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Selective oxidation of 1-octanol over gold supported on mesoporous metal-modified HMS: The effect of the support

S. Martínez-González[a], A. Gómez-Avilés[a], O. Martynyuk[b,c], A. Pestryakov[c], N. Bogdanchikova[b], V. Cortés Corberán[a,*]

[a] I. of Catalysis and Petroleumchemistry (ICP), CSIC, Marie Curie 2, 28049 Madrid, Spain
[b] Centro de Nanociencias y Nanotecnologia (CNN), Universidad Nacional Autónoma de México (UNAM), 22800 Ensenada, Mexico
[c] Tomsk Polytechnic University, Tomsk 634050, Russia

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ABSTRACT

Selective oxidation of long chain alkanols ($_{+}C_{8+}$) has deserved much less attention than that of more reactive benzylic or C_1–C_4 aliphatic alcohols. Supported gold nanoparticles (NP) are active for the oxidation of alcohols under green chemistry conditions, and high surface supports are used to maximize and stabilize their dispersion. In this work, we investigate hexagonal mesoporous silicas (HMS), pure or modified with metal cations having redox properties (Ce, Fe), as supports of gold NP catalysts for the aerobic oxidation of 1-octanol under green process conditions. Two ways of support modification were used, say, by introducing the modifying cations during the HMS synthesis or by post-synthesis impregnation.

Octanal was the main product on every catalyst under the conditions tested (80 °C, oxygen flow at atmospheric pressure, solvent base-free heptane); the ester also formed but no acid was detected. Both the composition and the preparation method of the support influenced the activity and stability of the catalysts: the best performance was found on catalysts with post-synthesis impregnated supports, where additional phases of the corresponding oxides are detected by XRD (X-ray diffractometry). IR (infrared) studies of CO adsorption on the catalysts revealed that is due to the different nature of the Au NPs, which are smaller (or positively charged) and preferentially deposited on the modifier oxidic phase in these catalysts.

1. Introduction

Selective oxidation of alcohols plays a key role in inorganic synthesis and in industrial practice. Conventional methods were based in the use of stoichiometric oxidants, mostly transition metal and halogenated compounds or sulfur oxides, producing great amounts of undesirable sub products. So, considerable efforts are being made to adapt it to the principles of green chemistry, by the implementation of processes based on catalysis and non-toxic oxidants, such as oxygen. Among the many types of heterogeneous catalysts reported for the aerobic oxidation of alcohols [1,2], supported gold nanoparticles (Au NPs) have attracted a great interest for their high product selectivity without any other metal addition [3–9].

Non activated, primary aliphatic alcohols (alkanols) are the most difficult type of alcohols to oxidize selectively, and 1-octanol is usually taken as a reference example of these alkanols in comparative studies of alcohol reactivity on different catalysts [2]. Prati et al. [7] reported that carbon supported Au NPs require a strong base and high pressure of oxidant to achieve and maintain catalytic activity for 1-octanol oxidation. However, the same group reported that the reaction can be conducted in the absence of alkali under 3 bar of O_2 when Au is supported on metal oxides [8], and that the activity depends not only on the basic properties of the support surface, but also in the particle size of the oxidic support. Recently, Ishida et al. reported the oxidation of 1-octanol in a base-free system on Au NPs catalysts supported on various metal oxides using 5 bar O_2 [10]: their catalytic activity and product distribution depend primarily on the nature of the support, and the best performances are found with catalysts supported on oxides with redox properties. However, as the results are obtained after a certain reaction time in a closed vessel, no information is obtained on the evolution of the activity with the run time. In addition, the use of oxygen at atmospheric pressure should be preferable, from the point of view of a green process.

Supported Au NPs catalysts frequently deactivate as the average size of the supported metal nanoparticles increases due to sintering, and usually the surface area of the oxidic support is moderate, which limits the dispersion of the metal. In this work we investigate the use of hexagonal mesoporous silica (HMS) as a high surface area support for maximizing the number and

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* Corresponding author. Tel.: +34 915854783; fax: +34 915854760.
E-mail address: vcortes@icp.csic.es (V.C. Corberán).

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dispersion of Au NPs, aiming to produce sinter-stable catalysts. HMS are mesoporous molecular sieves with wormhole like frameworks, with physical and catalytic properties substantially different from MCM-41 materials [11,12]. The interaction between gold and pure silica is weak. To improve this interaction, and to provide redox properties to the support surface, the HMS supports have been modified with cerium and iron, by two different ways: by introducing them in the initial synthesis of the HMS, or by depositing them by post-synthesis impregnation. The supported Au NPs catalysts prepared with these supports have been used for selective oxidation of 1-octanol as a model of longer chain alkanols. Looking to approach green processes principles, we investigated the catalytic reaction under demanding conditions, say, using oxygen at atmospheric pressure as oxidant and with no base addition to the reacting medium, and following the evolution of the catalytic performance with reaction time. The effects of the support, and its modifications, on the catalytic properties are then discussed in terms of the nature of the gold active centers, as studied by CO adsorption experiments.

2. Experimental

2.1. Supports preparation

Hexagonal mesoporous silica (HMS) was synthesized by a neutral S^0I^0 templating route (S^0: neutral primary amine surfactant; I^0: neutral inorganic precursor) [11,12]. Dodecylamine was employed as a surfactant and mesitylene as a swelling organic agent [13]. The reaction products were filtered, washed, with distilled water, and dried at room temperature for 24 h and at 100 °C for 2 h. The template was then removed by calcination at 550 °C for 3.5 h in air, at a heating rate of 2.5 °C min^{-1}.

The direct synthesis metal-modified HMS supports (M-HMS) were prepared similarly, incorporating the metal M in the synthesis using cerium nitrate hexahydrate or iron (III) nitrate nonahydrate as precursors, with an atomic ratio Si/M = 40. The reaction products were filtered, washed with distilled water and dried at room temperature for 48 h, followed by drying at 110 °C for 4 h, and then the samples were calcined at 550 °C for 4 h in static air.

The metal-impregnated supports (M/HMS) were prepared by impregnation of the pure HMS support by the pore filling method, with 1.5 cm^3/g of an aqueous solution of cerium nitrate hexahydrate or, iron (III) nitrate nonahydrate, having the concentration needed to obtain a final Si/M = 40. These impregnated samples were dried and calcined under the same conditions described previously.

2.2. Synthesis of $Au(en)_2Cl_3$

Ethylenediamine (0.45 mL) was slowly added to the solution of $HAuCl_4{\cdot}3H_2O$ (1.0 g) in deionized water (10 mL). The transparent brown solution was magnetically stirred for 30 min. Then, ethanol (70 mL) was added to it, resulting in the formation of a white precipitate. The suspension was stirred for other additional 20 min and filtered. The solid was washed with ethanol and dried at 40 °C under vacuum overnight.

2.3. Catalysts preparation

$Au(en)_2Cl_3$ (0.5 g) was dissolved in water (50 mL) and the pH of the solution was adjusted to 10.0 by the addition of the aqueous solution of NaOH (5.0 wt.%). This method was selected to deposit a cationic gold precursor onto the HMS surface (zero charge point of silica is 2.0). Then, the support HMS, M-HMS or M/HMS (1.0 g) was added. The pH of the solution, which dropped after the addition of the support, was re-adjusted to ca. 10.0. The suspension was stirred at 60–70 °C for 2 h and filtered. The solid was washed with distilled water and dried in vacuum at 70 °C for 5 h. Finally, the catalysts were thermally treated at 300 °C in air for 1.5 h to ensure a complete removal of the organic template.

2.4. Catalysts and supports characterization

Metal and gold loadings were measured by energy dispersive spectroscopy in a Jeol 5300 scanning electron microscope equipped with a Kevex Superdry detector.

The textural properties of supports and catalysts were determined from nitrogen adsorption–desorption isotherms (−196 °C) recorded with a Micromeritics TriStar 3000 apparatus. Prior to experiments, samples were degassed at 300 °C in vacuum for 5 h. The volume of the adsorbed N_2 was normalized to a standard temperature and pressure. The specific areas of the samples were calculated by applying the BET method to the nitrogen adsorption data within the P/P^0 range 0.005–0.25. An average pore diameter was calculated by applying the Barret–Joyner–Halenda method (BJH) to the adsorption and desorption branches of the N_2 isotherms. A cumulative pore volume was obtained from the isotherms at $P/P^0 = 0.99$.

Pure supports and the reduced (5% H_2/He, 300 °C, 1 h) catalysts were characterized by powder X-ray diffractometry (XRD) according to the step-scanning procedure (step size 0.02°; 0.5 s) with a Philips X'Pert PRO diffractometer, using Ni-filtered CuKα ($\lambda = 0.15406$ nm) radiation. Assignment of crystalline phases was based on the ICDD- 2013 powder diffraction database.

High resolution transmission electron microscopy (HRTEM) studies were carried out using a JEM 2100F microscope operating with a 200 kV accelerating voltage. The samples were ground into a fine powder and dispersed ultrasonically in hexane at room temperature. Then, a drop of the suspension was put on a lacey carbon-coated Cu grid. At least ten representative images were taken for each sample. A particles size distribution was obtained by counting ca. 100 particles for each sample. Particle size diameters were calculated from the following equation: $d_{avg} = \Sigma\,(n_i d_i)/\Sigma\, n_i$.

2.5. FT-IR spectra of adsorbed CO

Fourier transformed infrared (FT-IR) spectra of CO adsorbed on the catalysts were recorded at a resolution of 4 cm^{-1} by using a Bruker Tensor 27 FT-IR spectrometer in transmittance mode. In situ experiments were carried out in a quartz cell with NaCl windows capable of working at temperatures from −100 to 500 °C and pressures from 10^{-2} to 760 Torr. The powder catalyst samples were pressed into self-supporting disks 13 mm in diameter and <20 mg in weight and placed at the center of the cell. They were then exposed to set pressures of carbon monoxide (Matheson Research grade) without further purification. CO adsorption FT-IR experiments were performed after the sample pre-treatments in hydrogen (100 Torr) at 300 °C for 1 h. CO adsorption (30 Torr) took place at room temperature. CO FT-IR spectra of the samples were obtained by subtracting CO gas phase spectrum.

2.6. Catalytic oxidation of 1-octanol

Prior to tests, catalyst samples were prereduced with pure H_2 (10 mL/min) at 300 °C for 2 h [14]. In a typical test, catalyst was added (in a substrate/metal ratio (R) = 100 mol/mol) to 20 mL of 1-octanol solution (0.1 M) in n-heptane, in four-necked round bottom flask equipped with reflux condenser, oxygen feed, thermometer and a septum cap. The reaction mixture was stirred in a batch reactor operated under atmospheric conditions at 80 °C. Oxygen was bubbled through the suspension with a flow rate of 30 mL/min for 6 h. Small aliquots were taken from the