



Au₂₅(SPh-pNH₂)₁₇ nanoclusters deposited on SBA-15 as catalysts for aerobic benzyl alcohol oxidation



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ARTICLE INFO

Article history:

Received 10 October 2014

Revised 4 December 2014

Accepted 7 December 2014

Available online 27 December 2014

Keywords:

Gold clusters

Thiolate ligands

Aerobic oxidation

Dehydrogenation

Benzyl alcohol

ABSTRACT

Au₂₅(SPh-pNH₂)₁₇ clusters deposited on mesoporous silica SBA-15 (mean particle size 0.9 ± 0.2 nm) have been used as catalysts in the oxidation of benzyl alcohol. In the absence of radicals, fresh thiolate clusters are not active even in the presence of caesium carbonate. The activity strongly increases with calcination temperature and reaches a maximum when all ligands have been removed to form gold nanoparticles of ca. 1.8 nm. In the presence of radical initiators, functionalized clusters deposited on SBA-15 are very active, but the benzaldehyde formed is rapidly consumed by over-oxidation. The activity is attributed to the presence of –S–Au^I–S–bridges at the surface of the clusters. Upon calcination, the activity decreases due to reduction of Au^I species and the absence of radicals in the reaction medium. However, approximately 45% of alcohol is converted into benzaldehyde, with a selectivity of ca. 65% after 30 h.

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1. Introduction

Since Haruta's pioneer work on the CO oxidation reaction catalyzed by gold nanoparticles [1,2], catalysis by metal nanoparticles (NPs) has become a hot topic in chemistry. It has been reported that the catalytic performance of NPs was strongly depending on their size and that very small particles (<5 nm) possess specific properties, different from those of bulk metal. In particular, though gold has been considered as catalytically inactive for years, Au NPs smaller than 5 nm can activate molecular oxygen, and therefore have been used as catalysts in numerous reactions such as C–C bond formation, hydrocarbon combustion [3,4], hydrogen peroxide (H₂O₂) formation through the direct oxidation of H₂ by O₂ [5,6], ozone decomposition [7,8], selective oxidations of alcohols [9–11], alkenes [12,13] and alkanes [14–19], etc. Using O₂ as oxygen source instead of strong oxidants such as KMnO₄ or even stoichiometric quantities of hydroperoxides is a good way to achieve green chemistry. In this respect, aerobic oxidations are of greatest interest, because they also have the advantage to use air as limitless and free oxidizing agent. Therefore, aerobic oxidation reactions are also particularly interesting for industrial applications.

Benzaldehyde is a valuable product with many applications in pharmaceuticals, agro-chemistry and fragrance industries.

Industrially, the main routes to benzaldehyde production are dichloromethylbenzene hydrolysis and toluene vapour/liquid phase oxidation [20]. The first method involves complicated technical processes and disposal issues which consist mainly of corrosive gases and subsequently organic wastes plus chlorine as final product. The second industrial method requires high temperatures and pressures, and suffers from a carbon loss in the form of CO₂.

Research papers have reported the use of gold nanoparticles as effective catalysts for the oxidation of benzyl alcohol to benzaldehyde [21–28]. For this reaction, the different conditions involve temperatures generally above 100 °C and the use of 1–10 bar of pure O₂, and this energy-consuming set-up can be an obstacle for an industrial scale-up. Other studies which mention combinations of deposited gold nanoparticles with a strong oxidant, namely *tert*-butylhydroperoxide (TBHP), clearly show that gold can be an effective and interesting catalyst at relatively low temperatures, making it interesting for industrial applications [20]. However, despite extensive studies on this subject, the influence of the particles size, the effect of the support and the difficulty to obtain monodisperse particles with a narrow particle size distribution (PSD) make difficult to rationalize the mechanisms involved in this reaction. Moreover, it emerges from those studies that there are two different mechanisms to obtain benzaldehyde from benzyl alcohol, and by extension, any aldehyde/ketone from the corresponding alcohol. These two mechanisms are either a radical oxidation reaction using strong oxidant such as hydroperoxides or an oxidative dehydrogenation, in the presence of a strong homogeneous or

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heterogeneous base. Theoretical studies have shown that the dehydrogenation pathway is a two-site, structure sensitive reaction [11,29] and that the active species are O^* and OH^* formed on the metallic surface [30]. On the other hand, when peroxides are used as oxygen source, theoretical studies emphasized the importance of having positively charged Au atoms in order to have an efficient catalytic system. Liu et al. showed by DFT calculations that $-S-Au^+-S-$ moieties, formed by decomposition of Au_{25} clusters in the gas phase, seem to be the active species for the formation of epoxides from hydroperoxides [31].

Over the last decade, atomically well-defined thiolate gold clusters with the generic formula $Au_n(SR)_m$ – where n is the number of gold atoms and m that of the surrounding thiolate-based molecules – have attracted much attention due to their unique electronic, magnetic and optical properties [32–38]. Interests in these compounds also arose from the fact that some structures had been resolved, which enabled a better understanding of their catalytic properties in relation with the size and the structure of the nanoparticles [39,40].

In addition, although sulphur species are usually considered as a poison in catalytic reactions with gold NPs, it has been shown that gold clusters could be active even in the presence of thiolate ligands for the oxidation of CO [41,42] or sulphide [43], the reduction of nitrophenol [44] or the selective hydrogenation of ketones and aldehydes [45,46].

Herein, we have studied the influence of the presence of thiolate ligands around gold nanoclusters in the oxidation of benzyl alcohol following the two routes described above. First, gold nanoclusters were used as catalysts in the oxidative dehydrogenation of benzyl alcohol in the presence of a base (CS_2CO_3). Catalysts were prepared by deposition of gold clusters $Au_{25}(SPh-pNH_2)_{17}$ on a mesoporous silica SBA-15 [47]. The influence of the ligands in the reaction was studied by following the evolution of the activity with calcination temperature. For the radical oxidation route, catalysts were also used before and after removal of the ligands in the presence of *tert*-butylhydroperoxide (TBHP) as radical initiator. Data showed that the presence of ligands in $Au_{25}(SPh-pNH_2)_{17}@SBA-15$ catalysts was beneficial to the radical oxidation of benzyl alcohol, whereas their elimination was necessary to activate the dehydrogenation mechanism.

2. Experimental section

2.1. Materials

Tetraethyl orthosilicate (TEOS, 98%), poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (P123 Triblock Copolymer, \sim Mn 5800), hydrochloric acid (HCl, 37%), *N,N*-dimethylformamide (DMF, puriss. p.a. \geq 99.8% (GC)), tetrachloroauric acid trihydrate ($HAuCl_4 \cdot 3H_2O$, \geq 49.0% Au basis), lithium borohydride solution ($LiBH_4$, 2 M in THF) and THF (Chromasolv[®]) were purchased from Sigma-Aldrich. Absolute ethanol (technisolv) was purchased from VWR International.

Benzyl alcohol (99+%), caesium carbonate (99%), toluene (Chromasolv[®], 99.9%) and acetonitrile (Chromasolv[®], 99.9%) were purchased from Sigma-Aldrich. Dodecane (99+%) and benzaldehyde (98+%) were purchased from Acros. All products were used as-received without further purification.

4-aminothiophenol (4ATP) was purchased from TCI and has been purified through sublimation prior to use. The obtained white crystals were stored at $-10^\circ C$ under air atmosphere. Anhydrous, inhibitor-free THF was purchased from Sigma-Aldrich and dried over an MB-SPS-800 system device prior to use.

$Au@TiO_2$ -WGC (Sample 105-A) was purchased from the World Gold Council. Gold particles have an average diameter of 3.5 ± 1.5 nm. Gold loading is 1.5 wt%.

2.2. Characterization techniques

Gold loading was determined by inductively coupled plasma optical emission spectroscopy (HORIBA Jobin Yvon Activa ICP-OES). Solids were decomposed in H_2SO_4 + aqua regia solution + HF and then in HCl.

Powder X-ray diffraction (XRD) was carried out on a Bruker D8 Advance A25 diffractometer using $Cu K\alpha$ radiation. Small-angle X-ray scattering was recorded between 0.45° and 7° (2θ) with 0.01° steps and 2 s per step. Wide-angle X-ray scattering was recorded between 4° and 90° (2θ) with 0.02° steps and 0.5 s per step. Longer acquisition was recorded between 30° and 90° (2θ) with 0.02° steps and 4.0 s per step.

Thermogravimetric analysis (TGA) was performed with a TGA/DSC 1 STARE System from Mettler Toledo. Around 3 mg of sample was heated from 25 to $900^\circ C$ at a rate of $10^\circ C/min$ in a 70- μ l alumina crucible, under air atmosphere (20 ml/min).

For simulated calcinations, around 3 mg of the crude clusters were heated at a rate of $10^\circ C/min$ from $25^\circ C$ to the final considered temperature (200, 300, 400 and $520^\circ C$) in a 70- μ l alumina crucible, under air atmosphere (20 ml/min). Final temperature was maintained for 12 h. The weight loss was compared to the complete loss observed by TGA from 25 to $900^\circ C$.

Transmission electron microscopy (TEM) was carried out on a JEOL 2010 LaB₆ microscope operating at 200 kV. Catalysts were embedded in an epoxy resin and sectioned with an ultramicrotome to obtain thin slices.

Gas chromatography was carried out on a Shimadzu GC-2014, using an Equity TMS $30 m \times 0.25 mm \times 0.25 \mu m$ column programmed from $60^\circ C$ to $180^\circ C$, injector and FID detector set at $280^\circ C$ and $200^\circ C$, respectively, and He as carrier gas. External calibration was carried out by injecting distinct standard solutions containing benzyl alcohol, benzaldehyde and methylcyclohexanol (MCOH). Methylcyclohexyl hydroperoxide (MCOOH) calibration was taken from previous work (PPH₃ titration followed by ^{31}P NMR to determine the response factor) [48]. Internal standard (dodecane) was used to calculate the conversion and yield of the reaction.

2.3. Catalysts preparation

Clusters $Au_{25}(SPh-pNH_2)_{17}$ have been synthesized following a synthesis procedure previously reported [49]. SBA-15 was prepared using the recipe of Zhao et al. and exhibits 8-nm hexagonal channels with surface area of $570 \pm 5 m^2 g^{-1}$ (Fig. S1, ESI) [47,50,51].

2.3.1. Clusters deposition

Cluster deposition was performed using a wet impregnation protocol adapted from previous reported preparations [15,47,52]. Gold amounts corresponding to theoretical loadings of 2 wt% (Batch A) and 0.15% (Batch B), were dispersed in a minimum of solvent, and the solution was added dropwise into a stirred suspension of the silica support.

2.3.1.1. Batch A – 2 wt% theoretical gold loading. A solution containing $Au_{25}(SPh-pNH_2)_{17}$ clusters (44.7 mg, 6.4 μ mol of clusters) dispersed in DMF (6 ml) was added dropwise into a stirred suspension of the mesoporous silica support SBA-15 (1.520 g) in ethanol (50 ml). Within a couple of hours, a discoloration of the solution from black to brown was observed. After 24 h, the prepared catalyst was recovered by centrifugation (15 min, 8000 rpm) and washed successively two times with DMF and two times with ethanol. The catalyst was then left to dry under air at room temperature to obtain a grey solid.

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