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Review

Oxidation of olefins employing mesoporous molecular sieves modified with copper

Analía L. Cánepa[a,c], Corina M. Chanquía[a,b], Griselda A. Eimer[a,c], Sandra G. Casuscelli[a,c,*]

[a] Centro de Investigación y Tecnología Química (CITeQ)/Universidad Tecnológica Nacional, Facultad Regional Córdoba (UTN-FRC), Maestro López esq. Cruz Roja Argentina, S/N, X5016ZAA, Córdoba, Argentina
[b] Centro Atómico Bariloche - Comisión Nacional de Energía Atómica, CNEA-CONICET, Bustillo 9500, S.C. de Bariloche, R8402AGP, Río Negro, Argentina
[c] CONICET: Consejo Nacional de Investigaciones Científicas y Técnicas, Av. Rivadavia 1917, C1033AAJ, Buenos Aires, Argentina

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ABSTRACT

M41S type nano-structured materials prepared with Cu contents varying from 1.2 wt% to 6.9 wt% were synthesized by the template ion exchange method to be used as potential catalysts in the reaction of α-pinene oxidation with H_2O_2. The catalysts were evaluated in the test reaction of cyclohexene oxidation as a method of selecting the most active material. The material selected for the oxidation of α-pinene was the one with the highest content of Cu (~7%, w/w) due to its high activity and selectivity to allylic oxidation products. A reaction mechanism was proposed in order to explain the obtained results. The α-pinene conversion was closed to 25% being verbenone the major product. The stability of the catalyst to the leaching of the active species and the possibility of recycling were checked. The results confirm that the Cu species are not leached during the reaction. Thus heterogeneous catalyst can be recovered and reused many times without loss in catalytic activity and selectivity.

Contents

1. Introduction

The oxidative functionalization of olefins is a very useful reaction, both to organic synthesis and to industrial production of fine chemicals. The olefins can undergo several different modes of attack by the oxidant: epoxidation and oxidative cleavage of the double bond as well as oxidation of allylic C-H bond [1]. Typically, the electrophilic attack on the double bond of the cyclic olefin leads to epoxidation or ring cleavage. In contrast to epoxidation, allylic oxidation preserves the olefinic function in the product, which allows further processing even more useful. Allylic oxidation is a process which involves free radicals and which is more likely to occur when the oxidizing metallic species are in a low oxidation state. On the other hand, epoxidation is normally associated with peroxometallic species [2]. In practice, epoxidation and allylic oxidation are often competitive processes in the oxidation of cyclic olefins and frequently both processes occur simultaneously producing a mixture of reaction products [3]. However, allylic oxidation products are found when hydrogen abstraction is the dominant reaction.

* Corresponding author. Tel.: +54 351 4690585; fax: +54 351 4690585.
E-mail addresses: scasuscelli@scdt.frc.utn.edu.ar, sandracasuscelli@yahoo.com.ar (S.G. Casuscelli).

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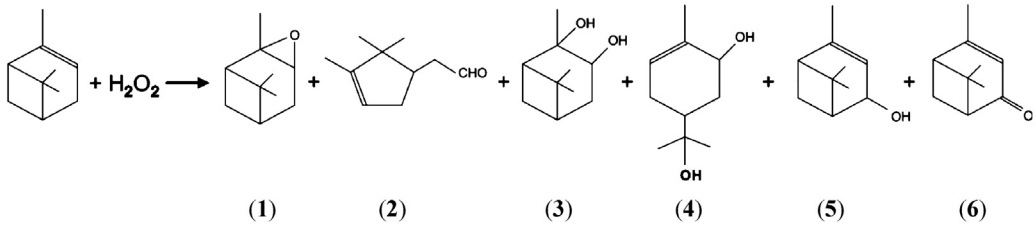


Scheme 1. Products obtained from α-pinene oxidation. α-Pinene oxide (**1**), campholenic aldehyde (**2**), 1,2 pinanediol (**3**), trans-sobrerol (**4**); verbenol (**5**), verbenone (**6**).

The cyclohexene is one of the most structurally simple cyclic olefins, which offers the opportunity to study the effects of different variables that lead to allylic oxidation and/or epoxidation. The oxidation of cyclohexene with hydrogen peroxide (H_2O_2) is frequently used as a test reaction to select the most active catalysts. Then these are evaluated in the oxidation of other more complex cyclic olefins, such as terpenes. The terpenes present in plants are generally composed of several "isoprene units"; the compounds that have two isoprene units are called monoterpenes. The turpertine oleoresin obtained from coniferous and terebinth trees and also essential oils from citrics are two of the most important sources of terpenes. Terpenes constitute a type of natural products that can be transformed into novel and valuable compounds commercially important for the industrial production of fragances, perfumes, flavors, and pharmaceuticals as well as useful synthetic intermediates and chiral building blocks [4]. The oxidative functionalization of monoterpenes represents an important way to value these natural products since terpenic aldehydes, alcohols and esters can be produced. These compounds often show high volatility and desired organoleptic properties; for that reason they are present in the composition of a great number of modern fragrances [5]. The α and β-pinene are bicyclical monoterpenes, which are constituents of the wood and oils of an extensive variety of plants [6] and they can also be obtained as sub product of paper industries. α-Pinene is the main component of gum turpentine, and it is also a low-cost and readily available renewable raw material for the production of a wide variety of fine chemicals, such as fragrances, flavors, drugs, and agrochemicals [7,8]. α-pinene gives valuable oxygenated products such as α-pinene oxide (**1**), campholenic aldehyde (**2**), verbenol (**5**) and verbenone (**6**) (Scheme 1). The campholenic aldehyde is obtained by the rearrangement of the α-pinene oxide, the verbenol and verbenone are obtained from the allylic C-H bond oxidation of α-pinene [9]. Among the oxidation products of α-pinene, verbenone is of great interest because it can provide a possible starting point for the synthesis of taxol, an important therapeutic agent. In addition, verbenone can also be used as an intermediate for the manufacture of pesticides and the flavor industry [10,11]. However, a limited number of investigations on the catalytic oxidation of terpenes have been reported [12–14].

Traditionally, the conventional production of many fine chemicals involves oxidations with oxidizing reagents stoichiometric, resulting in the generation of effluent pollutants. Therefore, it is very important replace to these antiquated technologies with cleaner alternatives. Thus the use of environmentally friendly oxidants in conjugation with heterogeneous catalysts, leads to efficient procedures to perform many oxidative reactions [2,15].

The incorporation of transition metals as active sites into the framework of mesoporous materials MCM-41, MCM-48, HMS, MSU and SBA-15) has been a significant advancement in oxidation reactions in liquid phase [16,17]. Since the discovery of the M41S family of mesoporous molecular sieves [18], a great number of researches have been devoted to the well-defined mesoporous molecular sieves that belong to the M41S family. One form of this series, MCM-41 nano-structured materials, which possesses a uniform arrangement of hexagonally shaped mesopores of diameter varying from 20 to 100 Å, have received great attention in materials science and as catalysts in oxidation reactions involving bulky molecules [9,19].

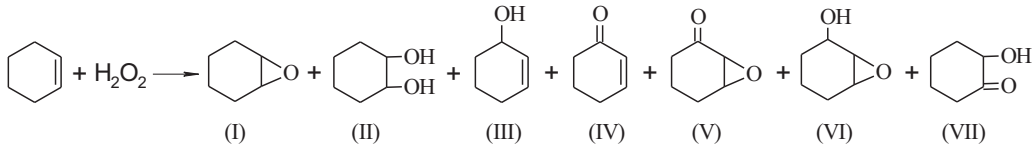
M41S type mesoporous materials modified with transition metals can be prepared by different synthesis methods such as: the direct hydrothermal (DHT) method and the template-ion exchange (TIE) method. The most extensively studied method is DHT, i.e. directly adding the metal ion precursors to the synthesis gel before hydrothermal synthesis. On the other hand, by the TIE method, the metal ions are implanted by exchanging the template cations embedded in the channels of the MCM-41 with the metal ions in solution. Thus, Wang and co-workers have applied these methods, i.e., DHT and TIE to the syntheses of V-, Fe-, Cr- and Mn-MCM-41 [20,21]. The two methods resulted in different locations and coordination environments of the incorporated metal cations. The TIE method provided highly dispersed metal ions on the wall surface of MCM-41 inside the mesopores and the DHT method tended to incorporate metal ions inside the framework of MCM-41. Finally, Liu et al. employed the TIE as one of the methods to prepare copper supported on MCM-41 and they examined the influence of metal introduction technique on the NO reduction [22].

There are numerous reports about the application of mesoporous catalysts modified with Ti and V by DHT in the processes for oxidation of olefins with H_2O_2, showing high conversion levels [23,24]. However, mesoporous materials modified with Cu have almost not been evaluated in this process [25], despite of its higher reduction potential with respect to other transition metals like Fe, Mn, Ni y Co [26] and particularly lower cost [27,28]. The nature and distribution of copper nanospecies in M41S type mesoporous molecular sieves prepared by the template-ion exchange method, as well as a preliminary catalytic testing in the oxidation of cyclohexene, have been recently presented and discussed by us [29]. In this work, we continue the study of the catalytic evaluation of the copper-containing MCM-41 synthesized by the TIE method, paying special attention to establish the relationships between the distribution of copper nano-species and the activity. A possible mechanism of interaction between H_2O_2 and the catalyst was proposed and tested in order to explain the formation of allylic oxidation products. Then, the most active catalyst was evaluated in the α-pinene oxidations under similar conditions of reaction. In order to improve the yield to allylic products, the influence of the molar ratio of α-pinene/H_2O_2 on the course of oxidation reaction was examined. Finally, the reaction heterogeneity and the possibility of reusing the catalyst were evaluated.

2. Experimental

2.1. Catalyst synthesis and characterization techniques

The parent siliceous mesoporous molecular sieve (Si-M) was synthesized using cetyltrimethyl ammonium bromide (CTABr, Aldrich) as template and tetraethoxysilane (TEOS, Fluka ≥98%) as Si source. In a typical synthesis, TEOS, a solution of CTABr in ethanol and a aqueous solution of the tetraethylammonium hydroxide (TEAOH, Sigma-Aldrich) were continuously stirring for



Scheme 2. Products obtained from cyclohexene oxidation. Cyclohexene oxide (I), 1–2 cyclohexanediol (II), 2-cyclohexen-1-ol (III), 2-cyclohexen-1-one (IV), 2,3-epoxy-cyclohexanone (V), 2,3-epoxy-cyclohexen-1-ol (VI) and 2-hydroxycyclohexanone (VII).

3 h. Finally, the remaining TEAOH and the water were further added dropwise to the milky solution which was then heated at 80 °C for 30 min to remove ethanol used in solution and produced in the hydrolysis of TEOS. The molar composition of initial gel was: TEAOH/Si = 0.3; CTABr/Si = 0.3; H_2O/Si = 60. In order to obtain the mesoporous molecular sieves modified with copper by TIE method, the as-synthesized Si-M was vigorously stirred with different concentrations of a $Cu(NO_3)\cdot 3H_2O$ (Anedra) aqueous solution at ambient temperature for 1 h, according to the procedure described by us elsewhere [29]. These copper-modified catalysts were named as Cu-M(x), where x indicates the copper content in wt.% in the final solids. The characterizations of the materials evaluated in this work were previously reported [29]. Here, we mention only those aspects which are relevant to the catalytic activity. In addition, the stability and the possibility of catalyst recycling were evaluated by Inductively coupled plasma optical emission spectroscopy (VISTA-MPX CCD Simultaneos ICP-OES – VARIAN) and by diffuse reflectance UV–vis spectroscopy (UV–vis-RD Jasco V 650).

2.2. Catalytic activity

2.2.1. Oxidation of olefins

The oxidation reactions of α-pinene and cyclohexene with H_2O_2 were performed as it was described in a previous report [29,30]. Reaction products were identified by mass spectrometry (Shimadzu GC MS-QP 5050) with a HP-5 capillary column. The percentage of each component in the reaction mixture was calculated by using the method of area normalization employing response factors. The relative uncertainties of the measurements were tested with repeated determinations. The percent relative uncertainty (CV (%)) of the result was calculated by dividing the corresponding absolute uncertainty with the average of the measurements.

A set of experiments was carried out changing the α-pinene/oxidant molar ratio to 4/1, 2/1 and 4/1 with a further addition of H_2O_2 after half an hour of reaction. This addition was carried out without opening the reactor to atmosphere and the added amount of H_2O_2 was the required to reestablish the starting molar ratio 4/1. The total conversion of H_2O_2 was measured by iodometric titration. The H_2O_2 efficiency was calculated as the percentage of this reactive converted to total oxidized products.

Finally, to check the stability and recycling ability as well as leaching of Cu species from mesoporous matrix under reaction conditions, several recycling experiments were carried out for the Cu-M(6.9). After the reaction was over, the catalyst was separated from the reaction mixture washed with CH_3CN and calcined in air at 500 °C overnight to be used again with fresh reaction mixture in different catalytic cycles.

3. Results and discussion

3.1. Catalytic test

The main products obtained during cyclohexene oxidation on Cu-M(x) catalysts are shown in Scheme 2. According to GC–MS analyses, the products mixture is composed of species formed by oxidation of double bond, oxidation of allylic C–H and overoxidation products. The formation of product I is attributed to the oxidation of π bond, specie II is formed by hydrolysis of oxirane ring, whereas species III and IV are generated by oxidation of allylic C–H bond. Meanwhile, the products V, VI and VII appear by a process of overoxidation. These products can be formed by a set of sequential reactions; thus, for example, the acetone (IV) and the alcohol (III) can then undergo a further epoxidation of the double bond leading to the formation of the overoxidation byproducts (V and VI). In addition, the glycol can be dehydrated into the allylic alcohol or dehydrogenated to corresponding α-keto-alcohol (VII).

Results of the catalytic activity of Cu-M(x) materials for cyclohexene oxidation after a reaction time of 5 h are shown in Table 1. As it can be seen, when the copper content increased from 1.2 to 6.9 wt% the cyclohexene conversion also increased, which could be mainly related to the increase in the amount of the isolated $Cu^{\delta+}$ species observed by UV–vis-DR [29]. However a linear relationship between this species and the catalytic activity was not observed. This feature can be attributed to the presence of clusters and oxides which accelerate the decomposition of H_2O_2 to O_2 and H_2O. In this sense, the low efficiency values observed along with the high H_2O_2 consumption are reflecting the high accessibility of these species mainly located on the pore wall surface. Regarding the products selectivity, the allylic oxidation has mainly taken place with the formation of 2-cyclohexen-1-one and 2-cyclohexen-1-ol as major products.

For comparative purposes, some other reactions were carried out: without using any catalyst and over the Cu-free siliceous mesoporous molecular sieve (Si-M). The reaction did not proceed in the absence of the catalyst and the cyclohexene conversion on Si-M was very low (~1 mol%), being also cyclohexenol (III) and cyclohexenone (IV) the main products.

According to selectivity obtained on Cu-M(x) catalysts, a possible mechanism of interaction between H_2O_2 and the catalyst for the formation of allylic oxidation products, via a redox mechanism is proposed below.

$$\text{M-Cu}^{+} + H_2O_2 \rightarrow \text{M-Cu}^{2+} + {}^{\bullet}OH + OH^{-}$$

$$\text{M-Cu}^{2+} + H_2O_2 \rightarrow \text{M-Cu}^{+}\,{}^{\bullet}O_2H + H^{+}$$

$$\text{M-Cu}^{+}\,{}^{\bullet}O_2H + H_2O_2 \rightarrow \text{M-Cu}^{+} + O_2 + {}^{\bullet}OH + H_2O$$

$$3\,H_2O_2 \rightarrow O_2 + 2\,{}^{\bullet}OH + 2\,H_2O$$

The reaction path for the present study involves a first stage, where the interaction of Cu-M(x) catalyst with H_2O_2 yields $^{\bullet}OH$ and $^{\bullet}O_2H$ species via a redox mechanism. Then the $^{\bullet}OH$ radical attacks the olefin where the formation of the allylic oxidation products, 2-cyclohexene-1-one (IV) and 2-cyclohexene-1-ol (III), shows the preferential attack of the C—H bond over the C=C bond. Thus, Cu-M(x) as catalysts promote the allylic oxidation pathway and epoxidation is unfavored. In addition, oxygen and water are formed as the side products by the decomposition of the hydroperoxy radical and H_2O_2, respectively. This mechanism is in accordance with that described by Parida et al. for the interaction of Cu/MCM-41 catalyst with H_2O_2 in the oxidation of benzene to phenol [31].

In order to verify the mechanism proposed, a set of experiments has been carried out by modifying the reaction conditions: in absence of light, under a N_2 atmosphere, adding the radical

Table 1
Catalytic performance of Cu-M(x) in the cyclohexene oxidation with H_2O_2.

Sample	Cu content (wt.%)	Conversion[a] (mol%)		H_2O_2	Products selectivity[c] (mol%)		
		Cyclohexene	H_2O_2	Efficiency[a,b] (mol%)	Epoxidation[d]	Allylic[e]	Over-oxidation[f]
Cu-M(1.2)	1.2	3.0	79.0	14.6	35.4	59.1	5.5
Cu-M (3.6)	3.6	5.1	89.3	22.6	35.1	57.3	7.6
Cu-M (6.9)	6.9	8.0	95.7	32.7	10.8	73.3	15.9
Cu-M (6.9) dark	6.9	7.9	96.0	32.8	9.2	74.6	16.2
Cu-M (6.9) N_2	6.9	7.9	93.1	32.8	11.6	72.9	15.5
Cu-M (6.9) BHT	6.9	2.5	82.2	11.5	18.8	71.0	10.2

Standard reaction conditions: cyclohexene/H_2O_2 molar ratio = 4/1, temperature = 70 °C, catalyst = 9 mg/mL, reaction time = 5 h.
[a] CV < 7%.
[b] H_2O_2 efficiency = (moles of cyclohexene converted/mol of H_2O_2 converted) × 100.
[c] Based on the substrate consumed CV < 5%.
[d] Cyclohexene oxide (I) + 1–2 cyclohexanediol (II).
[e] 2-Cyclohexen-1-ol (III) + 2-cyclohexen-1-one (IV).
[f] 2,3-Epoxy-cyclohexanone (V) + 2,3-epoxy-cyclohexen-1-ol (VI) + 2 hydroxycyclohexanone (VII).

scavenger 2,6-di-tertbutyl-4-methylphenol (BHT) and using a reduced catalyst. For this, Cu-M(6.9) catalyst has been selected due to the higher activity and allylic selectivity. The obtained results are summarized in Table 1. In the absence of light the activity and products selectivity were similar to those obtained at 70 °C in the standard conditions. This result indicates that the reaction under study is not fundamentally a photochemical process. When the experiment was repeated under a N_2 atmosphere, the results were not significantly different from those obtained in air. Therefore, the nature of the atmosphere has not influence on the reaction. With the addition of the radical scavenger (0.24% mol BHT), the conversion of cyclohexene decreases which confirms the idea of a free radical mechanism. Fig. 1 shows the cyclohexene conversion obtained with and without addition of BHT in function of reaction time. As it can be seen, in the presence of radical inhibitor, the initiation of the reaction was retarded by 1.5 h. Meanwhile, the cyclohexene oxide was the only product obtained during this reaction time. Then, the selectivity to oxide decreases with the increase of the allylic products. After that the radical inhibitor is consumed, the reaction is considered to proceed as in the standard condition. This confirms that the oxidation of cyclohexene over Cu-M(x) catalysts mainly occurs through the formation of free-radical. In order to attempt to confirm that the isolate Cu^+ and Cu^{2+} cations are the main active species, the catalyst was reduced taking into account the temperature programated reduction studies [32]. The employed conditions (H_2/Ar flow 20 ml/min at 450 °C) allowed the reduction of the oligonuclear clusters and bulky CuO oxides [32]. When we repeated the oxidation of cyclohexene with reduced Cu-M(6.9) the activity did not decreased. Thus, considering these results and the mechanism proposed, we can infer that Cu^{2+} and Cu^+ ($Cu^{\delta+}$) present in the catalyst [29] would be the active species in this oxidation reaction.

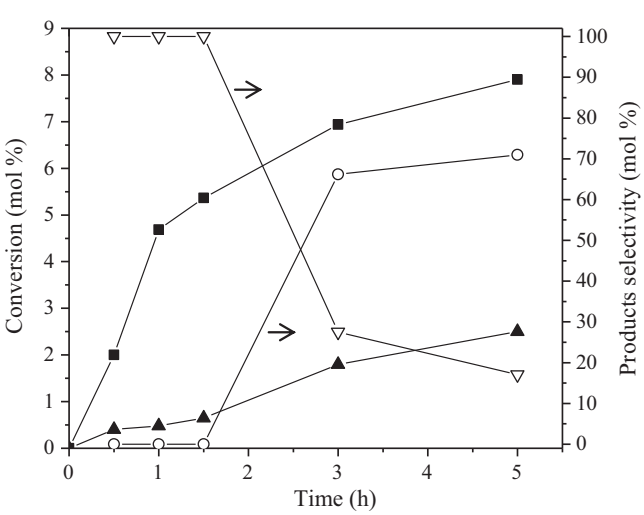


Fig. 1. Conversion of cyclohexene with (▲) and without (■) addition of BHT versus reaction time over Cu-M(6.9) (CV < 7%). Products selectivity for the reaction carried out with BHT: (▽) Cyclohexene oxide and (○) allylic oxidation products (CV < 5%). Reactions conditions: cyclohexene/H_2O_2 molar ratio = 4/1; temperature = 70 °C; catalyst = 9 mg/mL.

3.2. α-Pinene oxidation

In response to the increased activity and the selectivity toward allylic oxidation products obtained with the cyclohexene model reagent, we selected the catalyst with higher Cu content for studying the oxidative functionalization of α-pinene with H_2O_2. The influence of the molar ratio of α-pinene/H_2O_2 on the course of oxidation reaction was examined at the temperature of 70° C, while the other parameters were unchanged. These results are presented in Fig. 2 and Table 2. As it can be seen, when the α-pinene/peroxide molar ratio was modified from 4/1 to 2/1, the α-pinene conversion achieved a value close to 20 mol% and the H_2O_2 efficiency was of 43 mol% after 5 h of reaction. Although the conversion of α-pinene increased by an increase in the concentration of H_2O_2, the efficiency of peroxide decreased from 55% to 43% due to their higher decomposition. Thus, in order to improve both conversion of α-pinene and H_2O_2 efficiency, we have considered appropriate to employ a α-pinene/oxidant molar ratio of 4/1 performing a further addition of peroxide to the reaction medium after 0.5 h, in order to reestablish the initial concentration of H_2O_2 (limiting reactive). Under these conditions, the conversion of α-pinene and H_2O_2 efficiency were increased up to 23 mol% and 50 mol% respectively. Moreover, as it is shown in Table 2, an increase in the amount of hydrogen peroxide does not have a significant impact on the selectivity to allylic products, achieving values around to 65% mol in all of the cases. Therefore, the higher conversion of α-pinene was achieved using the optimized reaction conditions, through a H_2O_2 addition after 0.5 h, allowing reach the higher yield to the allylic products.

The influence of the reaction time on the selectivity to the oxidation products was examined in the range of 0–5 h (Fig. 3). The study showed that the main product obtained was the verbenone (**6**), which reaches 40 mol% after 0.5 h and then practically does not undergo any change, while the selectivity to verbenol (**5**) increases slightly. On the order hand, the α-pinene oxide (**1**) achieves a maximum at 0.5 h and then decreases because the same can be rearranged to aldehyde (**2**) or lead to the products of hydrolysis

Table 2
The influence of the molar ratio of α-pinene/H_2O_2 on the oxidation reaction.

α-Pinene/H_2O_2 mole ratio	Reaction time (h)	Conversion[a] (mol%)		H_2O_2	Selectivity[b] (mol%)		
		α-Pinene	H_2O_2	Efficiency[a] (mol%)	Epoxidation[c]	Allylic[d]	TON[a,e]
4/1	1	7.8	83.4	37.4	39.9	60.1	8.1
	5	13.8	97.2	55.1	33.9	66.1	14.4
2/1	1	9.8	96.2	20.4	40.2	59.8	12.2
	5	20.8	97.3	42.7	35.1	64.9	21.3
4/1[f]	1	12.0	70.1	34.3	40.5	59.5	12.3
	5	22.7	91.6	49.6	34.7	65.3	23.2

Standard reaction conditions: α-pinene/H_2O_2 molar ratio = 4/1, temperature = 70 °C, catalyst= 9 mg/mL, reaction time = 5 h.
[a] CV < 7%.
[b] Based on the substrate consumed CV < 5%.
[c] α-Pinene oxide (**1**) + campholenic aldehyde (**2**) + 1,2 pinanediol (**3**) + trans-sobrerol (**4**).
[d] verbenol (**5**) + verbenone (**6**)
[e] TON = moles of α-pinene converted/mol of copper.
[f] α-Pinene/H_2O_2 molar ratio = 4/1 with further addition of H_2O_2 at 0.5 h.

and opening of the oxirane ring (**3** and **4**). It seems probable that the side reaction of epoxide ring cleavage proceeds on the acid sites of the catalysts [28]. The present water in the reaction medium may compete with the reactant and be adsorbed on the Lewis sites of the catalyst generating Brønsted acid sites which aid this type of reactions [33–35].

Finally, in Fig. 4, the yield to product of interest, verbenone, is plotted versus the conversion of α-pinene under the best condition described above (α-pinene/H_2O_2 = 4/1 with further addition of H_2O_2). As it can be seen, the relation between the yield and the conversion follows a linear behavior. Thus, a further addition of peroxide to the reaction medium is necessary to increase the α-pinene conversion and consequently the yield into the desired product.

An important aspect to be studied in the oxidation process in liquid phase with solid catalysts is the stability of the catalyst to the leaching of the active species and the possibility of catalyst recycling. In fact, the leached species might contribute to the catalytic reaction, and the reaction might not be truly heterogeneous. Thus, to check the stability, heterogeneity and recycling ability of the copper modified mesoporous matrix under reaction condi-

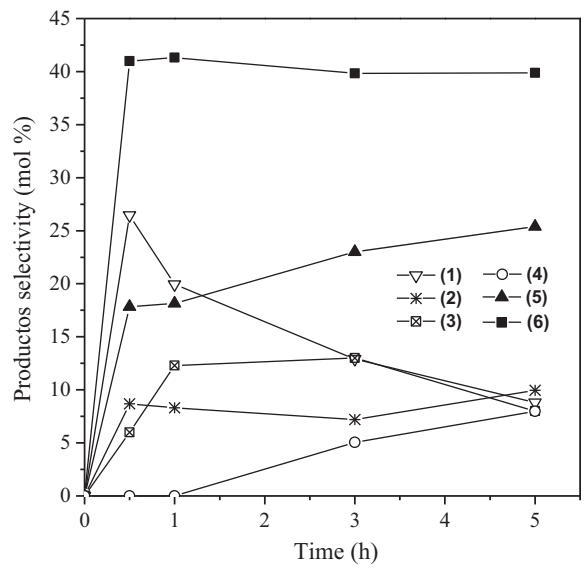


Fig. 3. Products selectivity for the α-pinene oxidation over Cu-M(6.9) with H_2O_2 extra dose after 0.5 h of reaction (CV < 5%). α-Pinene oxide (**1**), campholenic aldehide (**2**), 1,2 pinanediol (**3**), trans-sobrerol (**4**); verbenol (**5**), verbenone (**6**).

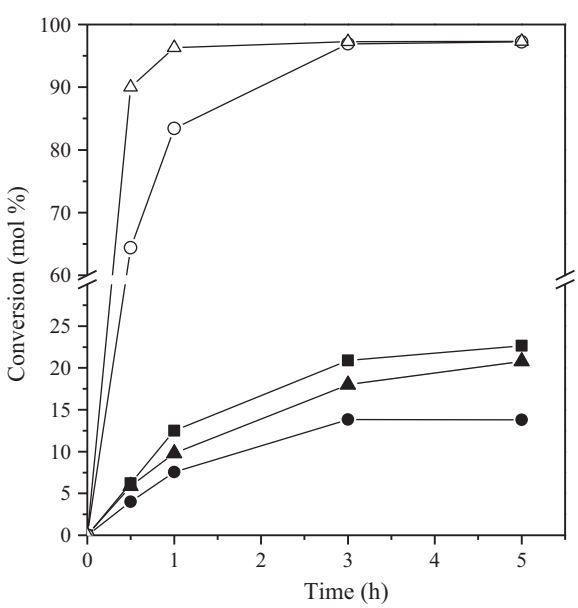


Fig. 2. Influence of different α-pinene/H_2O_2 molar ratios on the α-pinene conversion with Cu-M(6.9) (●) α-pinene/H_2O_2 molar ratio = 4/1, (▲) 2/1, (■) 4/1 with further addition of H_2O_2 at 0.5 h.(CV< 7%). H_2O_2 conversion: (○) α-pinene/H_2O_2 molar ratio = 4/1, (△) 2/1 (CV< 5%). Reactions conditions: temperature = 70 °C; catalyst = 9 mg/mL.

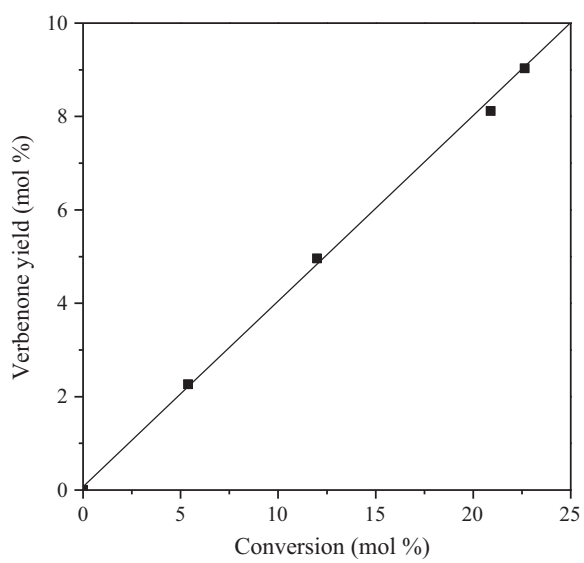


Fig. 4. Verbenone yield versus conversion in the oxidation of α-pinene with H_2O_2 extra dose after half hour of reaction over Cu-M(6.9). Reaction conditions: α-pinene/H_2O_2 molar ratio = 4/1; temperature = 70 °C; catalyst = 9 mg/mL, reaction time 5 h.

Table 3
Reuse of Cu-M(6.9) for α-pinene oxidation.

Cycles	Conversion[a] (mol%)		H_2O_2	Selectivity[b] (mol%)		
	α-Pinene	H_2O_2	Efficiency[a] (mol%)	Epoxidation[c]	Allylic[d]	TON[a]
1	22.7	91.6	49.6	34.7	65.3	23.2
2	22.4	91.4	49.0	36.5	63.5	22.9
3	23.1	92.2	50.1	40.2	59.8	23.6
4	22.9	91.3	50.2	41.9	58.1	23.4

Reaction conditions: α-pinene/H_2O_2 molar ratio = 4/1 with further addition of H_2O_2 at 0.5 h, temperature = 70 °C, catalyst= 9 mg/mL, reaction time = 5 h.
[a] CV < 7%.
[b] Based on the substrate consumed CV < 5%.
[c] α-Pinene oxide (**1**) + campholenic aldehyde (**2**) + 1,2 pinanediol (**3**) + trans-sobrerol (**4**).
[d] verbenol (**5**) + verbenone (**6**).

tions, four recycling experiments were carried out for Cu-M(6.9) in the oxidation of α-pinene (α-pinene/H_2O_2 = 4/1 with further addition of H_2O_2). As it can be seen in Table 3, the conversion and the selectivity of the catalytic reactions were not significantly modified through the first to the fourth use. Moreover, the Cu content in the solid, measured by ICP-OES before and after the reaction, remained constant.

On the other hand, the UV–vis–DR spectroscopy is known to be a very sensitive probe for the identification and characterization of metal ion coordination and its existence in framework and/or in extra-framework position of metal containing zeolites. UV–vis-DR spectroscopy has been used extensively to characterize the coordination circumstance of Cu ions in mesoporous materials [36]. A major aspect that should be taken into account is the modifications induced in the structure of the catalytic sites due to the interaction with the reaction medium. Thus, Fig. 5 shows the UV–vis-DR spectra of the Cu-M(6.9) sample used for four cycles (α-pinene/H_2O_2 = 4/1 with further addition of H_2O_2) together with the fresh corresponding one, after calcination in air at 773 K during 8 h. The spectra exhibit two bands centered at about 353 and 446 nm and a broad band between 600 and 800 nm. The first band is assigned to the isolated mononuclear $Cu^{\delta+}$ cations possibly in coordination with lattice oxygen, which suggests that some Cu ions are incorporated into the framework. The second band is assigned

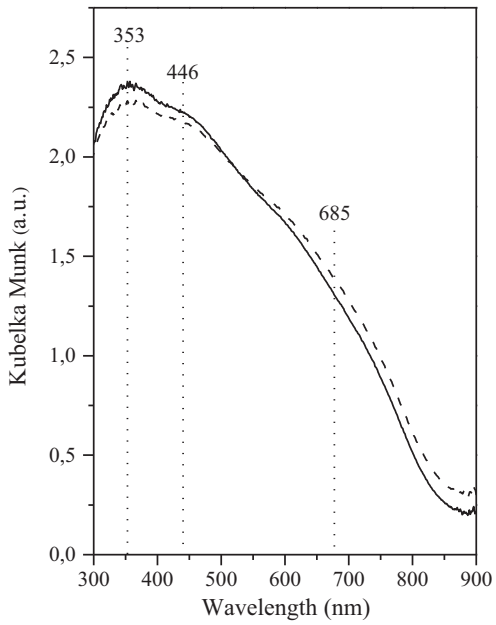


Fig. 5. Diffuse reflectance spectra in the UV–visible region of fresh (solid line) and used (dashed line) Cu-M(6.9) for four cycles. Reaction conditions: α-pinene/H_2O_2 molar ratio = 4/1 with further addition of H_2O_2 at 0.5 h, temperature = 70 °C, catalyst = 9 mg/mL, reaction time = 5 h.

Table 4
UV–vis-DR spectra peak intensity ratio I_{353}/I_{446} and I_{353}/I_{685} of samples fresh and used Cu-M(6.9).

	I_{353}/I_{446}	I_{353}/I_{685}
fresh Cu-M(6.9)	1.05	1.72
used Cu-M(6.9)[a]	1.06	1.82

[a] Catalyst used during four cycles. Reaction conditions: α-pinene/H_2O_2 molar ratio = 4/1 with further addition of H_2O_2 at 0.5 h, temperature = 70 °C, catalyst= 9 mg/mL, reaction time = 5 h.

to linear oligonuclear [$Cu^{\delta+}\cdots O^{\delta-}\cdots Cu^{\delta+}$] clusters like chains possibly inserted into mesoporous channel. Then the band between 600 and 800 can be attributed to d–d transitions of Cu^{2+} ions in a pseudo-octahedral ligand oxygen environment, which is assigned to copper species in the extra framework position (CuO particles). Similar bands are exhibited for the fresh and used catalysts and no significant changes in the intensity rations I_{353}/I_{446} and I_{353}/I_{685} (Table 4) were observed. This indicates the maintenance of the structure of the Cu species after the oxidation reaction which is a key factor for the reusable property of the catalyst. In this way, all the results confirm that the Cu-M(6.9) material certainly operates as heterogeneous catalyst and can be recycled.

Finally, Chattopadhyay et al. [37] reported α-pinene conversion using a copper (II) coordinated organic nanotube catalyst the 15% at 2 h using a high H_2O_2 concentration (α-pinene/oxidant molar ratio = 1/15). This conversion is comparable with the results that we obtained at same reaction time but using a much lower H_2O_2 concentration (α-pinene/oxidant molar ratio = 4/1). On the other hand we could improve the α-pinene conversion up to 23 mol% (TON = 23) for a reaction time of 5 h.

4. Conclusions

The Cu-M(*x*) catalysts were evaluated in the test reaction of cyclohexene oxidation using H_2O_2 as oxidant. The cyclohexene conversion obtained was increased when the Cu content increases, which could be mainly related with the increase in the amount of isolated $Cu^{\delta+}$ species observed by UV–vis-DR. The selectivity to allylic products was predominant this would be indicating that the reaction path involves the interaction of the Cu-M(*x*) catalyst with peroxide which yields mainly •OH species via a redox mechanism. The results did not show differences when some operative variables, such as the use of N_2 atmosphere, absence of light and reduced catalyst, were modified. When a radical scavenger (BHT) was added, the reaction was significantly affected, confirming the mechanism proposed. By using the reduced catalyst, we could infer that Cu^{2+} and Cu^{+} ($Cu^{\delta+}$) present in the catalyst would be the active species in this oxidation reaction.

Taking into account the increased activity and selectivity toward allylic oxidation products obtained with the model substrate, we selected the catalyst with higher Cu content to study the oxidative

functionalization of α-pinene with hydrogen peroxide. The highest yield to verbenone, was achieved for a α-pinene/oxidant molar ratio of 4/1 with a further addition of peroxide to the reaction medium after 0.5 h.

The recycling studies did not show loss in activity and selectivity. Moreover, the copper content in the solid, measured by ICP-OES before and after the reaction, remained constant. Also, it is important to mention that the metallic species of Cu present in the material remain unchanged after oxidation reaction which is a key factor for its reusable property. Thus, these Cu modified mesoporous materials behave as truly heterogeneous catalysts.

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