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Atomically well-defined $Au_{25}(SR)_{17/18}$ nanoclusters deposited on silica supports for the aerobic epoxidation of *trans*-stilbene

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ABSTRACT

Two atomically well-defined thiolate gold nanoclusters, $Au_{25}(SC_2H_4Ph)_{18}$ and $Au_{25}(SPhNH_2)_{17}$, having the same gold core but different thiolate ligands have been deposited on silica supports and the obtained catalysts have been tested in the aerobic oxidation of *trans*-stilbene. By properly selecting the support to maximize cluster/surface interactions, it was possible to prepare materials with small nanoparticles and very narrow particle size distributions. $Au_{25}(SPhNH_2)_{17}$@SBA-15 catalyst showed an activity and a *trans*-stilbene epoxide selectivity comparable to the best heterogeneous catalysts. Elimination of the thiolate molecules by calcination did not significantly modify the particle size but decreased the activity, pointing out the critical role of the ligands in the reaction.

1. Introduction

Since Haruta's work on CO oxidation catalyzed by gold nanoparticles [1], those materials have been widely used as catalysts in various catalytic reactions such as alcohols and aldehydes oxidation, alkenes epoxidation, hydrochlorination of ethyne, carbon–carbon bond formation, and so on [2]. When reactions can be performed in the presence of non-polluting oxidants, typically oxygen from the air, they are particularly important for industry. Aerobic oxidations can be carried out over supported gold nanoparticles [3] as well as colloids [4]. Among these oxidative reactions, selective alkenes epoxidation remains an important challenge in fine chemicals area and efficient catalysts are still needed. Gold nanoparticles deposited on different supports can efficiently catalyze the aerobic epoxidation of alkenes [5–7] but despite extensive studies on the subject, the understanding of the role of particles diameter, their surface, the effect of the support and the difficulty to obtain monodisperse particles with a narrow particle size distributions (PSD) makes difficult to rationalize the mechanisms involved in this reaction.

Over the past decade, atomically well-defined thiolate gold clusters, defined as $Au_n(SR)_m$, where n and m are number of gold atoms and surrounding thiolate-based molecules, respectively, have attracted intense research interests due to their unique electronic, magnetic and optical properties [8]. These atomically and structurally well-defined thiolate gold clusters have emerged as a new promising catalysts class to understand the relationship between the size, the structure of the nanoparticles and their catalytic activity [9]. Indeed, their atomically well defined composition and known structure can lead to a precise understanding of size, structural and electronic effects on the catalytic mechanisms.

In addition, although sulfur species are considered as a poison in catalytic reactions such as the oxidation of styrene [10], it has been shown that thiolate gold clusters can be active, even in the presence of thiolate groups, for the oxidation of CO [11] or sulfide [12], the reduction of nitrophenol [13] or the selective hydrogenation of ketones and aldehydes [14,15]. For the epoxidation of alkenes, thiolate gold clusters have been tested on styrene [14], and on both *trans*- and *cis*-stilbene substrates [16]. The conversion of styrene, with $Au_{25}(SC_2H_4Ph)_{18}$ clusters as the catalyst, in the presence of O_2, was of ca. 18 and 27% at 24 h, depending on whether clusters were supported or not on silica [14]. The major product in this reaction was the benzaldehyde (selectivity ~70%). On the contrary, for the *trans*-stilbene epoxidation with $Au_{25}(SC_2H_4Ph)_{18}$@SiO_2 and an excess of *tert*-butyl hydroperoxide used as the oxidant, the main product was the *trans*-epoxide (selectivity 94%) with a 51% conversion at 24 h [16].

In the present work, we have studied the effects of the presence of thiolate ligands around gold nanoclusters, their nature and the type of silica on which they are supported in the aerobic epoxidation of *trans*-stilbene. Reactions are carried out in

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methylcyclohexane at atmospheric pressure, 80 °C, using *tert*-butyl hydroperoxide (TBHP) as a radical initiator. Two gold clusters have been tested, namely $Au_{25}(SC_2H_4Ph)_{18}$ with hydrophobic external phenyl groups and $Au_{25}(SPhNH_2)_{17}$ with hydrophilic external amino functions. The two supports were AEROSIL® R 972, a hydrophobic fumed silica and SBA-15, a hydrophilic ordered mesoporous silica.

In liquid phase heterogeneous catalytic reactions involving supported nanoparticles, some of the main parameters that have to be considered to select the best catalysts are the wettability of the support in the reaction medium and the interaction between the nanoparticles and the support to prevent release of colloids in the solution. Because of their different surrounding thiolate ligands, the two Au_{25} clusters have been deposited on two different supports to maximize cluster-support interactions: $Au_{25}(SPhNH_2)_{17}$ on SBA-15, to favor hydrogen bond interactions between the silanol groups of the silica with the amino functions and $Au_{25}(SC_2H_4Ph)_{18}$ on Aerosil-R972 to promote hydrophobic interactions. These interactions are indeed of prime importance for the stability and recyclability of catalysts. The recent report on the adsorption of $Au_{25}(SC_{12}H_{25})_{18}$ on carbon nanotubes through weak hydrophobic interaction clearly shows the importance of selecting the appropriate support according to the clusters external functions [17].

Finally, the effect of ligands has been evaluated by comparing the activity of $Au_{25}(SPhNH_2)_{17}$ on SBA-15 before and after calcination at 400 °C.

2. Experimental

2.1. Materials

N,N-dimethylformamide (DMF, puriss. p.a. ≥99.8% (GC)), dichloromethane (Laboratory reagent, without stabilizer, >99.9%), methylcyclohexane (ReagentPlus® 99%), methanol (MeOH, puriss p.a.), tetrahydrofurane (THF, Chromasolv®), *trans*-stilbene (96%) and *tert*-butylhydroperoxide solution (TBHP, 70% in water) are purchased from Sigma–Aldrich Company. Ethanol absolute (technisolv) is bought from VWR International.

Gold nanoparticles deposited on TiO_2 (Au@TiO_2) (sample 105-A) is purchased from the World Gold Council [18]. The gold particles have an average diameter of 3.5 ± 1.5 nm with a gold loading of 1.5 wt% and the titania support is Degussa P25, a mixture of anatase (80%) and rutile (20%). This solid is used as a reference in the *trans*-stilbene epoxidation reaction [6].

All reagents and solvents are of commercial quality and used without further purification. The glassware used in the synthesis are cleaned with *aqua regia* (*aqua regia* is a very corrosive product and should be handled with extreme care), then rinsed with copious amount of distilled water and dried overnight prior to the use. All reactions are carried out in atmospheric conditions.

2.2. Equipments

Gold loading is determined by inductively coupled plasma optical emission spectroscopy (HORIBA Jobin Yvon Activa ICP-OES) and focused at 242.79 and 267.59 nm onto the detector. The solids are decomposed in H_2SO_4 + aqua regia solution + HF and then in HCl.

Standard X-ray diffraction (XRD) is carried out on a Bruker D8 Advance A25 diffractometer using Cu Kα radiation equipped with a 1-dimensional position-sensitive detector (Bruker LynxEye). X-ray pattern is recorded between 4° and 90° (2θ) with 0.02° steps and 2 s per step. Divergence slit is fixed to 0.2° and the detector aperture to 189 channels (2.9°).

Transmission electron microscopy (TEM) is carried out on a JEOL 2010 LaB_6 microscope operating at 200 kV. All samples are dispersed in ethanol with the help of an ultrasonic bath and then a drop is deposited on a copper grid and let to dry under ambient conditions of atmosphere and temperature. Samples **3** and **4** are embedded in an epoxy resin and sectioned with an ultramicrotome to obtain thin slices.

Gas adsorption isotherms for pressures in the range 0.01–1 bar are measured by using a Micromeritics ASAP2020 instrument. Powders of the compounds are transferred to a preweighed analysis tube, which is capped and evacuated by heating at 100 °C under dynamic vacuum for 12 h. The sealed tube is then transferred to the analysis port of the gas adsorption instrument. For all isotherms, warm and cold free-space correction measurements are performed by using ultra-high purity He gas (UHP grade 5.0, 99.999% purity). The N_2 isotherms at 77 K are measured in a liquid nitrogen bath, using UHP-grade gas sources. The specific surface area is calculated from the Brunauer–Emmett–Teller (BET) method and the pore size distribution by employing the Barrett–Joyner–Halenda (BJH) model on the desorption curve of the N_2 isotherm.

X-ray photoelectron spectroscopy (XPS) experiments are carried out on a Kratos Axis Ultra DLD spectrometer using monochromated Al Kα X-rays (1486.6 eV, 150 W), a pass energy of 20 eV, a hybrid lens mode and stainless steel sample holder in ultra-high vacuum ($P < 10^{-9}$ mbar). The analyzed surface area is 700 μm × 300 μm. Charge neutralization is required for all samples. Shirley background subtraction is performed with the Vision 2.2.8 Kratos processing program.

Gas chromatography is carried out on a Shimadzu GC-2014, using a Equity TMS 30 m × 0.25 mm × 0.25 μm column programmed from 60 °C to 180 °C, injector and FID detector set at 280 °C and 200 °C respectively, and He as carrier gas (26.6 mL min^{-1}). External calibration is carried out by injecting distinct standard solutions containing *trans*-stilbene (96%, Sigma–Aldrich), *trans*-stilbene oxide (99%, Aldrich) and benzyl alcohol (99+%, Sigma–Aldrich) in acetonitrile. Internal standard (dodecane) is used to calculate the conversion and yield of the reaction.

2.3. Catalysts preparation

Syntheses of the clusters $Au_{25}(SC_2H_4Ph)_{18}$ [19] and $Au_{25}(SPhNH_2)_{17}$ [20] have been done by following the previous reports. Hydrophobic silica (Aerosile® R972) is purchased from Degussa and is described with an average primary particle size of 16 nm and a surface area of 116 ± 2 $m^2\,g^{-1}$. SBA-15 is prepared by following a previous described synthesis [21] and Exhibits 8 nm hexagonal channels and a surface area of 570 ± 5 $m^2\,g^{-1}$ (Fig. S1).

Cluster deposition is carried out by following a wet impregnation. A calculated amount, for a theoretical gold loading of 2 wt%, is dispersed in a minimum of solvent and is added dropwise into a stirred suspension of the silica support.

2.3.1. Preparation of $Au_{25}(SC_2H_4Ph)_{18}$@SiO_2(R972) (**1**)

$Au_{25}(SC_2H_4Ph)_{18}$ clusters (7.5 mg; 1 μmol of clusters) are dispersed in dichloromethane (5 mL) and are added into a stirred suspension of the hydrophobic silica Aerosil R972 (251.5 mg) in 20 mL of a solution of dichloromethane/ethanol (v:v, 70:30). After 24 h, the solvent is evaporated and the solid is washed two times with ethanol and recovered by centrifugation (15 min, 8000 rpm). Catalyst is left to dry under air at room temperature to obtain a light gray solid.

2.3.2. Preparation of $Au_{25}(SPhNH_2)_{17}$@SiO_2(R972) (**2**)

$Au_{25}(SPhNH_2)_{17}$ clusters (7.5 mg, 1.1 μmol of clusters) are dispersed in dichloromethane (5 mL) with an ultrasonic bath, then