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Magnetically recoverable copper oxide catalysts for aerobic allylic oxidation of cyclohexene

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Graphical abstract



Highlights

- PVA-stabilized copper oxide NPs were used to obtain heterogeneous catalysts
- Aerobic oxidation of cyclohexene into α,β-unsaturated derivatives
- Effecient catalyst recovery and negligible metal leaching

Abstract

Magnetically recoverable copper oxide catalysts prepared by sol-immobilization method exhibited interesting properties for the allylic oxidation of cyclohexene with molecular oxygen as the sole oxidant. The catalysts were prepared by immobilization of presynthesized PVA (polyvinyl alcohol)-stabilized Cu₂O nanoparticles (NPs) on a magnetically recoverable support; the catalyst was further oxidized to CuO NPs after

calcination at 600 °C. Both catalysts can selectively oxidize cyclohexene through allylic oxidation to give 2-cyclohexene-1-one as the main product, but CuO was identified as the most active species providing 90% cyclohexene conversion and 96% selectivity for allylic products under 100 °C and 4 bar pressure of O_2 for 6 h of reaction time. The catalysts were magnetically recovered without metal leaching and could be reused in at least six consecutive runs.

Keywords Magnetic separation; Allylic oxidation; Cyclohexene; 2-cyclohexene-1-one; Copper oxide .

1. Introduction

The functionalization of allylic C–H bonds of alkenes represents a powerful approach to the synthesis of α , β -unsaturated derivatives, which find widespread application as synthetic intermediates and as products in the commodity chemical, fine chemical, and pharmaceutical industries [1-4]. The allylic oxidation of alkenes is a valuable organic transformations for the synthesis of value-added products such as α , β -unsaturated alcohols, esters and ketones from simple precursors [4]. Classically, these oxidations were performed using chromium reagents (first stoichiometric or then catalytic with the aid of oxidants), but due to the radical character, metals that undergo one-electron redox processes, such as Mn, Rh, Fe, Cu or Co, have been used in the development of environmentally friendly metal-catalyzed methods [4-8]. Many of these metal-catalyzed systems are not compatible with the use of molecular oxygen and require unfriendly oxidants, such as PhIO, NaClO, H₂O₂, tBuOOH; to achieve catalytic turnover [9-15]. Molecular oxygen should be preferred as an ideal oxidant due to its natural, highly economical, environmentally benign and abundant characters [16, 17]. Limitations in

reaction scope and selectivity as well as safety concerns have hindered the application of aerobic oxidations in the fine chemical, pharmaceutical, and related industries.

An ideal clean oxidation may use molecular oxygen as the primary oxidant along with catalysts that can be recycled and non-toxic solvents. Yin *et al.* [18] and Silva *et al.* [19] reported the allylic oxidation of alkenes using molecular oxygen as the sole oxidant with easily recoverable cobalt catalysts. Copper catalysis also received attention for selective aerobic oxidative functionalization of C-H bonds [20-22]. The facile aerobic oxidation of Cu(I) ions to Cu(II) is widely recognized, and a number of important synthetic Cucatalyzed aerobic oxidation reactions exist, including industrial applications, with high catalytic activities and a wide functional groups tolerance.

Herein we explored the preparation of supported copper oxide nanoparticles (NPs) as catalyst for the allylic oxidation of alkenes with molecular oxygen as the sole oxidant. Many catalytic processes with copper makes use of metal complexes or enzyme mimetics [23-25]; however, due to its excellent conductivity, availability and low cost, the use of copper as an heterogeneous catalyst receives attention. Metallic copper nanoparticles and cuprous oxide have been used as catalysts for various reactions, including Ullmann coupling [26-28], cycloaddition of terminal alkynes and azides [29, 30], hydrogenation of alkynes [31, 32], oxidative dehydrogenation of alcohols [33], degradation of pollutants [34] and oxidation of olefins [35]. Copper tetramers supported on alumina showed excellent activity in carbon dioxide reduction into methanol at low partial pressure of CO₂ [36]. Allylic oxidation of cyclohexene by copper supported on expanded graphite [22] or Cu-MOFs [37] exemplifies the chemistry of copper applied to allylic C-H bond functionalization.

2. Materials and methods

2.1. Catalyst preparation

The magnetically recoverable copper catalyst was synthesized by a sol-immobilization method. Initially the magnetic support, which is comprise of silica-coated magnetite nanoparticles (Fe₃O₄@SiO₂), was prepared as previously reported, followed by its functionalization using (3-aminopropyl)triethoxysilane (APTES) to obtain NH₂ groups in the surface of the support [19, 38]. Copper oxide nanoparticles were prepared by reduction of an aqueous solution of copper(II) nitrate (Cu(NO₃)₂.3H₂O, Sigma Aldrich) in the presence of polyvinyl alcohol (PVA, MW=9000-10000 g.mol⁻¹, Sigma Aldrich), according to the literature.[39] To an aqueous solution of copper(II) ions (200 mL, 1.2 mmol L^{-1}) was added an aqueous solution of PVA (2.25 mL, [Cu:PVA] = 1:1.5) under vigorous stirring. Then, a freshly prepared and cold aqueous solution of sodium borohidrate (12 mL, 0.1 mol L⁻¹, [Cu:NaBH₄]=1:5) was dropwise added. The resulting solution was stirred for 30 minutes and then 1 g of the functionalized support was added, and the solution was stirred for another 2 h. The solid was magnetically separated using an external magnet and washed several times with distilled water and acetone, and dried under vacuum. Part of this sample was used "as-prepared" and part was calcined at 600 °C for 2 h in air before the catalytic studies.

2.2. Catalytic oxidation experiments

The catalytic reactions were carried out in a modified Fisher-Porter glass reactor (50 mL) pressurized at the desired O₂ pressure. For each experiment, the glass reactor was loaded with the catalyst (0.04 mmol Cu) and 20 mmol of cyclohexene under inert atmosphere. The chosen temperature was maintained by an oil bath in a hot-stirring plate connected to a digital controller (ETS-D4 IKA). The reactor was loaded with O₂ at the desired pressure and kept connected to an oxygen supply reservoir (constant pressure during the catalytic experiment). The reaction was conducted under magnetic stirring (700 rpm) and

after the desired time, the catalyst was magnetically recovered by placing a permanent magnet in the reactor wall and the products were collected and analyzed by GC, using a Shimadzu GC-2010 gas chromatograph system with a 30-m RTX-Wax column and helium as carrier gas. The analyses were performed using the following conditions: initial temperature 40°C, rate 10°C.min⁻¹, final temperature 200°C and gas flow of 1.41 mL.min⁻¹. Conversion and selectivity were calculated based on peak areas of GC calibrated with an internal standard (biphenyl) added to the organic phase after separation of the catalyst. The validity of the identification and quantitation of the GC peaks was verified by comparison of the mass spectra and gas chromatographic retention times with those of the authentic compounds.

2.3. Characterization methods

X-ray powder diffraction (XRD) patterns were recorded on a Rigaku Miniflex with Cu K α radiation (λ =1.54 Å) at 2 θ = 25–80° with a 0.02° step size.

Transmission electron microscopy (TEM) and EDS analysis were performed with the JEM-2010 microscope operating at 200 kV. Samples for TEM observations were prepared by placing a drop containing the nanoparticles in a carbon-coated grid.

The quantification of Cu was performed via flame atomic absorption spectroscopy (FAAS) using a Shimadzu AA-6300 apparatus.

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements were performed at the Cu K-edge in the transmission mode (channel-cut Si (111) crystal monochromator and three ionization chambers to detect incident and transmitted photon fluxes) performed at XAFS beamline of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas,

SP) at proposal number XAFS1-16100. During data collection, the XAS spectrum of Cu metal foil was simultaneously measured and the energy was calibrated by aligning the respective absorption edges. All data processing was carried out using IFEFFIT [40, 41].

The X-ray photoelectron spectroscopy (XPS) experiments were carried out at SXS beamline of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, SP) at proposal number SXS-15172. The XPS spectra were collected using an incident photon energy of 1840 eV. The operating pressure in the ultrahigh vacuum chamber (UHV) during the analysis was 1×10^{-9} Pa. Energy steps was of 20 eV with 0.2 eV step energy and 200 ms per point acquisition time. The peak fitting was performed using a 70% Gaussian type curve and a 30% Lorentzian type curve, and a shirller nonlinear sigmoid type baseline. The C 1s peak of adventitious carbon was fixed at 284.8 eV to set the binding energy scale, and the data fitting was performed using CasaXPS software (Casa Software Ltd., UK).

3. Results and Discussion

PVA-stabilized copper oxide nanoparticles prepared by a well-known aqueous phase protocol for the preparation of a many others metal nanoparticles (Pd, Au, Rh, etc.) were used in this study as component for the preparation of supported catalysts. The immobilization of the metal nanoparticles in high surface area inorganic solids increases its stability and recyclability. Furthermore, if the metal nanoparticles are immobilized on a magnetic support, the handling and separation is tremendously facilitated [42]. Here we choose a support developed in our research group that is comprised by magnetite nanoparticles spherically coated with silica (final average size 35 nm) obtained by a reverse microemulsion method [38, 43]. The magnetic properties of this material were

extensively investigated and are adequate for the proposed application due to its superparamagnetic behavior and high saturation magnetization [43]. The support surface was functionalized with amino groups in order to facilitate the impregnation of the colloidal nanoparticles, as also previously discussed [44]. The functionalized support was added to an impregnation aqueous solution containing the desired amount of PVA-stabilized copper oxide NPs to give a solid containing 1.2 wt% Cu.

Morphological analysis of colloidal NPs by TEM (Figure 1a) showed that the copper oxide NPs have an average diameter of (3.1 ± 0.8) nm (Figure 1b), but the analysis of the supported catalyst (Figure 1c), which discloses the core-shell structure of the support, do not clearly show the copper oxide NPs on its surface. Two distinct regions were analyzed by EDS technique (Figure 1d), as highlighted in Figure 1c. EDS analysis of the region 1 shows the presence of the elements Si and Fe corresponding to the magnetic support and the analysis of region 2 revealed the additional presence of Cu, confirming the composition of the nanoparticles analyzed (the presence of Ni is due to the TEM grid).



Figure 1: (a) TEM image of PVA-stabilized copper oxide nanoparticles; (b) NPs size distribution histogram; (c) TEM image of the copper catalyst supported on silica-coated magnetite nanoparticles and (d) EDS analysis of the regions highlighted in (c) using a Nibased sample grid.

The crystalline structure of the PVA-stabilized copper oxide NPs was evaluated by X-ray diffraction analysis. Due to the presence of overlapping peaks between Fe_3O_4 core and Cu oxide species in XRD, we prepared a sample with the copper oxide NPs supported on silica spheres without the magnetic core. Figure 2a present the XRD patterns of asprepared copper oxide NPs supported on silica. The diffraction peaks identified at (1 1 1), (2 0 0), (2 2 0) and (3 1 1) crystal planes can be perfectly assigned to the Cu₂O phase by comparison with JCPDS 84-1286 database. The XRD for the calcined sample at 600

°C for 2 h (Figure 2b) showed strong diffraction peaks at 2 θ values 35.54 and 38.70° corresponding to (1 1 -1) and (1 1 1) planes of Cu₂O phase (JPCDS-65-3288). We expected to produce PVA-stabilized Cu(0) NPs, but after reduction of the copper(II) precursor with NaBH₄, the characterization confirmed the preparation of a nearly phase pure copper(I) oxide NPs.



Figure 2. X-ray diffraction patterns of PVA-stabilized copper oxide NPs supported on silica: (a) as-prepared and (b) after thermal treatment at 600 °C for 2 h samples.

In order to obtain information on the oxidation state and chemical environment of the surface of PVA-stabilized copper(I) oxide NPs supported on silica, a XPS analysis was carried out. Figure 3 shows the XPS data for Cu 2p core level for both as-prepared and thermal treated at 600 °C for 2 h samples. For the as-prepared sample the fitting peaks of Cu 2p region in Figure 3a shows clearly the presence of peaks at 951.6 eV ($2p_{1/2}$) and 931.7 eV ($2p_{3/2}$) corresponding to Cu¹⁺ specie and peaks at 953.3 eV ($2p_{1/2}$) and 933.6 ($2p_{3/2}$) corresponding to Cu²⁺ specie [45, 46]. These XPS result showed that the asprepared PVA-stabilized copper oxide NPs catalyst surface is composed of a mixture of

CuO and Cu₂O oxides. The existence of Cu²⁺ phases in as-prepared sample could not be detect using XRD analysis probably due to small concentration of this specie presented. However, the XPS analysis was enough to identify these two coexisting phase (Cu¹⁺ and Cu²⁺) present in the surface of the as-prepared sample. Thus, this result confirms that combine both methods to understanding the real composition of the sample is very important. In the Figure 3a, the peak of $2p_{3/2}$ for Cu¹⁺ is more intense, showing that most of the surface of the as prepared catalyst is composed of Cu₂O species. On the other hand, in the XPS spectra for thermal treated copper oxide NPs supported on silica at 600 °C for 2 h shown in Figure 3b it was only possible to identify peaks at 954.0 eV ($2p_{1/2}$) and 934.1 eV ($2p_{3/2}$) corresponding to CuO, along with a remarkably satellite peak at near 942 eV. This remarkably satellite peak is attributed to the binding energy of Cu²⁺ suggesting the full conversion of Cu¹⁺ in the Cu²⁺ species after thermal treatment. Therefore, calcination of the catalyst compound Cu₂O leads to full oxidation of copper species present on the surface of the material.



Figure 3: XPS spectra and deconvolution of the photoemission line for Cu 2p: (a) asprepared PVA-stabilized copper oxide NPs supported on silica e (b) copper oxide NPs supported on silica after calcination process (600 °C, 2 h) and XANES spectrum of Cu-K edge: (c) as-prepared e (d) after calcination process (600°C, 2 h).

The X-ray Absorption Near Edge Structure (XANES) is a powerful tool for determining the local atomic structure, giving information about the oxidation state of compounds. Herein, XANES measurements were used to determine the local atomic structure of Cu-species present in the as-prepared and after thermal treatment samples. The XANES spectra revealed that both samples, as-prepared and thermally treated, have a well apparent shoulder at 8981 and 8985 eV, respectively (Figure 3 c and d). The as-prepared sample showed a shift in the edge region to lower energy values when compared with the thermal treated sample at 600 °C for 2 h. The Cu K-edge shift to lower energies is characteristic of Cu¹⁺ species [47], which is in good agreement with XRD and XPS

results. The XANES spectrum for the sample after thermal treatment presents important changes in the characteristic shoulder position peak and white line compared to the spectrum of the sample as-prepared. It is observed that the thermal treated copper catalyst has a strong absorption at 8997.5 eV (white line) and a shoulder at 8985 eV indicating that it is comprised of species of CuO, as shown by XRD and XPS results [34].

Figure 4 shows the k-weighted EXAFS signal $\chi(k)$ and the corresponding Fourier transforms (FTs) for the as-prepared and thermal treated samples. The results from the Cu K-edge are shown in Table 1.



Figure 4: EXAFS spectra of the Cu-K edge for the catalysts before and after the calcination process. (a) Fourier Transform (FT) space-k and (b) FT space-R of asprepared PVA-stabilized copper oxide NPs supported on silica; (c) FT space-k and (d)

FT space-R for copper oxide NPs supported on silica after calcination process (600 °C, 2 h).

The FT of EXAFS oscillations obtained for the as-prepared PVA-stabilized copper oxide NPs supported on silica shows the presence of a peak at 1.4 Å and a peak at 2.6 Å (Figure 4b) corresponding to the Cu-O and Cu-Cu bonds, respectively. The oscillations obtained for the sample obtained after thermal treatment (600 °C, 2 h) demonstrates the presence of two main peaks at 1.4 Å and 2.5 Å (Figure 4d), corresponding to the same type of bindings described above. These results are in agreement with values reported in the literature for samples of Cu₂O and CuO, respectively [34, 47, 48]. The coordination sphere parameters (bond distance (R), coordination number (CN) and Debye-Waller factor (σ^2)) obtained by FT calculations for the EXAFS oscillations obtained are shown in Table 1. It may be noted that the bond distance values for both Cu-O and Cu-Cu are slightly lower for the as prepared sample (Table 1 - entries 1-2) when compared to the thermally treated sample (Table 1 - entries 3-4). These bond distances are actually lower for the cuprous oxide (Cu₂O) due to the high symmetry of the cubic structure of this compound, as well as the octahedral environment of the Cu in Cu₂O crystal. Finally, the Debye-Waller factor values represent the structural disorder of the material and, according to the literature, tend to be higher for small-sized nanoparticles [49]. The values obtained are higher than the ones reported in the literature for these types of structures, indicating the reduced size of the copper oxide NPs present in the synthesized catalysts. It is worth mentioning that the reduced size of the copper oxide NPs is probably responsible for lower Cu-O and Cu-Cu bond distance values obtained for the catalysts compared to the values reported for bulk Cu₂O and CuO [34].

Entry	Sample	Bond	R (Å) ^a	NC ^b	$\sigma^2(\text{\AA}^2)^{c}$
1	As_prepared	Cu-O	1.89 ± 0.03	2.4 ± 0.1	0.0032
2	ris prepared	Cu-Cu	2.81 ± 0.05	2.8 ± 0.1	0.0292
3	Calcined (600	Cu-O	1.90 ± 0.02	2.9 ± 0.2	0.007
4	°C, 2 h)	Cu-Cu	2.9 ± 0.5	2.7 ± 0.5	0.012

 Table 1: Structural parameters calculated by EXAFS of synthesized copper oxide catalysts.

^a bond distance in Angstroms; ^b coordination number; ^c Debye-Waller factor.

The magnetically recoverable copper oxide catalysts were tested in alkene oxidation reactions, using cyclohexene as a model substrate. Figure 6 shows the possible cyclohexene oxidation products. Since the mechanisms of allylic oxidation and epoxidation compete during the reaction, the catalysts were tested for their selectivity for the generation of allylic products or epoxide products.



Figure 6: Main products of cyclohexane oxidation: (1) 7-oxabicyclo-[4.1.0]-heptane or cycloexene oxide; (2) 2-cyclohexen-1-ol; (3) 2-cyclohexen-1-one e (4) 7-oxabicyclo-[4.1.0]-heptan-2-one.

We first tested the activity and selectivity of the as-prepared PVA-stabilized copper oxide NPs supported catalyst in the oxidation reaction and its behavior when used in successive reactions. In a typical experiment, the catalyst and the olefin were added to the reactor under inert atmosphere in a molar ratio of 500/1 (olefin/catalyst). The reactions were carried out in solventless conditions. The reactor was then charged with 4 atm of O_2

and placed in a silicone oil bath maintained at constant temperature of 100° C. The reaction was kept under a stirring rate of ~ 700 rpm with the aid of a magnetic stirrer. After 6 hours, the reactor was cooled, the remaining oxygen pressure relieved and the catalyst was recovered magnetically with the aid of a magnet placed against the wall of the reactor. The organic phase was easily separated and analyzed by GC. The reusability of the solid was measured by adding a new portion of the substrate to the reactor. The solid after each reaction was separated and dried under vacuum for 10 min. Table 2 shows the results obtained.

				Selectivity	r (%)						
Entry	Conv. (%)	O	°	OH		Sallylic	Sepoxide				
1	31.6	6.9	48.1	45.0	-	93.1	6.9				
2	46.1	5.6	52.8	41.6	-	94.4	5.6				
3	43.7	0.6	55.5	44.5	-	99.4	0.6				
4	32.0	13.6	58.6	23.8	4.0	82.4	17.6				
5	40.5	12.0	60.4	25.2	2.4	85.6	14.4				
6	48.4	2.0	66.1	30.8	1.1	96.9	3.1				

 Table 2: Cyclohexene oxidation using as-prepared PVA-stabilized copper oxide NPs catalyst.^a

7	13.2	3.1	63.8	31.8	1.3	95.6	4.4
8	13.5	6.5	19.7	72.2	1.5	92.0	8.0

^a Reaction conditions: 20.0 mmol substrate and 0.04 mmol Cu (substrate/catalyst: 500/1); $T = 100^{\circ}$ C, 4 bar pressure of O₂, 6 h. There was no conversion in the absence of catalyst.

The catalyst shows high selectivity to the allylic oxidation products formation, and the main product found was 2-cicloexen-1-one (3), as reported also for other non-noble metals [18, 19, 50]. The 2-cicloexen-1-one is a versatile substance used as the basis for the synthesis of a variety of products in the chemical industry, for example, pharmaceuticals and fragrances [51]. Other products obtained were the epoxide (1), derived from direct oxidation of cyclohexene and 2-cyclohexen-1-ol (2) is present in small amounts. It is believed that 2-cyclohexen-1-one is formed by the oxidation of 2cyclohexen-1-ol [52, 53], which is also a product of allylic oxidation of cyclohexene. An interesting finding is the presence of 7-oxabicyclo[4.1.0]heptan-2-one (4) among the epoxidation products, product of direct oxidation of 2-cicloexen-1-one, which according to the literature is not usually obtained except in the case of reactions with 100% conversion [53]. The as-prepared PVA-stabilized copper oxide NPs supported catalyst could be used for up to six consecutive reactions without losing activity and with high selectivity for the formation of allylic oxidation products. The conversion increased from the first cycle (32%) to the second cycle (46%), most probably due to removal of excess of PVA, and was maintained until the 6th cycle. The conversion was reduced to 13% in the 7th cycle and the catalyst lost its activity only in the 9th reaction cycle. The loss of activity may not be directly related to loss of catalyst mass as copper leaching was not noticed in the recovered organic phase (<0.01 ppm Cu detected by FAAS).

The calcined catalyst, which contains CuO NPs, was used to evaluate the stability after removing the organic groups present on the catalyst support as well as the stabilizer (PVA) present in the as-prepared catalyst. The CuO-based catalyst (calcined at 600°C for 2 h in air atmosphere) was tested in the cyclohexene oxidation using the same previously employed conditions (4 atm O₂ pressure, 100 °C and 6 h reaction). The results obtained are shown in Table 3. The catalyst was selective for the allylic oxidation products, and again the preferably obtained product was 2-cyclohexen-1-one (3). We observed an increase in substrate conversion to 90% in the first run, but there was also a loss of activity, reaching a conversion compared with the as-prepared catalyst after the 4th run. This result shows that the removal of organic ligands was favorable for the catalytic activity; however, another possible explanation for the increase in catalytic activity may arise from the change in copper oxidation state. The as prepared catalyst contains a mixture of Cu₂O and CuO, and the calcined catalyst became CuO, exclusively. Moreover, considering that the calcination step removed the organic stabilizer, morphological changes or aggregation of the non-protected nanoparticles are possible explanations for catalyst fast deactivation.

		Selectivity (%)								
Entry	Conv. (%)	O	°	OH		Sallylic	Sepoxide			
1	89.9	4.9	60.5	34.6	-	95.1	4.9			
2	79.2	3.9	63.6	31.3	1.2	94.9	5.1			

Table 3: Cyclohexene oxidation using calcined CuO-based catalyst.^a

3	61.8	2.5	66.2	30.3	1.0	96.5	3.5
4	37.2	2.3	65.9	29.4	2.4	95.3	4.7
5	36.8	3.1	67.6	28.8	0.5	96.4	3.6
6	19.5	-	68.5	31.5	-	100	-
7	10.2	-	70.2	29.8	-	100	-
8	-	-	-	-	-	-	-

^a Reaction conditions: 20.0 mmol substrate and 0.04 mmol Cu (substrate / catalyst: 500/1); T = 100° C, 4 bar pressure of O₂; ^b Selectivity for the main allylic and epoxides products, respectively. There was no conversion in the absence of catalyst.

The influence of temperature on the cyclohexene oxidation with the CuO-based catalyst (calcined at 600°C for 2 h in air atmosphere) was investigated by varying the temperature of 25 ° C to 100 ° C (Table 4, entries 1-4). The conversion and selectivity are highly dependent on temperature. At temperatures below 75 °C the conversion was very low compared with that obtained for the reaction carried out at 100 °C. It was also observed that at room temperature, and direct oxidation of the olefinic bond take place practically the same extent, thus impairing the selectivity of the catalyst studied for the allylic and epoxide products. Raising the temperature favors the allylic oxidation mechanism, the main product obtained cyclohex -2 -en- 1 -one (3). The influence of O₂ pressure on the cyclohexene oxidation with the CuO-based catalyst (calcined at 600°C for 2 h in air atmosphere) was also investigated (Table 4, entry 5-7). The conversion increased with

increasing the reaction pressure, but the selectivity was only slightly affected, forming preferentially the allylic oxidation products at all pressures studied.

Table 4: Oxidation of cyclohexene using calcined CuO-based catalyst at different T andP.

		D 0	G						
Entry	Τ (°C)	P O ₂ (bar)	(%)	$\langle \rangle$	°	OH		$\mathbf{S}_{allylic}$	S _{epoxide}
1	25	4	3.8	46.9	26.8	26.3	-	53.1	46.9
2	50	4	8.7	9.2	68.6	22.2	-	90.8	9.2
3	75	4	15.7	5.4	70.9	21.3	2.4	92.2	7.8
4	100	4	76.2	3.5	60.5	34.6	1.4	96.5	3.5
5	100	1	28.2	10.8	54.6	34.6	-	89.2	10.8
6	100	2	50.2	9.8	63.6	31.3	1.2	90.2	9.8
7	100	6	89.4	2.7	70.5	25.8	1.0	96.3	3.7

Conditions: 20.0 mmol cyclohexene and 0.04 mmol Cu each reaction cycle (cyclohexene / copper = 500/1).

Finally, the reaction conversion and selectivity was investigates at different reaction times (Figure 5). A typical cyclohexene oxidation reaction using the calcined catalyst at 4 bar of O_2 and 100°C was followed by a longer time interval in order to investigate the distribution of products throughout the reaction.



Figure 5: Profile of allylic oxidation of cyclohexene by calcined CuO-based catalyst activity as a function of time. Reaction conditions: substrate 500 mol/mol of Cu, 4 bar pressure of O₂ and 100°C. (\Box conversion, \bullet cyclohexen-1-one, \bigcirc cyclohexen-1-ol, \blacktriangle cyclohexen oxide, \triangle oxabicyclo-[4.1.0]-heptan-2-one).

An analysis of the data in Figure 5 reveals that even in 1 hour reaction the catalyst is selective for the formation of the allylic oxidation products. It is worth to note that after 1 h, there were equivalent amounts of 2-cyclohexen-1-ol (2) and 2-cyclohexen-1-one (3) being produced, which is in agreement with the proposed mechanism where two cyclohexenyl peroxy radicals combine, followed by decomposition of the resulting tetraoxide intermediate into a 1:1 ratio of the allyl alcohol and enone [54]. At longer reaction times, 2-cyclohexen-1-ol (2) is converted into 2-cyclohexen-1-one (3), which is the main reaction product. The other observed products were cyclohexene oxide (1) and 7-oxabicyclo-[4.1.0]-heptan-2-one (4). The first is formed in the beginning of the reaction, by the direct oxidation of the olefinic bond, and was consumed after long

reaction times, by a reaction pathway not yet elucidated. After 4 h of reaction, we also have noticed the decline of the selectivity of allylic products and an increase in selectivity of the epoxide product 7-oxabicyclo-[4.1.0]-heptan-2-one (4), which is a product of the direct oxidation of 2-cyclohexen-1-one (3). It is possible that the heterogeneously coppercatalyzed oxidation occurs via a radical-chain sequence mechanism with initiation at the catalyst surface, consistent with the proposed mechanism for the reaction in which some epoxides products are formed from their corresponding allylic product [52, 55, 56]. Moreover, the radicalar nature of the olefin oxidation mechanism by the copper oxide catalyst was confirmed by the interruption of an ongoing reaction after adding butylated hydroxytoluene (BHT). BHT is an antioxidant that reacts with free radicals, delaying oxidative processes. Here the addition of 1 equiv. of BHT, stopped the reaction and also did not changed the product distribution. We can also conclude that both mechanisms of oxidation (epoxidation and allylic oxidation) occur via radicals, as after the addition of the radical trap the product distribution remained the same.

4. Conclusions

Magnetically recoverable copper oxides catalysts were prepared by the immobilization of PVA-stabilized pre-formed NPs, which were fully characterized by TEM, XRD, XPS, XANES and EXAFS. The as prepared catalyst contains a mixture of Cu₂O and CuO, and the calcined catalyst (600 °C, 2 h) was completely oxidized CuO. The catalysts showed high activity towards cyclohexene oxidation and selectivity to the allylic oxidation product, which increases when the catalyst was calcined. The magnetic property allowed a facile and fast product separation with negligible Cu leaching into the products. The reaction method used has a strong environmental appeal as molecular oxygen is the only oxidant, and the catalyst is easily recovered. Allylic oxidations are particularly attractive for the valorization of terpenes through their conversion into allyl alcohols and enones.

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