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Synthesis and characterization of gold nanoparticles supported on thiol functionalized chitosan for solvent-free oxidation of cyclohexene with molecular oxygen

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ABSTRACT

The selective liquid phase oxidation of cyclohexene to 2-cyclohexe-1-one and 1,2-cyclohexanediol has been investigated over gold nanoparticles (GNPs) with molecular oxygen in a solvent-free condition. The gold nanoparticles were immobilized on thiolated chitosan derivative (TChD), by grafting thiol groups on the support. The catalyst was characterized by XPS, N_2 adsorption/desorption, TEM, FT-IR and UV–vis spectroscopy. TEM results show that the majority of Au particles have diameters in the range of 3–6 nm. X-ray photoelectron spectroscopy (XPS) revealed the coexistence of both oxidized and metallic gold species on the surface of TChD. The results show that the catalytic performance of GNPs/TChD is quite remarkable and the catalytic activity over recycled catalyst remains at a high level after at least 4 cycles. Activity tests were carried out in an autoclave at 80 °C without any solvent. In order to obtain maximum conversion, the reaction parameters such as reaction temperature and time were optimized. Under optimized conditions, a maximum of 87% conversion and 70% selectivity was achieved with the GNPs/TChD catalyst.

1. Introduction

Gold nanoparticles (GNPs), particularly with dimension less than 8 nm [1–5], have been widely used to catalyze many chemical transformations such as selective oxidation of alcohols and hydrocarbons, hydrogenation, dehydrogenation and redox reactions [6–11]. The unique catalytic properties of GNPs in comparison with bulk gold are closely related to their particle size and morphology which provide large surface to volume ratio with respect to the bulk system. However, GNPs are nearly unstable and difficult to separate from the reaction medium when they are used as a catalyst. By immobilizing them on a solid support, the nanoparticles can be effectively protected from aggregation and as a result of this strategy, improvement in selectivity and stability were obtained for many important chemical reactions such as, low temperature oxidation of CO [9,12–15], oxidation of alcohols [9,16–19], direct oxidation of hydrogen to hydrogen peroxide [20,21], epoxidation of alkenes [9,12,22–24], oxidation of olefins [4,9,25], oxidation of alkanes [9,26,27], oxidation of cyclohexane and cyclohexene [9,27–35]. Extensive studies on the oxidation of cyclohexene have been carried out due to the potential uses of the products, including 2-cyclohexene-1-ol, 2-cyclohexene-1-one and many other chemical intermediates [36]. Cyclohexene oxidation over the Au/C catalyst with oxygen gave a good conversion (approximately 50%) along with many notable products [34]. To improve the conversion and selectivity of Au as catalyst, choice of a support with good physicochemical properties and affinities is very important and plays crucial role for the overall stability of the supported catalyst. Therefore, we chose modified chitosan (MCh) to improve the efficiency of the gold catalyst for cyclohexene oxidation using oxygen as oxidant, and to explore the effect of composition of catalysts on oxidation of cyclohexene.

The chitosan (Ch) biopolymer and its derivatives are nowadays widely used for different purposes. As a naturally occurring biopolymer, chitosan has many advantages, such as biocompatibility, biodegradability, and non-toxicity, which make it an environmental friendly substrate [37,38]. Various chemical groups of Ch especially its amino groups which can be grafted by different ligands are responsible for site-selective chemical modification, such as Schiff base formation, N-acylation and reductive alkylation [39–41]. These modifications favor the continuous growth of Ch derivatives for various applications fields [40].

One of the chemical modifications of Ch involves grafting thiol groups in the polymer structure. Sulfur-containing covalent and

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noncovalent linkers (in particular, thiol, —SH) have attracted individual attention. Thiol groups due to the soft character of —SH group [42] that lead to the high affinity to gold [42–46], were successfully employed as a linker for anchoring GNPs to the support.

In this paper, we are reporting a new MCh which was synthesized by N-alkylation of Ch with methyl acrylate in the first step, and successively by 1,2-ethanedithiol. We have shown that the synthesized thiolated chitosan derivative (TChD) is a very effective ligand for anchoring GNPs. The resulting GNPs/TChD catalyst was compared with GNPs/Ch. The GNPs/TChD catalyst showed a better catalytic performance than GNPs/Ch and its related conversion was the highest reported conversion in solvent-free condition and using molecular oxygen as a cheap oxidant for oxidation of cyclohexene.

2. Experimental

2.1. Materials and physical measurements

All chemicals and solvents used in the synthesis were of reagent grade and were used without further purification. Chitosan (Sigma Aldrich medium molecular weight, 75–85% deacetylated) was used as the polymeric component. Methyl acrylate (MA), auric chloride ($AuCl_3$) and 1,2-ethanedithiol were purchased from Merck chemical company.

The Fourier transform infrared spectroscopy (FT-IR) analysis was performed using a Fourier transform infrared spectrometer (Jasco FT/IR-680 plus spectrophotometer). The powders were blended with IR-grade KBr in an agate mortar and pressed into tablets. The electronic spectra of solid samples were taken on a JASCO V-550 UV–vis spectrophotometer in the range of 200 to 800 nm, using the diffuse reflectance technique (DR UV–vis spectroscopy).

Particle size and morphology were evaluated from the transmission electron microscopy (TEM) images obtained in a JEM 2100F microscope operated with an accelerating voltage of 200 kV. The standard procedure involved dispersing 4 mg of the sample in ethanol in an ultrasonic bath for 15 min. The sample was then placed on a Cu carbon grid where the liquid phase was evaporated. The average diameter was calculated by measuring the diameters of no less than 500 randomly selected metal particles.

XP spectra were obtained with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer (constant pass energy of 50 eV) and a non-monochromatic ($h\nu = 1253.6$ eV) X-ray source, powered at 120 W. Wide scan data were collected using pass energy of 100 eV whereas high energy resolution spectra were recorded using pass energy of 20 eV. As the samples experienced variable degrees of charging the binding energy scale was referenced to adventitious carbon contamination using the C 1s line at 284.8 eV. The samples were analyzed after a base pressure of 2×10^{-9} mbar was reached within the analysis camber. Data processing was performed with the "*XPS peak*" software. The spectra were decomposed with the least squares fitting routine provided with the software, with Gauss/Lorentz lines (90G/10L) and after subtracting a Shirley background. Atomic ratios were calculated from the peak areas using sensitivity factors provided with the data system [47].

Elemental CHNS analysis was performed on a Perkin Elmer Carbon Hydrogen Nitrogen (CHN), 2400 Series II Elemental Analyzer.

The nitrogen adsorption isotherm recorded at −196 °C using a Quantasorb (Quantachrome, USA) equipment. Before nitrogen adsorption, the samples were degassed at 110 °C for 3 h to a residual vacuum of 10^{-3} mbar. The specific areas were calculated by the Brunauer–Emmett–Teller (BET) method using a value of 0.162 nm^2 for the cross section of adsorbed nitrogen molecule.

2.2. Reaction of methyl acrylate with Ch

Firstly, N-carboxyethyl chitosan methyl ester (CChME) was prepared successfully by the Michael addition as depicted by Scheme 1(A). Briefly, chitosan (2 g) was added to 50 mL methanol, and it was stirred overnight at 50 °C to be dispersed completely. The mixture was transferred to a 100 mL three-necked round-bottom flask fitted with a dropping funnel. Methyl acrylate (48 mmol; 4.3 mL) was dissolved in methanol (5 mL), and added to the reaction mixture dropwise over 10 min through dropping funnel under nitrogen atmosphere. The reaction was monitored using FT-IR spectroscopy. The unreacted methyl acrylate in the reaction mixture was removed completely by washing with methanol in a Soxhlet apparatus.

2.3. Grafting dithioethane to CChME

Once prepared, CChME was grafted with dithioethane. The procedure consisted in dispersing CChME in chloroform in a round bottom flask that was equipped with a reflux condenser. 1,2-Ethanedithiol (36 mmol; 3 mL) was added to the reaction mixture, which was refluxed for a period of 24 h. After the completion of the reaction, the product was rinsed several times with pure ethanol to remove unreacted 1,2-ethanedithiol and dried under vacuum at 30 °C overnight to obtain thiolated chitosan derivative (TChD) (Scheme 1(B)). The results of the CHNS analysis, FT-IR and XPS spectroscopy (Sections 3.1.1, 3.1.2 and 3.1.4, respectively) confirmed the presence of the thiol groups on the support.

2.4. Synthesis of GNPs on TChD

Next step consisted in the preparation of GNPs deposited on the TChD substrate. In a typical experiment, 2 g of the TChD were dispersed into 500 mL of distilled water (containing 2 wt% acetic acid), to which 5 mL of 10^{-2} M aqueous solution of $AuCl_3$ was added in 10 steps to the suspension during 24 h, under vigorous stirring for loading of 0.5 wt% of Au (III). The resulting product was separated via centrifugation, and washed few times with distilled water. The product was dried under vacuum at room temperature before characterization and catalytic activity measurements. In order to prepare 1 wt% of Au (III), 10 mL of aqueous solution of $AuCl_3$ (10^{-2} M) was added to suspension and all of the above processes was repeated again. To obtain the GNPs on the support, after addition of a given amount of aqueous metal salt ($AuCl_3$) to the suspension, an aqueous $NaBH_4$ solution (molar ratio of $NaBH_4$:Au = 10:1) was slowly added under vigorous stirring at room temperature, and left overnight; a bright red color was observed immediately after addition of reductant to the solution. Then the catalyst was separated by filtration, washed with distilled water, left overnight at room temperature and dried in oven at 90 °C.

Chemical reduction of Au (III) loaded on TChD with excess $NaBH_4$ results in formation of interdendrite-Au clusters (Scheme 1(C)) on TChD. Evidence for this reduction comes from the immediate change in solution color. It is noteworthy to mention that the same procedure was followed for Ch as a support without any modification to compare its catalytic activity with the new synthesized catalyst. The importance of modifying Ch on trapping the Au ions will be discussed in Section 3.1.3.

2.5. The selective oxidation of cyclohexene by molecular oxygen

In a typical experiment, 20 mL of cyclohexene and 50 mg of the solid catalyst were loaded in a titanium batch reactor. Proper pressure was provided with oxygen capsule (99.98%) and desired temperature selected and applied to the reaction mixture. After purging with O_2, the reactor was heated to 80 °C and the O_2