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Bimetallic Gold–Palladium vapour derived catalysts: The role of structural features on their catalytic activity

Claudio Evangelisti [a,*], Eleonora Schiavi [b], Laura Antonella Aronica [b], Anna Maria Caporusso [b,c], Giovanni Vitulli [c], Luca Bertinetti [d], Gianmario Martra [d], Antonella Balerna [e], Settimio Mobilio [f]

[a] CNR, Institute of Molecular Science and Technologies (ISTM), Via G. Fantoli 15/16, 20138 Milano, Italy
[b] Department of Chemistry and Industrial Chemistry, University of Pisa, Via Risorgimento 35, 56126 Pisa, Italy
[c] Advanced Catalysts S.r.l., Via Risorgimento 35, 56126 Pisa, Italy
[d] Department of Chemistry IFM & NIS Interdipartimental Centre of Excellence, Via P. Giuria 7, 10125 Torino, Italy
[e] INFN – Frascati National Laboratories, Frascati, Via E. Fermi 40, 00044 Frascati, Roma, Italy
[f] Department of Physics, University of Roma TRE, Via della Vasca Navale 84, 00146 Roma, Italy

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ABSTRACT

A procedure to synthesize new Au–Pd bimetallic catalysts using Au and Pd vapours as reagents (metal vapour synthesis, MVS) is reported. The simultaneous co-condensation of Au and Pd vapours with acetone vapour affords Au–Pd/acetone-solvated metal atoms which have been used to deposit Au–Pd bimetallic nanoparticles on γ-alumina and titanium oxide supports. Transmission electron microscopy (TEM) analysis determined the nanoparticles dimensions ($d_m = 2.2–2.4$ nm) and size distribution while the X-ray absorption spectroscopy (XAS) analysis showed the presence of small bimetallic Au–Pd nanoparticles with a large amount of Au–Pd bonds. The bimetallic co-condensed systems, tested in the selective oxidation of benzyl alcohol with molecular oxygen both in toluene solvent and in solvent-free conditions, showed higher catalytic activity and selectivity than the corresponding monometallic systems as well as of the analogous systems obtained by separate evaporation of the two metals.

1. Introduction

Bimetallic systems are of great interest from both scientific and technological point of view. Their catalytic, electronic and optical properties are different from those of their pure constituent metals and are influenced by different factors: not only from particles size and shape, as in monometallic nanoparticles, but also from the atomic ratio of the metals and the electronic and chemical structure of bimetallic nanoparticles [1–3]. Among the numerous metals which were investigated in combination, gold–palladium systems have been extensively studied because of their peculiar catalytic properties [4]. Bimetallic gold–palladium catalysts have been recently reported as promoters of processes such as oxidation of alcohols to corresponding aldehydes or ketones [5–7], production of hydrogen peroxide [8,9], production of vinyl acetate [10,11], hydrogenation of unsaturated compounds [12,13] and hydrodechlorination of chloro- and chlorofluorocarbons [14].

Recently, several investigations towards the relationship between catalytic activity and structural and electronic features of Au–Pd bimetallic catalysts have been reported. Au and Pd can form solid solutions at any ratio [15] and depending on their preparation method, Au–Pd bimetallic systems can contain different structural features including core–shell structure [8,16–18], segregated Au and Pd monometallic domains [19], uniform Au–Pd alloys [20,21] or a mixture of them [22,23].

In this work, we report the preparation of supported Au–Pd bimetallic systems by using Pd and Au vapours as reagents (metal vapour synthesis, MVS) [24] following two different synthetic procedures. In the first one, Au and Pd vapours were co-condensed simultaneously with acetone vapour in order to obtain a close interaction between the two metals, leading to a bimetallic Au–Pd/acetone solvated metal atoms (SMAs) solution. Then, Au–Pd/acetone SMA was used as starting material to synthesize bimetallic [Au–Pd] catalysts supported on γ-alumina and titanium oxide, respectively. In the second one, Au and Pd were evaporated separately in two different evaporation reactions; therefore, Pd/acetone and a Au/acetone SMA were achieved. Afterwards, Pd and Au SMA were mixed together and used as starting materials to obtain supported [Au][Pd] bimetallic systems.

In order to have a further insight into the morphology and the structural properties of the Au–Pd bimetallic nanoparticles and to rationalize the role played by the two different MVS procedures used, Au–Pd bimetallic systems supported on γ-alumina and on titanium oxide were investigated by the transmission electron microscopy (TEM) and X-ray absorption spectroscopy (XAS) analyses.

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* Corresponding author. Present address: CNR, Institute of Molecular Science and Technologies, Via C. Golgi 19, 20133 Milano, Italy. Fax: +39 050 2219260.
E-mail address: claudio@dcci.unipi.it (C. Evangelisti).

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The catalytic activity of Au–Pd bimetallic systems was studied in the selective oxidation of benzyl alcohol to benzaldehyde, chosen as test reaction, evidencing a close relationship between the structural features of these bimetallic systems, induced by the different preparation procedures used, and their catalytic behaviour. The selective oxidations of alcohols to their respective aldehydes or ketones are a processes of great relevance from a laboratory and industrial point of view [25,26]. It is well known that both highly dispersed palladium [27] and gold [28] catalysts promote these processes using molecular oxygen as environmental friendly reagent respect to stoichiometrical reagents such as permanganate or dichromate, which are traditionally employed [29,30].

Recently, Au–Pd bimetallic catalysts have shown to be very active in these reactions evidencing a beneficial interaction between the two metals depending on the structural characteristics of these bimetallic systems. Significant advances in the field has been reported by Dimitratos et al. [31] and Enache et al. [6] which achieved high catalytic efficiency under solvent and solvent-free conditions, respectively, with supported Au–Pd bimetallic nanoparticles obtained by reduction in Au and Pd salts.

2. Experimental

2.1. General

All operations involving the MVS products were performed under a dry argon atmosphere. The co-condensation of gold, palladium and acetone vapours was carried out in a static reactor similar to those previously described [32]. In the case of co-evaporation experiments, the MVS apparatus was equipped with two alumina-coated tungsten crucibles heated by Joule effect with two Rial AEJ2 generators, respectively, with a maximum power of 2 kW that allowed to evaporate independently two metals. The acetone-solvated metal atoms solutions were handled under argon atmosphere with the use of the standard Schlenk techniques. The amount of palladium and gold in the above solutions was determined by inductively coupled plasma–optical emission spectrometers (ICP–OES) with a Spectro-Genesis instrument equipped with a software Smart Analyser Vision. For ICP–OES, a sample (1 mL) of SMA solutions was heated over a heating plate in a porcelain crucible in the presence of *aqua regia* (2 mL) for four times, dissolving the solid residue in 0.5 M aqueous HCl. The limit of detection (lod) calculated for palladium and gold was 2 ppb. Acetone was purified by conventional methods, distilled and stored under argon. Commercial γ-Al_2O_3 (Chimet product, type 49, 3.1 μm average particle size, surface area 110 $m^2\,g^{-1}$), TiO_2 (Degussa product, powder containing anatase (80 wt.%) and rutile (20 wt.%), P99.5%, 21 nm average particle size, surface area 50 ± 15 $m^2\,g^{-1}$) were dried in a static oven before use. Benzyl alcohol was supplied from Aldrich and used as received. The GLC analyses were performed on a Perkin–Elmer Auto System gas chromatograph, equipped with a flame ionization detector (FID), using a SiO_2 column (BP-1, 12 m × 0.3 mm, 0.25 μm) and helium as carrier gas.

Electron micrographs were obtained by a Jeol 3010-UHR high-resolution transmission electron microscope (HRTEM) equipped with a LaB_6 filament operating at 300 kV) equipped with an Oxford Inca Energy TEM 300 EDS X-rays analyser. Before the introduction in the instrument, the samples, in the form of powders, were ultrasonically dispersed in isopropyl alcohol and a drop of the suspension was deposited on a copper grid covered with a lacey carbon film. Histograms of the particle size distribution were obtained by counting onto the micrographs at least 300 particles; the mean particle diameter (d_m) was calculated by using the formula $d_m = \Sigma d_i n_i / \Sigma n_i$ where n_i was the number of particles of diameter d_i. TEM analysis was performed on both monometallic and bimetallic samples supported on Al_2O_3 and TiO_2. The instrument condition at the time of the measurements resulted in a minimum cross section of the electron beam during EDX analysis of ca. 5 nm.

The X-ray absorption spectroscopy (XAS) measurements at the Au L_3 edge (11,919 eV) and at the Pd K-edge (24,350 eV) were performed at the GILDA beamline [33] of the European Synchrotron Radiation Facility (ESRF, Grenoble). The X-ray beam was monochromatized and horizontally focused by using a double crystal Si(3 1 1) monochromator [34]; two Pd mirrors at the Au L_3 edge and two Pt mirrors at the Pd K-edge were used to reject the higher harmonics and focus the beam in the vertical direction [33]. XAS measurements at the Au L_3 and at the Pd K edges were performed on the two reference samples (Au and Pd foils) and on a complete set of two monometallic (Au (1%) and Pd (0.5%) and two bimetallic [Au][Pd], [AuPd] samples supported on γ-Al_2O_3. Two bimetallic [Au][Pd], [AuPd] samples supported on TiO_2 were measured only at the Au L_3 edge. The catalytic samples were prepared for the X-ray absorption spectroscopy (XAS) experiments mixing their fine powders with boron-nitride and pressing them into pellets. The different sample amounts were calculated [35] in order to achieve appropriate edge jumps.

Both reference samples and the catalysts at the Au L_3 edge were measured in transmission mode with two Ar-filled ionization chambers to detect the incident (I_0) and transmitted (I_T) X-ray beam. The catalysts at the Pd K-edge were measured in fluorescence mode (I_F) by using a 13-element high-purity Ge multi-detector coupled to an X-ray pulse digital analyser for a more accurate dead-time effect correction [36].

The absorption coefficients were calculated as $\mu(E) = \ln(I_0/I_T)$ in transmission mode and as $\mu(E) = (I_F/I_0)$ in fluorescence mode. All spectra were recorded at 20 K in order to reduce the thermal effects.

2.2. Preparation of the [AuPd] catalysts

In a typical experiment (Scheme 1), palladium and gold vapours generated by resistive heating of two different alumina-coated tungsten crucibles filled with ca. 150 mg of Pd powder and 300 mg of Au pellets, respectively, were co-condensed simultaneously at liquid nitrogen temperature with acetone (100 mL) in the glass reactor chamber of the MVS apparatus for a chosen time. The reactor chamber was warmed to the melting point of the solid matrix, and the resulting red–brown solution was siphoned at a low temperature into a Schlenk tube and kept in a refrigerator at −40 °C. The metal amount recovered in SMA was about the 80 wt.% of the evaporated metal. The palladium and gold content, obtained by ICP–OES analysis, were 0.5 mg/mL of Pd and 1.0 mg/mL of Au, corresponding to a Pd/Au molar ratio = 1. 70 mL of the [Au–Pd]/acetone SMA (0.33 mmols, 35 mg of Pd and 0.35 mmols, 70 mg of Au) was added to a suspension of γ-Al_2O_3 or TiO_2 (7.00 g) in acetone (30 mL). The mixture was stirred for 12 h at room temperature. Au–Pd bimetallic nanoparticles were quantitatively deposited on the supports; the colourless solution was removed, and the light-brown solid was washed with *n*-pentane and dried under reduced pressure. By this way Au–Pd bimetallic catalysts containing 1 wt.% of Au and 0.5 wt.% of Pd, represented as [AuPd]/γ-Al_2O_3 and [AuPd]/TiO_2, respectively, were obtained.

2.3. Preparation of the [Au][Pd] catalysts

In a typical experiment (Scheme 2), palladium vapour generated by resistive heating of an alumina-coated tungsten crucible filled with ca. 200 mg of Pd powder was co-condensed at liquid nitrogen temperature with acetone (100 mL) in the glass reactor chamber of the MVS apparatus for a chosen time. The reactor