### Catalysis Today xxx (xxxx) xxx-xxx



Contents lists available at ScienceDirect

# Catalysis Today



journal homepage: www.elsevier.com/locate/cattod

# Gold nanoclusters prepared from an eighteenth century two-phases procedure supported on thiol-containing SBA-15 for liquid phase oxidation of cyclohexene with molecular oxygen

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# ARTICLE INFO

Keywords: Gold nanoclusters Catalysis Cyclohexene Oxidation Transmission electron microscopy Allylic oxidation

# ABSTRACT

The present work describes the incorporation of finely divided and well-dispersed Au species into SBA-15 mesoporous silica functionalized with mercaptopropyl groups, and the catalytic activity of the resulting Au-materials in the liquid phase oxidation of cyclohexene with molecular oxygen at atmospheric pressure. The gold entities have been prepared through a two-phase system described in the eighteenth century involving a solution of gold in a mixture of nitric acid and ammonium chloride (*aqua regia*) and rosemary oil. Gold nanoclusters, which present a disordered structure and sizes below 3 nm, and even single gold atoms which may be anchored/ stabilized through sulphur groups are found immobilized on the mesoporous support, but no gold nanoparticles (with well-defined structure and usually over ~ 5 nm) are detected. Such observations have been carried out by  $C_s$ -corrected STEM-HAADF where the visualization of bright spots is attributable to these individual entities. These materials are active in the oxidation of cyclohexene, but their relative activity is governed by the synthesis conditions. Partial aggregation of the gold entities into nanoparticles has been observed during the reaction, which are mainly responsible for the catalytic activity. The allylic oxidation of the cyclohexene ring over the double bond epoxidation is strongly favored, and at high conversion the two dominants products are 2-cyclohexen-1-one and 2-cyclohexen-1-ol.

# 1. Introduction

The behavior of gold nanoparticles as catalysts for a large variety of organic chemical reactions have been extensively explored [1-3]. The catalytic activity and selectivity of these nanoparticles are dependent upon their size and shape, the specific chemical environment they are exposed during reaction and, if immobilized on a support, their interaction with the carrier. In this context, a key challenge is to prepare stable gold nanoparticles with controlled size and shape, and several methods have been developed along the time to meet this objective [4]. One of these is the two-phase Brust-Schiffrin method introduced in 1994 [5], which allows the in situ preparation of thiolate-stabilized gold nanoparticles with small size and very narrow particle-size distribution. It is acknowledged in that publication that the preparation of colloidal metals in a two-phase system was introduced by Michael Faraday in the nineteenth century [6], consisting in the reduction of an aqueous gold solution with phosphorous in carbon disulfide. However, it has been found that in the 1757 edition of the then well-known French textbook of chemistry Cours de Chymie by N. Lemery, the editor M. Baron

included a recipe claiming that, after prolonged contact between a solution of gold in *aqua regia* (consisting in this old formulation in a mixture of nitric acid and ammonium chloride) and rosemary oil, the upper oil layer mixed with alcohol got red colored. This red solution was called the "potable gold of Mademoiselle Grimaldi" and it was supposed to have medicinal properties. Recent replication of this recipe has revealed the presence in the rosemary oil of gold nanoparticles (which adopted decahedral, icosahedral or twinned fcc structures) of an average size of 5 nm, disordered gold clusters of < 1 nm and even isolated gold atoms [7].

Based on these findings, in this paper it is reported the immobilization of the gold species produced by this eighteenth century recipe on a mesoporous SBA-15 material functionalized with mercaptopropyl groups and the use of the resulting gold-containing materials as catalysts for the oxidation of cyclohexene in liquid phase by using molecular oxygen as oxidant [8,9].

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http://dx.doi.org/10.1016/j.cattod.2017.09.045

Received 10 May 2017; Received in revised form 1 September 2017; Accepted 24 September 2017 0920-5861/@ 2017 Elsevier B.V. All rights reserved.

#### 2. Experimental

### 2.1. Synthesis of thiol-containing SBA-15

Propyl-thiol mesoporous SBA-15 was prepared from a gel with molar composition: 1.0 TEOS:0.111 MPTMS:0.0186 P123:6.42 HCl:180H<sub>2</sub>O, where TEOS stands for tetraethyl orthosilicate (Sigma-Aldrich, > 99%);MPTMS 3-mercaptopropyltrimethosysilane for (Sigma-Aldrich, 95%); P123 for Pluronic 123, the triblock co-polymer PEO<sub>20</sub>PPO<sub>70</sub>PEO<sub>20</sub>, m.w. ~5800 (Sigma-Aldrich); and HCl for hydrochloric acid (Panreac, 37 wt%), according to the procedure described in Ref. [10], as follows: 125 mL of 1.9 M HCl were placed in a 500 mL plastic bottle provided with a cover having a hole for allowing the insertion of a PTFE (Polytetrafluoroethylene) stirrer blade, and 4 g of P123 were added. Then, the bottle was heated at 40 °C in a silicone oil bath, and 8.2 mL of TEOS were added. After 45 min, 764 µL of MPTMS were added, and the mixture was stirred for 22 h. Then, the mixture was poured into a stainless-steel autoclave provided with a Teflon liner, and heated statically at 100 °C for 24 h. After that, the autoclave was cooled and its content filtered, washed with ethanol and dried at room temperature overnight. The dried sample was treated with ethanol (200 mL of ethanol per g of sample) under stirring in a 1L round-bottom flask at 90 °C for 24 h in order to remove the surfactant. Following this procedure, two different batches of SH-SBA-15 precursor materials were prepared, denoted L1 and L2, respectively.

# 2.2. Synthesis of the gold nanoparticles

Gold nanoparticles were prepared from a two-liquid phase system according to a procedure described in the Lemery's textbook [7]. A gold lump (0.1657 g, Johnson-Matthey, 99.99%) was dissolved under gentle stirring in 53 g of aqua regia, prepared following this old formulation by mixing (4:1 w/w) nitric acid (Panreac, 65 wt%) and ammonium chloride (Sigma-Aldrich, > 98 wt%), heated at 40 °C in a sand bath. This solution has a 1:320 gold-to-aqua regia weight ratio. After cooling, the resulting golden yellow solution was placed in a 50 mL decanting funnel, and then 13.50 g of rosemary essential oil were gently added, which remains as a top layer over the gold solution. The same procedure was followed with a more concentrated gold solution in aqua regia, 1:64. The rosemary essential oil (supplied by the Spanish company El Granero Integral (The Integral Barn) has the following chemical composition (wt.%) as determined by GC-MS employing a gas chromatograph (Agilent 6890) coupled with a mass spectrometer (Agilent 5973N) using a capillary column made of methylpolysiloxane (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu m$  ), heating from 70 to 290 °C at 6 °C/min: 24.9% 1,8-cineole, 21.9% alpha-pinene, 20.91% camphor, 9.06% camphene, 3.81% borneol, 3.34% verbenone, 2.59% myrcene, 2.41% beta-pinene, 2.01% caryophyllene, 2.00% p-cymene, 1.16% alpha-humulene, 0.98% bornyl acetate, 0.94% gamma-terpinene, 0.63% 4-terpineol, 0.63% alpha-terpineol, 0.29% alpha-terpinolene, 0.28% fenchone.

## 2.3. Immobilization of the gold nanoparticles on SBA-15

24 h and 8 days after the addition of the rosemary oil, 3.75 mL of the organic layer were mixed with 18.75 mL of ethanol, to the resulting solution 0.500 g of the extracted SBA-15 material were added, and the mixture was stirred at room temperature for 3 h. After that, the solid was separate by centrifugation and washed with four portions of 40 mL each of ethanol. The samples were denoted as L1-1 and L1-8 for those obtained from L1 precursor and the less concentrated gold solution after 1 and 8 days, respectively, while L2-1 and L2-8 correspond to those prepared from L2 and the more concentrated gold solution after 1 and 8 days.

For comparison purposes, a gold catalyst supported on L1 precursor was prepared by the sol-immobilization method described in [11], based on the reduction of HAuCl<sub>4</sub>·3H<sub>2</sub>O (Johnson Matthey) in an aqueous solution of polyvinyl alcohol (Sigma-Aldrich) with NaBH<sub>4</sub> (Sigma-Aldrich, > 96%). The Au content of this catalysts is 1.2 wt%. It will be denoted as RefCat.

#### 2.4. Catalytic tests

The oxidation of cyclohexene with molecular oxygen was carried out by following a procedure based on that reported in [8]. The catalytic reaction was carried out in a 50 mL glass three-neck round-bottom flask provided with an additional vertical neck to adapt a condenser through which water at 5 °C was circulated to minimize the evaporation of reagents and products. The flask was immersed in a silicone oil bath to keep the reaction temperature at 65 °C, measured inside the reaction mixture by a thermometer inserted in one of the necks. The experimental set-up was not protected against environmental light. The reaction mixture was formed by 0.049 mol of cyclohexene (4.055 g, Sigma-Aldrich, 99%), 0.4055 g of octane (10 wt% referred to cyclohexene; Sigma-Aldrich, > 99%), 0.2027 g of a ter-butyl hydroperoxide solution (TBHP, 5 wt% referred to cyclohexene; ~5.5 M in decane, Sigma-Aldrich), 3.041 g of toluene (75 wt% of the cyclohexene; Panreac, > 99.5%), and 0.050 g of catalyst. O<sub>2</sub> (1.8 mL/min) was bubbled through the stirred reaction mixture. The catalysts were previously heated at 100 °C for 1 h in the reaction flask provided with a tube containing molecular sieve 5A as water trap, cooled down to the reaction temperature of 65 °C, and then the reagents added. The trap was removed before the reaction starts. Aliquots of 0.20 mL of the reaction mixture were taken at given time intervals and analyze by GC in a Varian CP-300 instrument, by using a FactorFour™ (Varian VF-1 ms) dimethylpolysiloxane capillary column, 15 m of length and 0.25 mm of i. d. Octane was used as internal standard. Five reaction products were identified; two of them result from the addition of oxygen to the cyclohexene double bond, namely cyclohexene epoxide and cyclohexanediol, and three coming from the allylic oxidation of the cyclohexene ring: 2-cyclohexen-1-ol, 2-cyclohexen-1-one and 2-cyclohexenyl hydroperoxide. Cyclohexene conversion was calculated from the yields of these five products.

## 2.5. Characterization techniques

Powder X-ray diffraction studies were done using a PANalytical X'pert Pro instrument (CuKa radiation). Gold content of the solid was determined by inductively coupled plasma (ICP-OES) spectrometry with an ICP Winlab Optima 3300 DV Perkin-Elmer spectrometer. Thermogravimetric analyses were performed in a Perkin-Elmer TGA7 instrument, in an air flow of 40 mL/min, with a heating ramp from 25 to 900 °C at 20 °C/min. CHNS elemental analyses were obtained in a LECO CHNS-932 analyser provided with an AD-4 Perkin-Elmer scale. Nitrogen adsorption-desorption isotherms where measured in a Micromeritics ASAP 2420 apparatus at the temperature of liquid nitrogen (-196 °C). The samples were degassed in situ at 120 °C in vacuum for 16 h prior to analysis. Surface areas were determined using the BET method. The pore volume and the average pore diameter were calculated by applying the BJH protocol to the adsorption branch of the isotherm. Diffuse reflectance UV-visible (UV-vis) spectra were recorded on a Cary 5000 Varian spectrophotometer equipped with an integrating sphere with the synthetic polymer spectralon as reference.

Transmission electron microscopy analyses were performed in a XFEG FEI Titan 60–300 which was operated at 300 kV in scanning transmission electron microscopy (STEM) mode using a High Angle Annular Dark Field detector (HAADF). The spherical aberrations were corrected using a CEOS corrector for the electron probe achieving a spatial resolution of 0.8 Å. The column was fitted with an EDAX detector for EDS chemical analyses and a Gatan Tridiem Energy Filter (GIF). The samples were prepared by deeply crushing the powders obtained using mortar and pestle for several minutes. Subsequently,



Fig. 1. XRD patterns of representative samples L1and L1-8.

they were dissolved in EtOH and a few drops of the suspension were placed onto a holey carbon copper microgrid.

#### 3. Results and discussion

## 3.1. Thiol-containing SBA-15 precursors

Two different batches of SBA-15 functionalized with mercaptopropyl moieties, denoted as L1 and L2, were synthesized and used to prepare L1 and L2 gold-containing samples, respectively. XRD of the representative precursor material L1 (Fig. 1) shows the characteristic profile of well-ordered SBA-15 materials, and only minor differences among them in d(100) spacing and  $a_0$  (Table 1) were found. They show the characteristic N2 adsorption-desorption isotherms of SBA-15 (Fig. 2), a surface area in the range 540–660  $m^2/g$  and pore volume  $0.64-0.82 \text{ cm}^3/\text{g}$ , and practically the same pore diameter, 5.8-5.9 nm(Table 1). Average pore diameter is clearly smaller than that of 7.0 nm reported for pure silica SBA-15 [12] which strongly supports the presence of mercaptopropyl moieties decorating the pore surface, which would hence reduce the free pore aperture. Chemical analysis evidences the presence of sulphur and carbon (Table 2), which indicates the effective incorporation of mercaptopropyl groups. Moreover, TG (Fig. 3) shows an abrupt weight loss centered at ~340 °C, which can be assigned to the decomposition/desorption of these groups. From chemical and TG analysis, the number of thiol groups per Si atoms can be estimated in an approximate way, and the results are collected in Table 2. It can be seen that nearly 10% of the Si atoms of the materials are

Table 1

Structural and textural pro-	erties of SH-SBA-15	supports and	catalysts
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Sample	d-Spacing d <sub>100</sub> (nm)	Unit cell parameter $a_0(nm)$	$S_{BET} (m^2/g)$	Vp (cm <sup>3</sup> /g)	Dpnm
L1	9.7	11.2	542	0.64	5.9
L2	9.2	10.6	660	0.82	5.8
L1-1	9.6	11.1	515	0.61	5.7
L1-8	9.5	10.9	454	0.55	5.6
L2-1	9.1	10.5	637	0.78	5.7
L2-8	8.9	10.3	488	0.62	5.5

bonded to mercaptopropyl moieties. Taken into account that only a small fraction of the total Si atoms would be present at channels interface, the thiol groups would be covering in a very effective way the channels surface. This aspect would be relevant for binding the gold nanoparticles upon contacting these materials with the gold solutions. Moreover, under the reasonable assumption that propyl groups are only present at channel surface, their density can be roughly determined from surface area and sulphur content, and it turns to be in the range 1.1-1.4 S atoms/nm<sup>2</sup>, or 1 S atom per 0.9 and 0.7 nm<sup>2</sup>, respectively. The area of thiol head groups of self-assembled alkanethiol layers on flat Au(111) surface has been reported to be  $0.214 \text{ nm}^2$  [13], while it has been calculated as 0.114 nm<sup>2</sup> for octadecanethiol-derivatized Au clusters of 2.2 nm in size modeled as spheres [14]. These values are much smaller than the surface density of mercaptopropyl groups present at the SBA-15 surface, and therefore suggest that they are far apart each other. However, low average density values would not exclude the presence of closer mercaptopropyl groups. Nonetheless, the low density of thiol groups would eventually make feasible the binding and stabilization of very small gold clusters formed by just few gold atoms, provided they would be present at the solution where they are generated.

From the chemical analysis data collected in Table 2, it can be seen that the C/S ratio is around 9, *i.e.*, much higher than that corresponding to mercaptopropyl moieties, even considering the possibility that some methoxy groups of the precursor were not hydrolyzed during the synthesis process. This excess of carbon could be accounted by the partial covering of the surface with ethoxy groups during the prolonged treatment of the sample in refluxing ethanol for surfactant removal, which has been previously observed for thiol-functionalized MCM-41 [15]. However, it could also be attributed to the presence of residual block copolymer species which were not completely removed by ethanol extraction [10].

# 3.2. Gold-containing samples

After contacting the SH-SBA-15 materials with the rosemary oil/ ethanol precursor gold solution following the procedure described in the experimental section, gold was indeed found in the resulting solid, ranging from 0.2 wt% to 2.6 wt% (Table 2). The amount of immobilized metal seems to be governed by the initial concentration of [AuCl<sub>4</sub>]<sup>-</sup> in the aqua regia solutions and their contact time with the rosemary oil. For samples L1, prepared from the less concentrated gold solution, the amount of this metal immobilized in the mesoporous material increased if the contact time between the [AuCl<sub>4</sub>]<sup>-</sup> solution and the rosemary oil before the impregnation step of SBA-15 with the oil phase was prolonged from 1 to 8 days, while the opposite was observed for samples L2 prepared from the more concentrated gold solution. Moreover, for 1 day of contact, the content of gold in the sample increased with its concentration in the aqua regia solution. For the gold-containing samples, the SBA-15 structure was preserved (Fig. 1), with nearly no variation in a<sub>0</sub> parameter and pore diameter (Table 1 and Fig. 2). However, both the surface area and pore volume decreased for the two samples prepared from 8 days, which also show some noticeable differences in the TG pattern as compared to both the precursor and 1 day samples (Fig. 3). The weight loss at T < 140 °C corresponding to the desorption of water is higher, and a more complex pattern of weight loss starts already at T > 140 °C, in such a way that four weight losses centered at 230 °C, 350 °C, 530 °C and 630 °C can be distinguished. A similar TG pattern has been reported for thiol-containing MCM-41 materials after oxidation with H<sub>2</sub>O<sub>2</sub>, where sulfonic and disulfide species were detected [15]. Therefore, in the gold-containing materials prepared from rosemary oil that was in contact for 8 days with the [AuCl<sub>4</sub>]<sup>-</sup> solution, the original mercaptopropyl groups would have been oxidized in considerable extension.

The absorption spectra of the catalysts in the UV-vis region are presented in Fig. 4. It can be seen that in none of them the surface



Fig. 2. Representative N2 adsorption/desorption isotherms of sample L1 (top) and L1-8 catalyst (bottom). Inset: pore size distribution.

plasmon resonance band at ~ 520 nm characteristic of Au NPs is detected [16], which means that the gold aggregates, if present, should be smaller than  $\sim 2$  nm in size [17]. In the spectra of samples L1-8 and L2-8, a band of weak intensity is observed at  $\sim$  370 nm, accompanied by a shoulder at  $\sim 270$  nm. In the L1-1 and L2-1 samples, the band at higher wavenumber is not observed, while the shoulder is more intense in sample L1-1. UV-vis bands of thiol-stabilize gold clusters with core diameter of 0.8 nm are detected in the range 300–450 nm [18], which are slightly blue-shifted for 1–2 nm size gold clusters capped with meso-2,3-Dimercaptosuccinic acid [19]. Moreover, UV bands at ~250 nm have been attributed to partially charged Au nanoclusters [20]. Therefore, the optical spectral features of the catalysts would be consistent with the presence of thiolate-gold nanoclusters of sub-nanometer size, or even thiolate-monoatomic gold species [21]. In order to elucidate the nature of the gold entities present in these materials, spherical aberration corrected (Cs-corrected) electron microscopy studies have been carried out and data corresponding to L2-8 material are depicted in Fig. 5. Fig. 5a corresponds to a typical image of SBA-15 displaying the hexagonal arrangement of the pores in a similar to a honeycomb structure; the FFT shown inset can be indexed assuming p6mm space group symmetry, obtaining a unit cell value of approximately

 $a_0 = 9.12 \text{ nm}$ . A closer look (Fig. 5b) of the system allows the observation of a strong contrast particularly on the walls of the conforming channels attributed to the presence of gold due to its higher scattering factor respect the silicon and oxygen that compose the SBA-15 [22]. Considering that the images have been acquired using a high annular dark field detector (HAADF) the contrast obtained is directly related to the atomic number of the elements through Rutherford scattering [23]. This approach, especially after the implementation of spherical aberration correctors, has been widely used for the analysis of incorporated species down to atomic level into lighter supports, just by image analysis or combined with spectroscopic measurements [24,25]. Fig. 5c and d show another SBA-15 particle orientated with the pore channels perpendicular to the electron beam, where the Au entities can be also identified. Fig. 5d depicts the atomic resolution data, with a magnified image shown inset, where gold clusters below 2 nm are and even single Au atoms can be observed.

These  $C_s$ -corrected STEM-HAADF findings are in agreement with the reported high surface disorder of thiol protected gold particles in the range 1–4 nm, due to the strong S–Au bond [26]. It can be noticed that the average S-to-S distance calculated as indicated above is 0.7–0.9 nm, which would be within the approximate value range of gold clusters

Table 2

Chemical co	omposition (	(wt%) and	TG results	of the	SH-SBA-15	supports	and	catalysts.
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Sample	С	Н	S	Au	C/S <sup>a</sup>	S/Au <sup>a</sup>	Si/S <sup>a</sup>	Weight loss T $< 140 \degree C$	Weight loss T $> 140$ °C.
L1	14.7	3.3	4.2	-	9.3	-	8.9	1.87	28.16
L2	13.2	2.8	3.7	-	9.4	-	10.4	1.88	26.09
L1-1	-	-	-	0.19	-	-	-	2.23	27.41
L1-8	-	-	-	2.57	-	-	-	6.32	25.53
L2-1	12.5	3.0	3.5	1.54	9.6	13.9	-	4.76	24.52
L2-8	12.5	2.9	3.2	0.53	10.5	36.9	-	4.71	25.44

<sup>a</sup> Mol ratio.



Fig. 3. TG/DTG curves of samples: L1 (left); L1-1 and L1-8 catalysts (right).

size as determined by STEM. Moreover, the average S/Au ratio is in the range 14–37 for L2 samples (Table 2), as a function of the gold content. A cluster formed by 11 gold atoms would have a size of ~0.8 nm [18], which would be therefore linked to one mercaptopropyl surface group on average at least for the lowest S/Au ratio. On the other hand, the observed differences in the optical spectra among the four catalysts suggest that the nature of the gold clusters depends on the specific conditions operating in the two-liquid phase system formed by the [AuCl<sub>4</sub>]<sup>-</sup> solution in *aqua regia* and the rosemary oil, where the contact time between both phases seems to be a more determinant factor than the starting [AuCl<sub>4</sub>]<sup>-</sup> concentration in the aqueous phase. On this

regard, it can be noticed the similarities of the UV–vis spectra of the samples prepared at the same contact time, 1 or 8 days, regardless their disparities in gold content. Therefore, the immobilization process of the gold species present in the impregnating rosemary/ethanol solution does not seem to alter significantly the nature of the gold clusters present in that solution. According to this, thiol groups anchored on the SBA-15 surface would capture the gold species present in the solution, though whether this "fishing" process discriminate among the several gold species that presumably are present in that solution cannot be said.

The remarkable presence of such small Au entities suggests that the rosemary oil would act not only as a reductant agent of the gold present

**Fig. 4.** UV–vis spectra of samples L1-1 (■); L1-8 (□); L2-1 (●); L2-8 ( $\bigcirc$ ); L1-8 after reaction ( $\blacklozenge$ ).





#### Catalysis Today xxx (xxxx) xxx-xxx

Fig. 5. C<sub>s</sub>-corrected STEM-HAADF images of L2-8 catalyst. a) High-resolution image of the pore system recorded along the [001] with the FFT shown inset. b) Magnified region of the edge of the SBA-15 particle. c) High-resolution image recorded perpendicular to the pore system (FFT is shown inset). d) Closer inspection of the image shown in c, showing the presence of the Au entities.

at the aqueous phase, but some of its components would also behave as efficient capping agents preventing massive gold aggregation, whether they are naturally present at the oil or they come from the slow reaction between the upper oil layer and the underneath strongly acid and oxidant aqueous solution. Additional research would be needed to elucidate details of the mechanism leading to the formation of the gold entities in this particular two-liquid phase system, which would help gaining control on the output of the process.

It can be mentioned that gold nanoparticles of sizes in the range 2–4 nm immobilized on SBA-15 functionalized with mercaptopropyl groups have been prepared by one-pot synthesis procedure after the gold-containing materials were calcined and therefore the thiol groups removed [21].

# 3.3. Catalytic tests

The four gold-containing SH-SBA-15 materials described above were used as catalysts for the liquid phase oxidation of cyclohexene using molecular oxygen as oxidant at atmospheric pressure, in the presence of a small amount of toluene as solvent and TBHP as initiator (Table 3). The four catalysts (Fig. 6) are active in this reaction, but they show noticeable differences concerning their activity pattern. Only catalyst L1-8 shows a conversion level significantly above that of goldfree thiol-SBA-15 support used as a reference or blank experiment. On the other hand, the conversion is much higher than the amount of initiator TBHP present in the reaction mixture, hence the oxidation of cyclohexene necessarily involves the participation of molecular oxygen. For the two 8-days catalysts, the conversion increases with the gold content (Table 2). The two 1-day catalysts show lower activity than those of 8-days ones, and also in this case the activity increases slightly with the gold content, thought the difference in catalytic activity is smaller than that of gold. These results indicate that the activity per gold atom shows a great disparity among the two series of catalysts. Moreover, as practically no differences are observed in the average pore size among them, which is close to 6 nm, nearly one order of magnitude larger than the molecular size of cyclohexene or TBHP, the reaction would not be influenced by eventual differences in the accessibility of the reagents to the gold active sites. Therefore, the observed variation in the specific activity (conversion per gold atom) among the several catalysts would be related to differences in the surface properties of the gold clusters, which could be governed by their size but also by their effective charge and the chemical interactions stablished with the sulphur-containig groups of the support. It is interesting to notice on this regard that the two 8-days samples present quite similar UV-vis spectra, as well as the two 1-day ones, which are nevertheless distinct from those of the former (Fig. 4), as they do not present the band at  $\sim 370$ nm. Therefore, it could be tempted to connect the catalytic activity with the size and nature of the gold clusters present in the as-prepared catalysts. However, it has been observed that the color of the 8-days catalysts changes during the reaction, being white to pale yellowish before reaction, to pink and then to purple as the reaction proceeds. This observation evidences that the particle size of the gold increases in the reaction medium, as it is confirmed by UV-vis spectroscopy of the L1-8 and catalyst after reaction (Fig. 4), which presents an absorption band at  $\sim$  520 nm. In agreement with this result, gold particles in the range 5-20 nm are clearly observed by STEM in this catalyst after reaction (Fig. 7), although gold nanoclusters are still present. Fig. 7 shows the Cs-corrected STEM-HAADF images also recorded along the [110] and

### J. Agundez et al.

Table 3				
Conversion	and	coloctivity	for	color

Catalyst	Conversion% (24 h)	Conversion% (48 h)	Selectivity (24 h)					Selectivity (48 h)				
				OH	°	$\bigcirc \circ$	СССОН	ООН	OH	°	$\bigcirc \circ$	OH OH
L1	17.6	29.6	61.1	11.3	15.8	11.2	0.6	36.1	17.5	32.7	10.1	3.6
L1-1	9.9	15.7	72.5	8.3	14.5	4.1	0.5	55.4	13.2	22.4	8.0	1.0
L1-8	30.1	33.4	32.7	17.8	38.0	7.5	3.9	9.6	26.6	60.0	1.5	2.2
L2-1	12.3	28.4	48.2	15.1	24.6	7.8	4.2	13.9	22.1	47.6	4.2	12.1
L2-8	13.8	26.5	62.3	12.8	19.4	4.5	1.0	44.1	15.7	30.1	7.1	3.0
L1-8 reused	22.6	31.0	35.3	18.6	34.5	8.7	2.9	8.4	28.5	58.5	2.3	2.3
RefCat	40.0	39.9	25.6	21.4	41.4	7.8	3.8	6.1	28.8	60.5	2.2	2.4

[001] crystal orientations proving that after reaction the material retained its original structure with no significant damage (Fig. 7a and b). From these images it can be clearly appreciated the presence of large Au nanoparticles of several tenths of nm. A closer look of two particles (Fig. 7c and d) confirms the presence of nanoparticles of 10-20 nm, which in some cases fit the pore size, in addition to the initial metallic clusters of around 2 nm. The atomic-resolution data shown in Fig. 7e and f allow the visualization of the metallic cluster together with isolated single Au atoms. In order to unambiguously determine the presence of the Au as isolated entities, different intensity profiles were extracted over three distinct high contrast units. The significant contrast changes observed over the 3 signals measured corroborates the heavier nature of those elements, which in the current case can only correspond to gold atoms. Although these entities are denoted as isolated gold atoms, the fact that they are anchored onto the mesoporous support before and after reaction, suggests good physical-chemical stability probably through the coordination of sulphur, and therefore the Au single atoms should be part of a bit more complex compound with sulphur linked to the gold atom.

ted reaction times

In an attempt to determine whether the observed increase of gold particle size is responsible for the higher activity of L1-8 catalyst, a catalyst was prepared by the sol-immobilization method described in [11] by using L1 as support, which has been described to led to Au nanoparticles when supported on graphite. In our case, gold nanoparticles in the range 2–12 nm are indeed observed, with most of the particles of 5 nm in size, in agreement with the presence of the characteristic  $\sim$  520 nm band in the UV–vis spectrum (not shown). It can be

observed in Fig. 6 that the reaction is faster with this catalyst as compared with L1-8, and the conversion is close to 40% after 24 h, although it does not progresses further.

This experiment strongly suggests that the higher activity of the L1-8 catalyst is due to in situ growing of the gold nanoclusters initially present in the fresh catalyst to form active gold nanoparticles. This phenomenon would also operate for L2-8 catalyst, although its lower Au content led also to smaller conversion. It can also be taken into account that very small clusters and single gold atoms are still present in the used catalyst, which means that the Au growing process has not been completed yet in the course of the reaction. In contrast to the 8days catalysts, no noticeable color change is observed for the 1-day catalysts during the reaction, being their activity very low, even that of L2-1, which contains 1.5 wt% of gold (Table 2). These results point to differences among the two series of catalysts concerning the interaction strength between the gold entities and the sulphur-bearing moieties to which they are linked. This interaction would be much stronger for the two 1-day than for the 8-days ones, preventing the growing of the gold nanoclusters toward active nanoparticles in the former. The reason for these differences could be found in the different chemical state of the sulphur in both cases. As it has been discussed above, the TG results (Fig. 3) shows that the thiol groups present in the support are preserved for the 1-day samples, while they are largely oxidized for the 8-days ones. Hence, the interaction of the thiol group with the gold entities of the former would be strong enough to avoid their partial reduction and growing in the reaction mixture. These differences in the Au-S interaction would also be reflected in the UV-vis spectra, where the band



**Fig. 6.** Conversion as a function of time for catalysts L1-1 (**()**); L1-8 (**()**); L2-1 (**()**); L2-8 (**()**); L1-8 reused ( $\delta$ ); blank reaction carried out with support L1(**()**); RefCat (\*). Solid lines have been drawn as visual aid only.



Fig. 7. Cs-corrected STEM-HAADF images of the catalyst L1-8 after reaction. a) Low-magnification micrograph with the channels perpendicular to the electron beam. SBA-15 particle orientated with the pores perpendicular to the electron beam. c) and d) Closer inspections of the particles shown in 7a and b respectively. e) Ultra-high resolution data extracted from figure c. f) Image of the edge of the SBA-15 showing isolated Au atoms.

at  $\sim$  370 nm is only observed for the two 8-days fresh catalysts. In this way, the strong Au-SH interaction would not only to prevent the growth of the gold entities, but would poison in large extension their oxidizing ability. Therefore, not all the Au present in the L1-8 catalyst would be active, because gold nanoclusters are still detected in the used catalyst.

On the other hand, it can also be observed in Fig. 6 that the L1-8 catalyst can be reused with no loss of activity. Therefore, once the nanoparticles are formed in the first run, they keep active for reusing.

Among the five reaction products, two of them result from the addition of oxygen to the cyclohexene double bond, namely cyclohexene epoxide and cyclohexanediol, and three are coming from the allylic oxidation of the cyclohexene ring: 2-cyclohexen-1-ol, 2-cyclohexen-1one and 2-cyclohexenyl hydroperoxide. As it can be seen in Table 3, the allylic oxidation pathway is dominant, and for conversion higher than  $\sim$  30%, the selectivity to the corresponding products is nearly 90%. The predominance of the allylic oxidation is in agreement with what has been previously reported for 1% Au/carbon catalysts containing 5–50 nm gold nanoparticles [8]. The selectivity to the reaction products is plotted in Fig. 8 as a function of the conversion for the seven reactions carried out. For conversion  $< \sim 20\%$ , 2-cyclohexenvl hydroperoxide is the major product, followed by cyclohexen-1-one and 2-cyclohexen-1-ol. However, the selectivity to this peroxide decreases rapidly as the conversion increases, and the cyclohexen-1-one is the dominant product beyond  $\sim 25\%$  of conversion. The enone/enol molar ratio is always > 1 and it increases with the conversion, reaching a value of  $\sim 2$  as the conversion approaches to  $\sim 40\%$ . From Fig. 8 it can be concluded that the 2-cyclohexenyl hydroperoxide is a primary product of the oxidation of cyclohexene, as well as the cyclohexene epoxide, but the former is much more favored. 2-cyclohexen-1-one is a secondary and stable product coming from 2-cyclohexenyl hydroperoxide, while 2-cyclohexen-1-ol could be a primary + secondary stable product. Cyclohexene epoxide is a primary but unstable product, which

transforms most probably into cyclohexanediol which is a secondary and unstable product. We have not been able to identify the product(s) coming from cyclohexanediol reaction. The scheme in Fig. 9 shows a tentative reaction pathway of the aerobic oxidation of cyclohexene under the reaction conditions prevalent in this work.

### 4. Conclusions

Gold nanoclusters can be conveniently prepared by a two-liquid phase system from a gold solution in aqua regia by using rosemary oil as oil phase and reductant agent according to a technique reported in eighteenth century. These gold entities can be immobilized in hybrid mesoporous SBA-15 materials functionalized with mercaptopropyl groups, where gold nanoclusters and single atoms are found, but no gold nanoparticles are detected. While the structural features of SBA-15 remain unaffected by the immobilization procedure, some thiol groups can be partially oxidized in the process, as a function of specific synthesis parameters. These gold-containing materials are active catalysts for the liquid phase oxidation of cyclohexene with molecular oxygen in the presence of small amounts of ter-butyl hydroperoxide and toluene as solvent, though their activity is strongly dependent upon the specific synthesis conditions of the precursor gold solution. It has been found that part of the gold nanoclusters present in the fresh catalysts evolves toward larger gold nanoparticles during the reaction, which are mainly responsible for the catalytic activity. The growing process of these nanoparticles is governed by the chemical nature of the sulphur groups attached to the gold entities in the as made catalysts. The cyclohexene is oxidized to two main stable reaction products, 2-cyclohexen-1-one and, 2-cyclohexen-1-ol, with a molar enone/enol ratio of 2, via 2-cyclohexenyl hydroperoxide as primary but unstable product. Beside these major products coming from the allylic oxidation of cyclohexene, a minor oxidation route involves the formation of

#### J. Agundez et al.

#### Catalysis Today xxx (xxxx) xxx-xxx



Fig. 8. Selectivity vs total conversion for 2-cyclohexenyl hydroperoxide
(●); 2-cyclohexen-1-ol (●); 2-cyclohexen-1-one (▲); cyclohexene epoxide (♦) and cyclohexanediol (+). Data collected for the seven reactions describe in this work at different reaction times.

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cyclohexene epoxide and cyclohexanediol, both unstable products.

## Acknowledgements

The authors gratefully acknowledge the Spanish Ministry of Economy and Competitiveness for the funding through Projects MAT2012-31127, MAT2016-77496-R (AEI/FEDER, UE). And Government of Aragon and the European Social Fund under the project grant number E/26 "Construvendo Europa desde Aragón" 2014–2020.

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