The use of gas chromatography coupled with mass spectrometry (GC-MS) for identification of fine chemicals

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Introduction

Controlled partial oxidation of natural products, such as terpenes, is one of the most important technologies to obtain cosmetic ingredients. For economic reasons, these processes mainly involve the use of molecular oxygen as the primary oxidant. Their success depends mostly on the use of a catalyst containing metal species in order to promote both the rate of reaction and the selectivity to partially oxidated products [1]. Both homogeneous and heterogeneous catalysts have been tested for this purpose over the last few decades [2].

The positive contribution of heterogeneous catalysis to fine chemistry is related to the characteristics role of the catalyst, i.e. [3]:

- to specifically activate a selected functionality; to make a chemical reaction more efficient, faster and more selective, and thus, to lower the raw material costs and/or increase the productivity
- to allow certain transformations to new molecular structures which are otherwise low-yielding, or even impossible by classical means. This often allows spectacular shortcuts through the synthetic pathways
- to have obvious ecological advantages, whenever the use of stoichiometric amounts of sometimes hazardous reagents can be avoided.

In this context, the use of heterogeneous catalysis in the liquid phase reactions towards the production of large amounts of chemicals is an obvious ambitious objective.

A wide variety of terpenes make a renewable, sustainable feedstock for the fine chemical industry [4]. These compounds are plentiful in the nature, i.e. in spice oils, citrus oils, pine oils and other natural products. Terpenes are an important source of ingredients and intermediates for flavors and fragrances and vitamins (e.g. A and E) [1]. The main structures of terpenes, which are used in the cosmetic manufacture are shown in Figure 1.

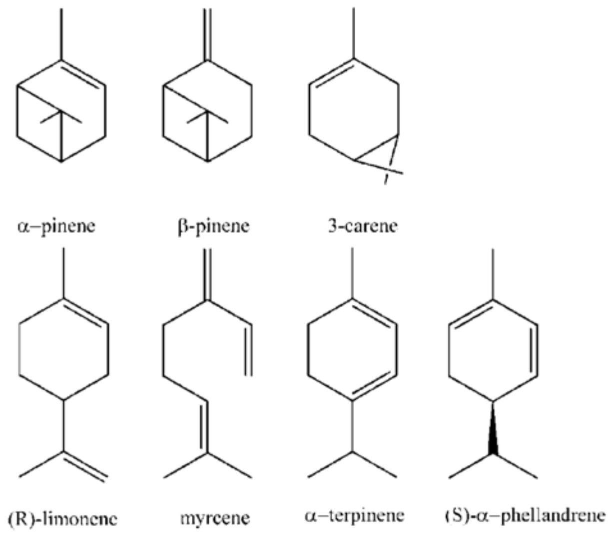


Fig. 1. The main structures of terpenes [5]

Catalytic transformations of terpenes are well documented [4 ,6, 7], comprising a wide variety of reactions: oxidation, hydrogenation, dehydrogenation, hydroformylation, hydration, carbonylation and etc. Terpenes can also be converted to the corresponding epoxides by reactions with hydrogen peroxide in the presence of various catalysts.

In our work we used mesoporous materials as catalysts. In this study we would like to test the activity of niobium species in epoxidation reactions of some terpenes using heterogeneous catalysts, i.e., mesoporous materials containing niobium and an environmentally friendly oxidant – hydrogen peroxide. Moreover, as the non-toxicity, of course, is *a conditio sine qua non*, thus the one-pot synthesis of Nb–type mesoporous materials was carried out using low cost and biodegradable surfactants as structure directing agents.

The synthesis of mesoporous materials is mostly related with "building mesopores" [8]. 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 accessible in a wide variety of different chemical structures. They are extensively used in industry because of attractive characteristics like low price, nontoxicity, and biodegradability [e.g. 9]. One of them is the SBA-15 porous structure that represents a 2D hexagonally organized network. The open frameworks and tunable porosities endow mesoporous materials with accessibility to chemical reagents, so these characteristics are really important in the field of catalysis.

Experimental

To this end niobium-containing mesoporous materials of SBA-15 type have been synthesized. The procedure for the synthesis of NbSBA-15 involves the addition of tetraethyl orthosilicate (TEOS) and ammonium tris(oxalate) complex of niobium(V) to a solution of commercially available surfactant Pluronic P-123 (ig.2). The Si/Nb ratio was kept as 64.

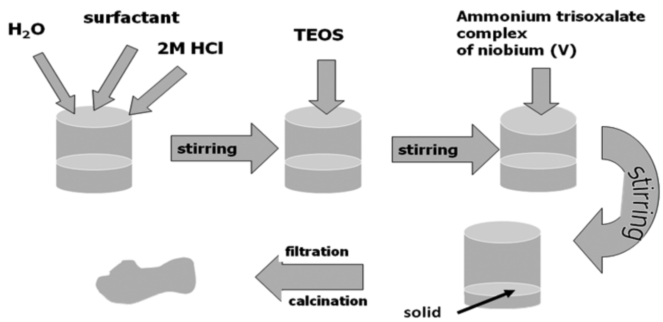


Fig. 2. NbSBA-15 synthesis scheme

The epoxidation reactions were carried out in a glass batch reactor at 313K using ethanol as a solvent (10 cm^3), 2 mmols of terpene (geraniol or α-pinene), hydrogen peroxide as an oxidant

(oxidant:substrate molar ratio = 1) and 40 mg of solid catalyst. Samples were taken after a reaction time of 1, 2, 3, 4, 5 or 24 h and analyzed by Varian GC3800 gas chromatograph using a flame ionization detector and VF-5MS column. The final product identification was made by GC-(EI)MS-MS. The analysis was performed with a Varian GC3800 gas chromatograph coupled with a Varian 4000 ion trap mass spectrometer.

Results

The synthesized material was characterized according to the standard physico-chemical methods for mesoporous materials (not shown here). It should be mentioned that NbSBA-15 catalyst exhibited the XRD pattern with five well-defined hk0 reflections that were indexed to a p6m hexagonal lattice of pores. Nitrogen sorption isotherms exhibited type-IV isotherms typical of mesoporous materials. The framework confined mesopore diameters, volumes and surface areas were typical of SBA-15-type mesoporous materials and are presented in Table 1. Additionally Nb-containing SBA-15 revealed in TEM micrographs hexagonally organized channels with a size of about 8 nm.

Table 1

Textural properties of the NbSBA-15 material

Surface area m^2g^{-1}	Pore, volume $cm^3 g^{-1}$			Pore size, nm	Wall thickness, nm
	total	meso	micro		
900	0.88	0.80	0.08	8.40	3.12

Oxidation reactions are very important in the syntheses of fragrances. The epoxidation reaction discovered in 1980 by Sharpless and Kazuki [10] is a very fine example of the strategy of using a reagent to control stereochemistry. When achiral allylic alcohols are employed, the Sharpless reaction exhibits exceptional enantiofacial selectivity and provides convenient access to synthetically multifunctional epoxy alcohols. The NbSBA-15 samples that were used for catalytic oxidation in the liquid phase of geraniol and α-pinene with hydrogen peroxide showed good activity. Moreover, NbSBA-15 showed very high activity and high selectivity towards oxidation of terpenoid compounds (Fig. 3).

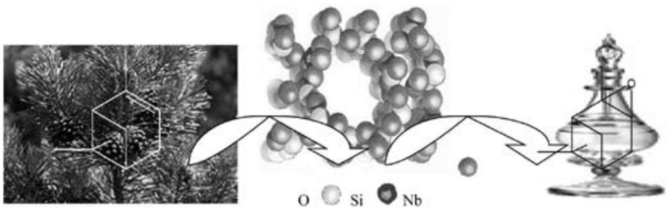


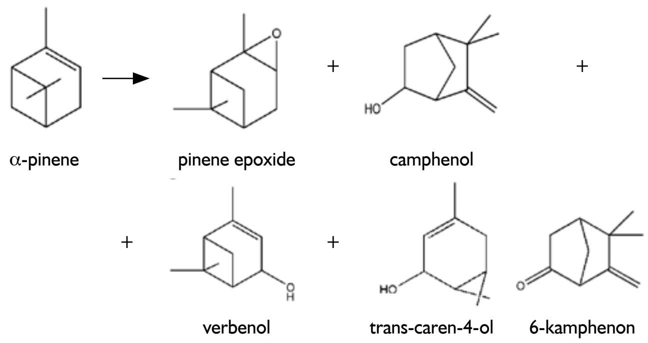
Fig. 3. Application of mesoporous molecular sieves for the synthesis of fragrance ingredients

The catalytic epoxidation of α-pinene was one of the reaction that has been chosen for study. The use of 35% hydrogen peroxide with Nb-based catalysts yielded around 65% of pinene epoxide. The other products were also: verbenon (~20%), camphenol (~10%) or trans-caren-4-ol (5%). The oxidation pathway is presented in scheme 1.

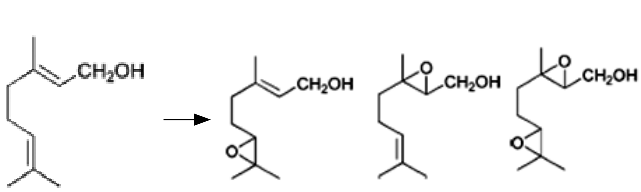
Geraniol was another interesting substrate that can be epoxidized to epoxy- or diepoxygeraniol (scheme 2).

Figure 4 shows the data on the catalytic activity of the NbSBA-15 materials till 24 h of the reaction .

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.This reactivity can be attributed to a highly active niobium-oxo species. With the niobium systems the epoxidation takes place exclusively at the more nucleophilic double bond. This is a typical behavior of an oxy species, which reacts faster with electron richer olefins. In these reactions we obtained new compounds – terpenoid, which we can use in cosmetic industry.



Scheme 1. α-Pinene oxidation pathway



Scheme 2. Geraniol oxidation pathway

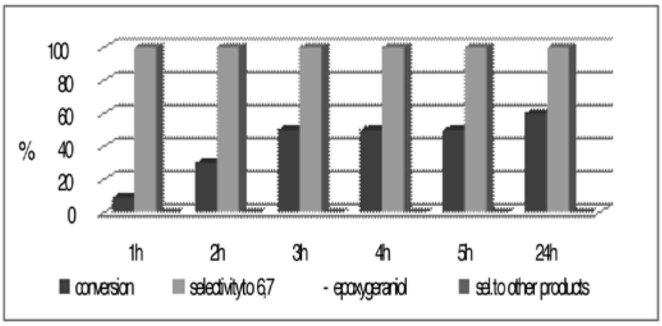


Fig. 4. Geraniol conversion and selectivity to monoepoxide over NbSBA-15 catalyst after the first to fifth hours and after 24 h of reaction

Summary

The results obtained have shown that NbSBA-15 materials can be used in the epoxidation of "bulky" terpenoic olefins molecules using hydrogen peroxide as oxidant agent.

Acknowledgement

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English translation by the Author

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Izabela NOWAK – D.Sc., is an Associate Professor and Head of the Applied Chemistry Group at the Faculty of Chemistry, the Adam Mickiewicz University (AMU) in Poznań. She was granted from TEMPUS a scientific fellowship at the University of Reading, U.K., in 1992-1993, where she wrote her M.Sc. thesis. She received her M.Sc. in chemistry in 1993 from the AMU, where she also obtained a Ph.D. in chemistry in 1996. She received a postdoctoral training at the Leverhulme Centre for Catalysis in Liverpool. In 2006, she was awarded the degree of D.Sc. (habilitation) for the research on synthesis, characterization and catalytic properties of nanoporous materials for the liquid-phase oxidation processes. Her current scientific interests are focused on synthesis and modification of novel ordered materials, textural/structural/surface/acid-base/redox properties of thereafter, heterogeneously catalyzed synthesis of fine and intermediate chemicals and modern synthesis strategies for cosmetics and cosmeceuticals. She has published more than 80 papers, 3 patents, and made more than 140 presentations at symposiums and conferences.

„Schools of Leaders" received certificates

Representatives of 43 Polish universities received "School of Leaders" certificates, awarded to universities for combining education quality with practical education of students and conducting studies in a manner that best prepares graduates for their future careers. Certificate ceremony was held at the Jagiellonian University. The competition was organised under the auspices of the European Parliament.

"The competition +School of Leaders+ awards universities that educate creative graduates, equipped with extensive knowledge and practical skills, and thus attractive on the labour market.

"School of Leaders" certificates were awarded in three categories: public university, private university, and public higher vocational school. Seven of certificates awarded in the "public university" category, 28 - in the "private university" category, and eight went to "public higher vocational schools".

After many years of contacts with young people I know how much the students appreciate the education at the universities cooperating with their environment, providing practical education, how much they care about having skills that can be successfully +sold+ in the labour market when they graduate. It seems clear that universities should remember and provide this. However, vary often they do not. Universities often educate in isolation from market realities, current trends in the economy. They are often not sufficiently flexible, they do not react to the reality that surrounds them as quickly, as students and candidates would expect them to. In this respect, you are leaders, and for that you receive these awards.

"School of Leaders" certificates were awardedby the jury composed of scholars from Polish public and private universities. The jury was chaired by Prof. Dariusz Rott, a member of the Higher Education Council, professor at the University of Silesia and an expert of the Ministry of Education.

Certificates were given to schools, which scored at least 50 ranking points in the competition procedure, in 90 points possible to obtain. Points were given by reviewers evaluating applications of universities. Each application was verified independently by three competition reviewers.

10 universities received "Primus" awards: Maria Curie-Skłodowska University in Lublin, the University of Białystok, Łazarski School in Warsaw, Gdańsk University of Technology, Wrocław University of Environmental and Life Sciences, Wrocław School of Banking, Jan Amos Comenius State Higher Vocational School in Leszno, the Witelon University of Applied Sciences in Legnica, Andrzej Frycz Modrzewski Kraków University and Stanisław Staszic College of Public Administration in Białystok.

"Aurea Praxis" awards went to: Rector of Collegium Civitas in Warsaw Prof. Edmund Wnuk-Lipiński, in recognition of "activities aimed at improving the quality of teaching and heading the university implementing a modern and flexible curriculum based on practical education, preparing for life and career in a globalised world".

The second winner was the rector of Jan and Jędrzej Śniadecki University of Technology and Life Sciences in Bydgoszcz Prof. Antoni Bukaluk. He received the award for "the creation in Bydgoszcz of the Regional Innovation Centre, with a purpose of initiating the distribution of innovative information for the entire Kujawsko-Pomorskie region and establishing and strengthening relations between science and economy".

The third winner of the "Aurea Praxis" award was Rector of Nicolaus Copernicus University in Toruń Prof. Andrzej Radzimiński for "the creation at the Nicolaus Copernicus University in Toruń of the most modern online public university career office for students and graduates".

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