

## Perspective

## Gold nanoparticles deposited on surface modified carbon materials as reusable catalysts for hydrocarboxylation of cyclohexane

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## ABSTRACT

Gold nanoparticles were deposited on different carbon materials and used as catalysts for the alkane hydrocarboxylation reaction. Cyclohexane hydrocarboxylation to cyclohexanecarboxylic acid was carried out in the presence of CO and water, peroxodisulfate, in water/acetonitrile medium, at ca. 50 °C, with gold nanoparticles deposited by a colloidal method on carbon nanotubes and activated carbon with three different surface chemistries: in their original forms (CNT or AC, respectively), oxidized with HNO<sub>3</sub> (-ox) or oxidized with HNO<sub>3</sub> and subsequently treated with NaOH (-ox-Na). Au/CNT-ox-Na was the best catalyst, yielding cyclohexanecarboxylic acid up to 88.2% yield, with excellent recyclability (97.5% of the initial activity was maintained after five consecutive catalytic cycles).

## 1. Introduction

The carboxylation of C<sub>n</sub> alkanes to C<sub>n+1</sub> carboxylic acids, using CO, is an attractive process for alkane functionalization [1–17] that might have important applications in industry and surpass the disadvantages of the present synthesis procedures [2,5,7,15]. However, this reaction is very challenging from the chemical point of view, due to the need of C-H activation, that is very difficult to achieve for the least reactive lower alkanes (with 1–6 carbon atoms). Some authors [1,3,4] reported on the carboxylation of cyclohexane to cyclohexanecarboxylic acid (achieving 4.3% yield relative to the substrate) using CO and peroxodisulfate in trifluoroacetic acid (TFA), at 80 °C, using a Pd(II)/Cu(II) system as catalyst. A strongly acidic medium is needed, since the alkane is rather inert.

More recently, many works dealt with the improvement of alkane carboxylation towards the sustainable production of carboxylic acid, using greener and safer solvents [12–14,16,17]. Other authors reported on the hydrocarboxylation of cyclohexane to cyclohexanecarboxylic acid (with a 72% yield), using CO and water, in the presence of peroxodisulfate oxidant, in water/acetonitrile medium, at ca. 50 °C, on a tetracopper(II) catalyst, where water acts both as reagent and solvent [12]. Additionally, and contrarily to the reaction carried out in TFA [4,6,9,11], the carboxylation of cyclohexane by CO in the H<sub>2</sub>O/MeCN/

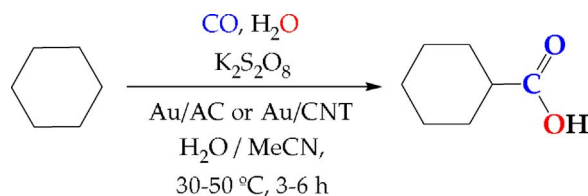
K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> system proceeds without catalyst up to a certain point, producing cyclohexanecarboxylic acid (up to 12% yield).

Naturally, the reaction proceeds more effectively in the presence of a catalyst (V, Mn, Fe or Cu) [12–14], with higher yields of carboxylic acid being achieved. Nevertheless, the homogeneous catalytic systems studied so far [13] cannot be re-used. Therefore, the quest for more efficient and eco-friendly heterogeneous methods that would allow catalyst recycling is still a challenge.

Supported gold catalysts have found application in different reactions of environmental and industrial importance [8,10,18–23]. Their catalytic activity is mainly influenced by the preparation method, the nature of the support and, in particular, the gold nanoparticle size [8,10,18–21]. However, the hydrocarboxylation of alkanes, using gold nanoparticles (supported on carbon nanotubes or activated carbon) as catalysts, has not been previously reported. Only alkyne hydrocarboxylation using gold complexes (not gold nanoparticles) [24,25], and the hydrocarboxylation of 1,3-butadiene catalyzed by a Rh(I) complex immobilized on activated carbon [26] can be found in the literature. The hydrocarboxylation of cyclohexane using gold nanoparticles on carbon xerogels was very recently reported by us [27]. However, the results found in the present work, for gold on activated carbon and carbon nanotubes, using the above-mentioned protocol [12] (Scheme 1), are far superior than those previously published for xerogels.

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**Scheme 1.** Hydrocarboxylation of cyclohexane to cyclohexanecarboxylic acid catalyzed by gold nanoparticles supported on carbon materials (AC = activated carbon; CNT = carbon nanotubes).

## 2. Experimental

### 2.1. Materials preparation

All the reagents and solvents were purchased from commercial sources and used as received. The water used for all reactions and analyses was double distilled and deionised.

#### 2.1.1. Carbon materials (supports)

Activated carbon (AC) from Sigma-Aldrich Norit<sup>®</sup> RO 0.8, and multi-walled carbon nanotubes (CNT) from Nanocyl<sup>™</sup> NC3100, were used in their original form, oxidized (-ox), and oxidized with nitric acid and subsequently treated with sodium hydroxide (-ox-Na). The -ox materials were obtained by refluxing 5 g of AC or CNT with 375 mL of a 5 M nitric acid solution, for 3 h, then separated by filtration and washed with deionized water until neutral pH, similarly to what was reported earlier [23,28–30]. The -ox-Na samples were obtained by treating 2 g of the -ox ones with 150 mL of a 20 mM NaOH aqueous solution, in reflux for 1 h, as reported in the literature [23,29,30]. These materials were also separated by filtration and washed until neutral pH.

#### 2.1.2. Gold catalysts

Gold (3% nominal wt.) was loaded on the carbon supports by a colloidal method [22,31–33]. This procedure consisted in dissolving 0.053 g of the gold precursor, HAuCl<sub>4</sub>·3H<sub>2</sub>O (Alfa Aesar), in 350 mL of water, adding 0.05 g of polyvinyl alcohol (Aldrich) and 0.023 g of NaBH<sub>4</sub> (Aldrich), previously dissolved into 5 mL of water, resulting in a ruby red solution to which the carbon support was added under stirring. The solution of the carbon material started to lose colour, as Au was deposited on the support. The stirring was maintained until total loss of colour (2–3 days in the case of carbon nanotubes and around 1 week for activated carbon samples). The colourless solution was filtered, the catalyst washed thoroughly with distilled water until the filtrate was free of chloride (around 1.5 L of water were used) and dried at 110 °C overnight. The organic scaffold was removed from the supports by a heat treatment under N<sub>2</sub> flow for 3 h at 350 °C, and then, the catalyst was activated by further treatment under hydrogen flow for 3 h, also at 350 °C.

### 2.2. Materials characterization

#### 2.2.1. Carbon materials (supports)

The carbon materials were characterised by N<sub>2</sub> adsorption at –196 °C in a Quantachrome Nova 4200e apparatus, using the Brunauer-Emmett-Teller (BET) method for total surface area determination, Barrett-Joyner-Halenda (BJH) for pore size distribution and Boer's t-method for micropore volume and external surface area.

The determination of oxygenated surface functional groups was performed by temperature programmed desorption–mass spectrometry (TPD–MS), according to procedures already established in previous publications [32–35]. CO and CO<sub>2</sub> TPD profiles were obtained with a fully automated Altamira AMI-300 equipment. The sample (100 mg) was placed in a U-shaped quartz tube inside an electrical furnace. A flow of He (25 cm<sup>3</sup>/min) was passed through the sample for 1 h at room temperature. Afterwards, the material was heated up to 1100 °C, at

5 °C/min linear temperature increase also under He flow (25 cm<sup>3</sup>/min). A quadrupole mass spectrometer (Ametek Dycor DyMaxion) was used to monitor CO and CO<sub>2</sub> signals, with temperature increase. For quantification of the CO and CO<sub>2</sub> released, calibration of these gases was carried out at the end of the analysis.

#### 2.2.2. Gold catalysts

The Au/CNT and Au/AC samples were imaged by transmission electron microscopy (TEM). The analyses were performed on a JEOL 2010F Field Emission Gun Transmission Electron Microscope (FEG-TEM), working in both High Resolution TEM (HR-TEM) and Scanning-Transmission (STEM) modes at 200 kV accelerating voltage. The average gold particle size was determined from measurements made on up to 100 particles (depending on sample). Gold size distribution histograms were also obtained. The dispersion was calculated from the formula [36]:

$$D = \frac{6Mn_s}{\rho Nd} \approx \frac{1.17}{d(\text{nm})},$$

where M represents the molar mass of Au (197 g/mol), n<sub>s</sub> the number of atoms of Au per unit area (1.15 × 10<sup>19</sup> m<sup>-2</sup>), ρ the density of Au (19.3 g/cm<sup>3</sup>), N is Avogadro's number, and d (nm) the average particle size, determined by TEM, considering the spherical gold nanoparticles.

X-ray photoelectron spectroscopy (XPS) analyses of the Au 4f region were carried out for selected samples in order to confirm the expected reduced state of gold. The equipment used was a VG Scientific ESCALAB 200A spectrometer using Al Kα radiation (1486.6 eV). The charge effect was corrected taking the C 1s peak as a reference (binding energy of 285 eV). CASAXPS software was used for data analysis.

SEM analyses were carried out on a scanning electron microscope JEOL 7001F with Oxford light elements EDS detector and EBSD detector.

In order to determine the loading of gold, samples were incinerated at 600 °C and the resulting ashes were dissolved in a concentrated HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> mixture. The resulting solution was diluted and analysed by atomic absorption spectroscopy (AAS) using a Unicam 939 atomic absorption spectrometer and a hollow cathode lamp Heraeus 3UNX Au. The amount of Na on selected samples was determined using a similar procedure.

### 2.3. Catalytic tests

The single-pot reactions were undertaken in stainless steel auto-claves, by reacting, at typical temperatures of 30–80 °C and in a water/acetonitrile medium with cyclohexane, carbon monoxide (pressures from 2 to 20 atm), gold catalyst (2–20 μmol) and potassium peroxodisulfate. The reaction mixture was stirred for 3–6 h (typically 6 h) using a magnetic stirrer and an oil bath, whereupon it was cooled in an ice bath, degassed, opened and the contents transferred to a Schlenk flask. Diethyl ether (9.0–11.0 mL) and 90 mL of cycloheptanone (GC internal standard) were added. The obtained mixture was vigorously stirred for 10 min, and the organic layer was analysed typically by GC. Chromatographic analyses were undertaken by using a Fisons Instruments GC 8000 series gas chromatograph with a DB-624 (J & W) capillary column (flame ionization detector) and the Jasco-Borwin v.1.50 software. GC–MS analyses were performed in a gas chromatograph Perkin Elmer Clarus 600C instrument GC–MS, using He as the carrier gas, equipped with a 30 m × 0.22 mm × 25 μm BPX5 (SGE) capillary column. The internal standard method was used to quantify the organic products.

Blank tests *i*) without any catalyst, *ii*) only with CM, CM-ox and CM-ox-Na (CM = CNT or AC), and *iii*) using only one of the solvents (H<sub>2</sub>O or NCMe) were also performed, to assess if the carboxylation reactions proceeded in the absence of metal catalyst and the importance of each support and solvent. Moreover, aqueous solutions of the gold precursor were also tested for comparison (homogenous medium).

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