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Magnetically recoverable copper oxide catalysts for aerobic allylic oxidation of cyclohexene

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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 pre-synthesized PVA (polyvinyl alcohol)-stabilized Cu_2O 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.

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, H_2O_2, 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 Cu-catalyzed 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 make 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 CO_2 [36]. Allylic oxidation of cyclohexene by copper supported on expanded graphite [22] or

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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 (Fe_3O_4@SiO_2), was prepared as previously reported, followed by its functionalization using (3-aminopropyl)triethoxysilane (APTES) to obtain NH_2 groups in the surface of the support [19,38]. Copper oxide nanoparticles were prepared by reduction of an aqueous solution of copper(II) nitrate ($Cu(NO_3)_2{\cdot}3H_2O$, Sigma Aldrich) in the presence of polyvinyl alcohol (PVA, MW = 9000–10,000 g mol^{-1}, Sigma Aldrich), according to the Ref. [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:$NaBH_4$] = 1:5) was dropwise added. The resulting solution was stirred for 30 min 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 O_2 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 O_2 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 Kα radiation ($\lambda = 1.54$ Å) at $2\theta = 25$–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 were 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 1 s 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 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 are 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 (Fig. 1a) showed that the copper oxide NPs have an average diameter of (3.1 ± 0.8) nm (Fig. 1b), but the analysis of the supported catalyst (Fig. 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 (Fig. 1d), as highlighted in Fig. 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).

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. Fig. 2a presents the XRD patterns of as-prepared 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 Cu_2O phase by com-