geraniol was oxidized with hydrogen peroxide mainly to monoepoxide (2,3-monoepoxide:6,7-monoepoxide:2,3:6,7-diepoxides ratio of 0:99:1 at ~38% conversion), whereas in the homogeneous systems mainly diepoxides and mixture of products (10:69:21 at 40% conversion) were registered over methyl trioxorhenium and DMD systems, respectively [17].

A series of experiments was devoted to assessing the true heterogeneity of the (Nb)MSU-7-2 catalyst (Table 2). Several approaches were followed. First, the catalyst recycling was studied. The material was used in four subsequent runs. The oxidation of geraniol was tested with a fresh sample followed by a series of recycling using the solid isolated from the previous reaction mixture by simple hot filtration. The recovered solid was washed four times with ethanol, dried for 5 h in the oven at 383 K, calcined at 723 K and reused. As can be seen from Table 2, after four cycles there is no loss of activity (conversion was unchanged), while the selectivity to epoxide seems to benefit to some extent from recycling (a small increase was observed if one compares 2nd entry versus 1st entry). In a second type of experiment, the catalyst was removed from the reaction mixture after 23 h and extra amount of H_2O_2 was added to the clear filtrate (6th entry). After 10 more hours of stirring, the substrate conversion was still the same, proving that the filtrate does not contain catalytic niobium species (1st entry versus 6th entry). In a final test, the catalytic experiment was conducted with catalyst, H_2O_2, and solvent, but in the absence of geraniol. After 23 h the catalyst beads were removed by filtration and geraniol was added to the clear solution, which was stirred for 23 h at 313 K. This results in a conversion of 0.9%, which is hardly distinguishable from the background reaction (0.6%) with H_2O_2 in the absence of any catalyst (entries: 7 and 8). It can therefore be stated that the catalytically active compounds do not leach from the niobosilicate catalysts.

Limonene is one of the molecules of choice to study chemo- and regioselective catalytic oxidations. The oxidation of limonene, in principle, yields a variety of products (Scheme 2). Epoxides (1,2- and 8,9-epoxylimonene) are considered to be the selective products if the oxidation occurs at olefinic positions. Carveol and carvone will be the products if the oxidation takes place at allylic position. In addition, limonene has two olefinic bonds (1,2 and 8,9) and the oxidation can take place at either or both of these



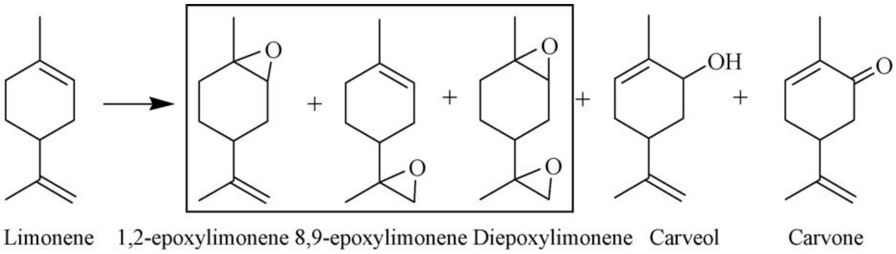
(Nb)MSU-7-6

	1h	2h	3h	4h	5h	23h
■ conversion	3,3	5,2	8,5	9,8	25,4	29,2
□ 6,7-epoxygeraniol	100,0	100,0	100,0	98,7	99,5	98,0
■ others	0,0	0,0	0,0	1,3	0,5	2,0

(Nb)MSU-14-6

	1h	2h	3h	4h	5h	23h
■ conversion	1,9	3,4	4,2	5,3	21,4	25,1
□ 6,7-epoxygeraniol	100,0	100,0	100,0	100,0	99,3	99,0
■ others	0,0	0,0	0,0	0,0	0,7	1,1

Fig. 2. The conversion and selectivity to monoepoxide as a function of reaction time over (Nb)MSU-7-6 and (Nb)MSU-14-6.



Scheme 2. Possible limonene oxidation pathway (the observed products are grouped in a square layout).

Table 2
Effect of catalyst recycling in the oxidation of geraniol with hydrogen peroxide catalyzed by (Nb)MSU-7-2.

Recycle	Conversion (%)	Epoxide selectivity (%)
Fresh cycle	38	97
First cycle	38	100
Second cycle	37	99
Third cycle	38	98
Fourth cycle	37	99
Filtrate after first run + H_2O_2	37	100
Filtrate after first run (reaction without geraniol) + geraniol	0.9	100
Blank (no catalyst)	0.6	100

sites. Most of the known solid catalysts [e.g., 18] yield significantly low limonene conversions and epoxide selectivities (~30%); carveol, carvone and polymeric products are formed in large quantities. The use of 34% hydrogen peroxide with a Nb-based catalyst yielded between 65% and 80% of the 1,2-limonene epoxide (70–100% selectivity), thus a high regioselectivity was observed. This could be possibly due to differences in the electron density of the olefinic (C1–C2) versus the (C8–C9) double bonds. The former is more electron-rich due to the neighboring methyl group than the latter. One has to mention, that the selectivity for these 1,2-epoxides is very high at the beginning of the reaction (100%). However, during the reaction it drops to 70% (after 23 h) due to the formation of diepoxide. It is well known that in the reactions with metal Schiff base complexes in homogeneous medium one often encounters catalyst deactivation due to the formation of oxo-bridged dimer complexes [19], whereas such characteristic was not present in our heterogeneous system (almost the same conversion was achieved in few consecutive oxidation reactions).

The oxidation of limonene with 1 equiv. of 34% H_2O_2 in the presence of a catalytic amount of (Nb)MSU-X proceeded regioselectively, but not stereoselectively, to afford a nearly 1:1 mixture of *cis*- and *trans*-limonene oxides in almost quantitative yield. Again, the presence of ruthenium besides niobium in MSU-X materials had a very negative effect on both conversion and monoepoxide selectivity in the oxidation of limonene.

A mixture of terpene and terpenoid, i.e., limonene (58%) and α-terpineol (42%) was also considered for the oxidation study. Such challenge, i.e., oxidation of two organic molecules in one batch, is not commonly employed. At the beginning of the reaction, the obtained mixtures have the monoepoxide as one of the most abundant products (see Fig. 3). At moderate conversions of the terpenic mixture, however, a production of monoepoxide is considerably reduced and hydroxyderivatives are the major products. The figures for product distribution suggest that the allylic products are being formed in consecutive processes (Scheme 3). The main product was 1-hydroxyterpineol formed by the acid catalyzed hydrolysis of the epoxy product in the presence of both Nb species and H_2O molecules. The other product – 1,3-cyclohexadiene-1-methanol – is considered to be formed via an intramolecular cyclization and hydrogen abstraction of 1-hydroxyterpineol or terpin-4-ol [19]. It is worthy to stress that 1,3-cyclohexadiene-1-methanol is a rather new fragrance ingredient that adds a leathery, spicy (clove), minty note to the formulation and enhances the leathery character thereof [20].

Obviously, a comparison of heterogeneous catalysts (Fig. 4) shows that materials prepared at pH~0.1 are less active in the

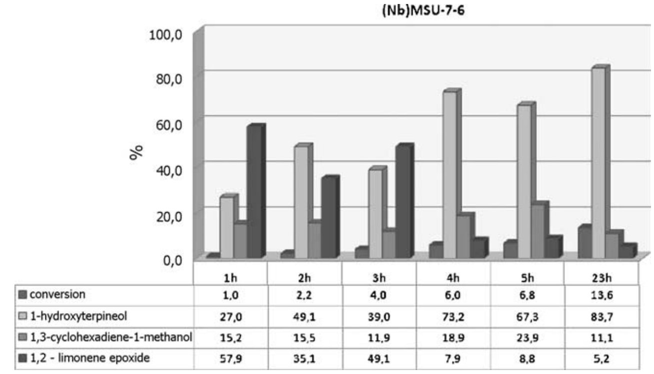
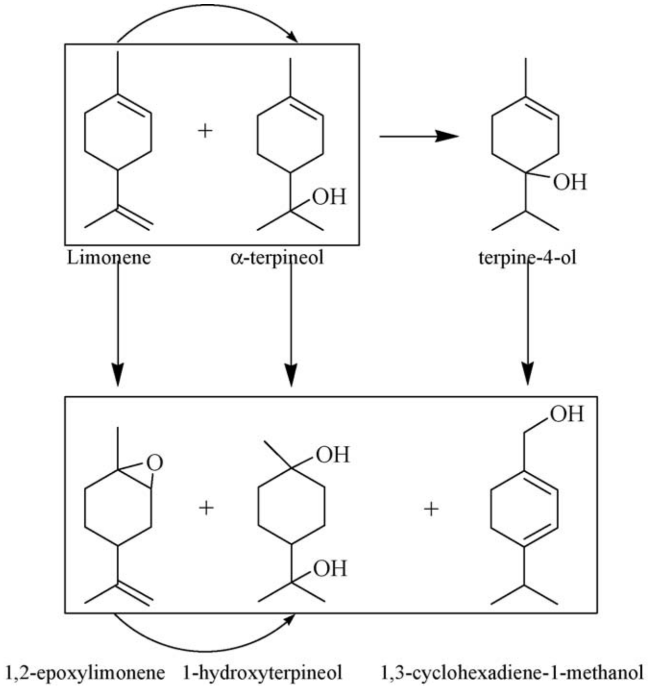


Fig. 3. The conversion and selectivities to main oxidation products for the oxidation of the mixture consisting of limonene (58%) and α-terpineol (42%) as a function of reaction time over (Nb)MSU-7-6.



Scheme 3. Limonene and α-terpineol oxidation pathways (the substrates and observed products are grouped in a square layout).

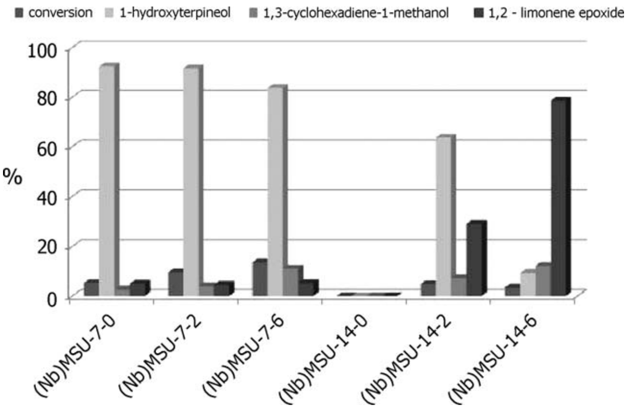


Fig. 4. The conversion and selectivities to main oxidation products for the oxidation of the mixture consisting of limonene (58%) and α-terpineol (42%) over (Nb)MSU-X catalysts after 23 h of reaction time.

oxidation of terpene/terpenoid compounds than those ones obtained at higher pH values. This hierarchy is a function of the surface area and probably the niobium dispersion/isolation and follows the same order as the epoxidation of geraniol. One can point out that for (Nb)MSU-X-7-0 and (Nb)MSU-X-14-0 supermicroporous “worm-like”-type porosity was registered that can explain lower activity of these materials in the oxidation of terpenes/terpenoids.

To summarize, the (Nb)MSU-X catalysts allowed higher conversions with a better selectivity for the terpene epoxides. The reasons for such better catalytic performance can be related to the suitable acidity and textural properties of the materials surface for the oxidative transformations. It was found that in all systems the starting monoterpenes as well as the primarily formed products could undergo various concurrent transformations, such as cyclization, H_α abstraction, addition, etc. with the balance between the reaction pathways being delicate.

4. Conclusions

Niobium and/or ruthenium containing mesoporous materials of MSU-X type have been synthesized. As a result supermicroporous and/or mesoporous molecular sieves of the (Nb)- and (Ru,Nb)MSU-X types have been synthesized by neutral templating route in strong acidic, acidic or almost neutral medium. The nanostructure of these materials can be monitored by the accurate control of the synthesis parameters. The worm-like pores and large pore volume of the (Nb)MSU-X materials facilitate the diffusion of the reactants and products molecules in the pore channels. The oxidations of terpenes showed good site- and chemoselectivity giving mono-epoxides as the major products. The optimal conversion was obtained for the (Nb)MSU-14-6 and (Nb)MSU-7-6 samples. The selectivity for epoxides could be understood through electronic structure assumptions, which is confirmed on the basis of the results that the most nucleophilic group of each terpene is predominantly epoxidized. This fact indicates that the oxygen transferred to the olefin acts as an electrophile.

Due to the simplicity of preparation, flexible particle size and adjustable pore size/wall thickness (Nb)MSU-X materials are expected to provide potentially high catalytic activity for a number of catalytic processes.

Acknowledgements

The authors would like to thank the Polish Ministry of Science and Higher Education for the partial financial support (COST Action D40; 2008-11). ROKITA (Poland), Companhia Brasilia de Metalurgia e Mineraçáo, and International Flavors & Fragrances (IFF) are acknowledged for donating surfactant, source of niobium and terpenes/terpenoids used in this study, respectively.

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