

Redox catalysts based on Au and Pd/PdO bimetallic nanoparticles confined in mesoporous silica SBA-15

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ABSTRACT

Au and Pd/PdO bimetallic nanoparticles supported on mesoporous molecular sieve SBA-15 were prepared by the modification of the silica surface with amino moieties, bonding of the metal precursors on these groups and calcination of the final material. The composition of the samples was analyzed by ICP-AES and their structures and morphologies were characterized by XRD, UV-Vis spectroscopy and electronic microscopy. It was observed that Au was always found alloyed with Pd, whereas excess Pd was found in the form of PdO nanoparticles. Oxide nanoparticles were frequently located near the alloy nanoparticles, suggesting that Pd exudates from the alloy in the form of PdO during the calcination process. It is possible to reduce Pd(II) to Pd(0) using a simple reduction process. These catalysts can be very useful in redox processes such as alcohol oxidations.

Keywords: bimetallic catalysts, Au-Pd alloy, oxide nanoparticles, mesoporous silica, transmission microscopy.

1 INTRODUCTION

Redox reactions are usual processes on the synthesis fine chemicals and of intermediary products; for instance, primary alcohols oxidation to aldehydes is of fundamental importance in laboratory and industrial procedures [1]. The use of heterogeneous catalysts supported with metal nanoparticles has been proposed as an alternative to stoichiometric oxidations, which involve the use of toxic reactants and are major sources of waste. The choice of the catalyst support, as well as of the metal species, are decisive because they greatly influence the catalytic activity.

Since the catalytic activity of nanoscale gold was discovered [2] many studies on this subject have been done. Meanwhile, since the 70s the concept of catalysis using a combination of two different metals is being developed [3]. The bimetallic systems turned out to be very important because of the synergistic effect between the two species. However, when bimetallic catalysts based on a combination of nanoparticles of two different metals are prepared, the system can become much more complex than when only one kind of metal is present. The different characteristics

between the metals can lead to materials with varied morphologies, such as core-shell, alloy or aggregated particles [4]. A very interesting bimetallic system, based on alloyed Au-Pd bimetallic nanoparticles (NPs) has emerged, and it was discovered that there is a synergistic effect between both metals, since Pd is able to promote, for certain reactions, the activity of Au, and vice versa [5].

The choice of a support for the nanoparticles is of crucial importance, since the support itself can influence the size and dispersion of the particles. Moreover, the higher the interaction between the support and the nanoparticles, the lower will be the leaching of the metals to the reaction media. The use of mesoporous silica such as SBA-15 as heterogeneous catalysts support is particularly interesting, mainly for the possibility of confining the nanoparticles, which lowers metal leaching and limits the nanoparticles growth [6].

In this work, Au-Pd/PdO NPs with varying molar ratios were supported on mesoporous molecular sieve SBA-15 which, besides having high thermal and hydrothermal stability, limits the growth of nanoparticles inside the mesochannels.

2 EXPERIMENTAL

2.1 SBA-15 Synthesis and Modification

SBA-15 synthesis was performed according to the method proposed by Zhao *et al.* [7] At 35 °C, a mixture containing 4.08 g of triblock copolymer EO₂₀PO₇₀EO₂₀ (Pluronic 123, Aldrich) and 30 mL of deionized water was stirred until total dissolution (about 30 h). It was then added 120 mL of 2 mol L⁻¹ HCl solution and maintained under stirring for 1 h. 9.1 mL of tetraethylorthosilicate (Aldrich) were added and the system was stirred at 35° C for 24 h. At the end of this period the suspension was transferred into inox-lined teflon vessels and placed in an oven at 100 °C for another 24 h period. After the hydrothermal treatment, the precipitated solid was exhaustively washed with deionized water by vacuum filtration and dried at 60 °C for 24 h. This sample was then subjected to a calcination procedure at 500 °C for 12 h.

For the modification with amino groups, 1 g of dry SBA-15 was dispersed in a solution containing 29.6 mL of toluene and 3.97 mL of 3-aminopropyltriethoxysilane

(Aldrich). After stirring for 6 h at 80 °C, under reflux, the resulting solid was isolated by filtration, repeatedly washed with absolute ethanol and then dried at 60 °C overnight [8].

2.2 Metal Nanoparticles Preparation

1.0 g of amino-modified SBA-15 was dispersed into 50 mL of a metal salt precursor aqueous solution. The metal salt precursors used were HAuCl_4 (30% solution, Aldrich) and PdCl_2 (5% solution, Aldrich). The system was stirred at 80 °C for 5 h under reflux. The solids were then isolated by vacuum filtration, washed with deionized water and dried at 60 °C overnight. The samples were subjected to a calcination procedure at 500 °C for 6 h.

2.3 Characterization Techniques

X-ray powder diffraction was performed on a Bruker, D8 Focus equipment (Cu $K\alpha$, 40 kV, 40 mA). Thermal analyses were carried on a Netzsch STA 409 PC/PG at a rate of 10 °C/min. UV-Vis spectroscopy was carried on a Varian Scan 50 spectrophotometer coupled with fiber optic accessory for solid analysis. Elemental analysis (Au and Pd) was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Spectro Ciros CCD equipment. SEM microscopy was performed on a FEI Inspect F-50 field emission scanning electron microscope and TEM micrographs were taken using a JEOL JEM-2100F transmission electron microscope at 200 kV.

3 RESULTS AND DISCUSSION

The process of preparation of SBA-15 supported metal nanoparticles is based on the functionalization of the silica surface with 3-aminopropyltriethoxysilane (APTES) molecule. The negative charged gold/palladium species bind to the positive ammonium sites that are generated due to the use of an acidic media. The samples are then calcined in order to decompose the APTES molecules and to form the nanoparticles. The metal content in the Au-Pd/PdO-SBA-15 samples prepared in this work have been analyzed by ICP-AES, and the results are listed in Table 1. It is important to observe that the total metal content in relation to the support is always superior to 1% (nominal value), because of the decomposition of APTES during the calcination procedure. The APTES content in the functionalized samples is about 15% wt. according to thermo gravimetric analysis. The name of the samples is based on the molar fraction of the metals determined using the data on Table 1.

The materials were also analyzed by X ray diffraction, in the 30° - 70° 2θ range (Fig. 1). The peak centered at $2\theta = 38.3^\circ$, which can be assigned to the (111) planes of cubic crystalline structure of gold, indicates the predominant presence of this kind of structure in the samples $\text{Au}_{0.97}\text{Pd}_{0.03}$ -SBA-15 and Au-SBA-15. When the Pd content is raised, it is possible to observe that the peak is shifted to

$2\theta = 38.9^\circ$, indicating the formation of alloy between the two metals. The samples that contain Pd molar fractions higher than 0.50 show a peak at 33.8° , characteristic of the presence of PdO nanoparticles. PdO is formed because of the use of oxidant atmosphere during calcination. The oxide can be easily reduced to Pd using either NaBH_4 solution or thermal treatment with H_2 (an example is shown on Fig. 2). It is important to notice that Au always form alloys with Pd, even when Pd is present in small amounts. Pd, on the other hand, forms alloys with Au until approximately 0.5 molar fraction. When higher Pd amounts are present, a segregated PdO phase is formed. Mean diameter of the nanoparticles were not calculated from XRD data because the Scherrer formula is, in general, inadequate for alloy particles smaller than 5 nm [9].

Table 1: Composition of the Au-Pd/PdO-SBA-15 samples, determined by ICP-AES.

Sample	wt.% Au	wt.% Pd	total wt. %
Au	1.17	0.00	1.17
$\text{Au}_{0.97}\text{Pd}_{0.03}$	1.20	0.02	1.22
$\text{Au}_{0.51}\text{Pd}_{0.49}$	0.96	0.51	1.47
$\text{Au}_{0.40}\text{Pd}_{0.60}$	0.94	0.75	1.69
$\text{Au}_{0.14}\text{Pd}_{0.86}$	0.41	1.41	1.82
Pd	0.00	1.25	1.25

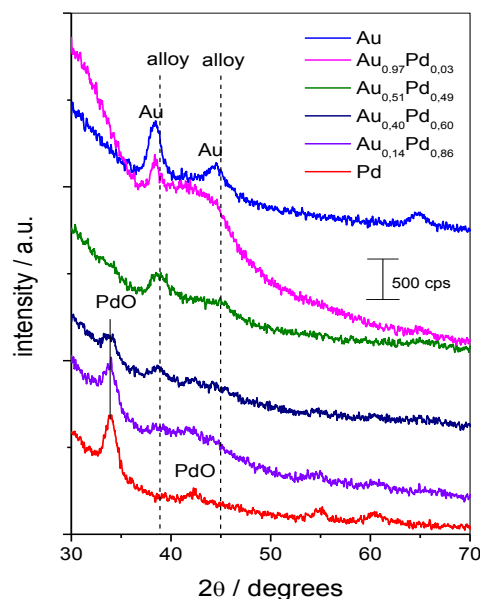


Fig. 1: XRD of Au-Pd/PdO-SBA-15 samples

The sample $\text{Au}_{0.51}\text{Pd}_{0.49}$ -SBA-15 presents a very small PdO contribution at $2\theta = 33.5^\circ$ that is evident only when it is compared to the diffractogram of a sample that has been subjected to a reduction process (Fig. 2). After the reduction the peak disappears because PdO is converted to metallic Pd, which can either be in the form of isolated Pd

nanoparticles or aggregate with the already present Au-Pd alloy nanoparticles.

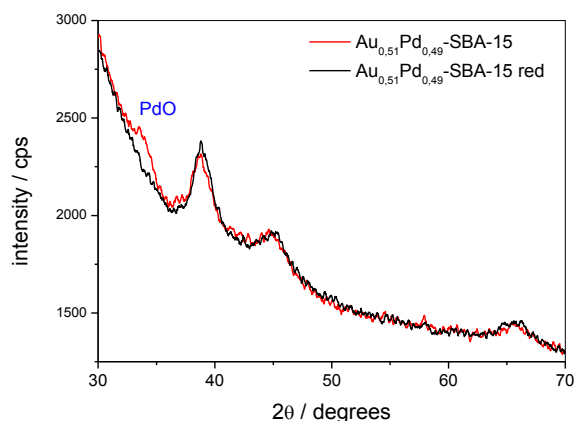


Fig. 2: XRD of the sample $\text{Au}_{0.51}\text{Pd}_{0.49}\text{-SBA-15}$ prior and after reduction with NaBH_4 (0.5 mol.L^{-1})

The formation of alloy from small Pd molar fractions can be confirmed by UV-Vis spectroscopy (Fig. 3). It can be clearly observed that the surface plasmon resonance (SPR) band typical of Au nanoparticles is present only for the sample Au-SBA-15. The sample $\text{Au}_{0.97}\text{Pd}_{0.03}\text{-SBA-15}$ presents a very low intense SPR band, and all the other samples do not present any contribution, which corroborates the formation of Au-Pd alloy in these samples [10].

The photographs of the powder materials (Fig. 3) also give an indication of the species present in the samples. The sample Au-SBA-15 is the only one that presents a red color typical of Au nanoparticles. Small fractions of Pd change the color of the samples to gray, because of the formation of alloy, and larger Pd amounts give rise to a yellow color typical of the presence of PdO.

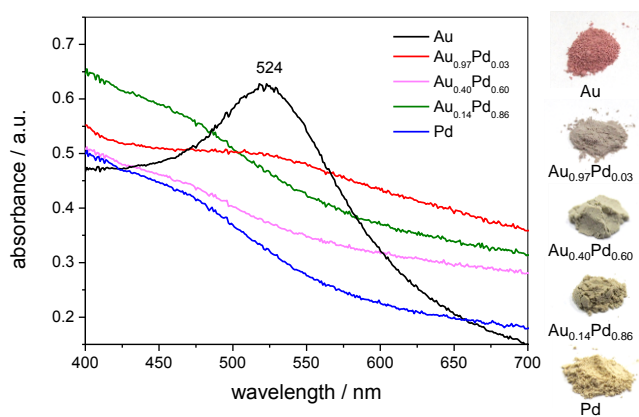


Fig. 3: DR-UV-vis spectra and photographs of Au-Pd/PdO-SBA-15 samples.

The samples present the typical rod-like morphology of SBA-15 materials [11] and there is a good distribution of the metal nanoparticles through the support (Fig. 4). HAADF-TEM images of the samples $\text{Au}_{0.97}\text{Pd}_{0.03}\text{-SBA-15}$,

$\text{Au}_{0.51}\text{Pd}_{0.49}\text{-SBA-15}$ and $\text{Au}_{0.40}\text{Pd}_{0.60}\text{-SBA-15}$ are shown in Fig. 5. In all the materials it can be observed that the majority of the particles are smaller than 5 nm.

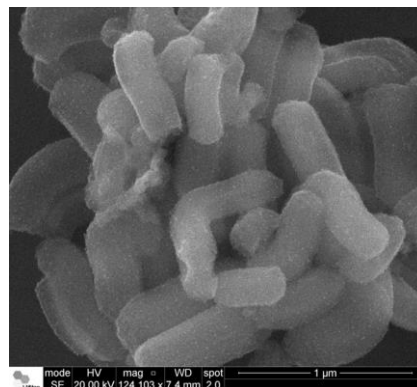


Fig. 4: SEM image of the sample $\text{Au}_{0.51}\text{Pd}_{0.49}\text{-SBA-15}$.

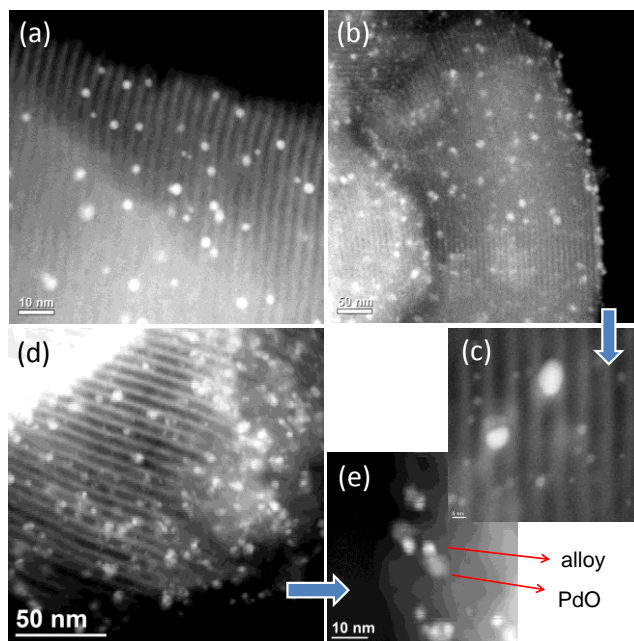


Fig. 5: HAADF-TEM images of the samples (a) $\text{Au}_{0.97}\text{Pd}_{0.03}\text{-SBA-15}$, (b, c) $\text{Au}_{0.51}\text{Pd}_{0.49}\text{-SBA-15}$ and (d, e) $\text{Au}_{0.40}\text{Pd}_{0.60}\text{-SBA-15}$.

The sample $\text{Au}_{0.97}\text{Pd}_{0.03}\text{-SBA-15}$, with higher Au content, presents a more uniform distribution of particles sizes, whereas the samples with higher Pd contents present more complex features. The sample $\text{Au}_{0.51}\text{Pd}_{0.49}\text{-SBA-15}$, for instance presents two different nanoparticle populations, one with particles of ca. 5 nm and other with very small particles in the order of 1 nm or less (Fig. 5c). The image on Fig. 5b also evidences a considerable amount of particles located on the external surface of the support, as can be seen on the edge of the material at the right side of the image. The presence of PdO, as verified by XRD, is not clearly evidenced on the micrographs, which may be an indication that the oxide is aggregated with the alloy

particles. The sample Au_{0.40}Pd_{0.60}-SBA-15 (Fig. 5d and e) also presents more than one population of particles. There can be observed a population of small isolated particles of 1 nm or less and a population of aggregated particles, constituted of alloy particles (bright spots in Fig. 5e) and oxide particles (less bright spots in Fig. 5e). Those composite particles suggest that, during calcination, excess Pd exudates as PdO from the alloy.

4 CONCLUSIONS

The morphology and the composition of bimetallic Au-Pd nanoparticles supported on SBA-15 mesoporous molecular sieve were investigated in this work. It was observed that Au forms alloy particles with Pd, originating materials composed of nanoparticles smaller than 5 nm. When Pd molar fraction exceeds that of Au, an increase in complexity of the systems occurs, because part of the Pd alloys with Au and part is separated in the form of PdO. These catalyst materials are very good candidates for redox reactions such as alcohol oxidations.

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