



Influence of pretreatment atmospheres on the performance of bimetallic Au-Pd supported on ceria-zirconia mixed oxide catalysts for benzyl alcohol oxidation

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ABSTRACT

Monometallic Au, Pd and bimetallic Au-Pd catalysts supported on a Ce_{0.62}Zr_{0.38}O₂ mixed oxide have been synthesized by the sol-immobilization method. An in-depth Scanning-Transmission Electron Microscopy (STEM) study has been performed to reveal the structural and chemical nature of the metal nanoparticle system present in these catalysts. Attention has been paid both to the evolution of the particle size distribution and the degree of Au-Pd interaction as a function of the treatment used to activate the catalysts. This characterization work has been complemented by results coming from other macroscopic techniques like Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), N₂ physisorption, Temperature Programmed Oxidation (TPO) or X-ray Photoelectron Spectroscopy (XPS). The whole set of characterization data evidences the intrinsic structural complexity of this type of bimetallic systems, in which a fraction of monometallic Au, monometallic Pd and bimetallic nanoparticles of varying compositions coexist. This picture, which clearly contrasts with other much more homogeneous situations described in previous literature on bimetallic catalysts, also indicates the requirement of combining both atomic scale and macroscopic techniques to understand the structure of these catalysts.

Concerning catalytic performance, a synergistic effect between Au and Pd has been observed in the selective oxidation of benzyl alcohol on ceria-zirconia. Moreover, the catalytic activity of these bimetallic Au-Pd catalysts is higher than that on other commonly used supports, such as activated carbon or carbon nanotubes. The treatments in oxidative and inert atmospheres at 250 °C improve the catalytic activity with respect to the fresh, un-pretreated, catalyst. Subsequent reduction of the oxidized bimetallic catalyst leads to an activity similar to that of the fresh catalyst, which is reduced at room temperature with H₂ bubbles.

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1. Introduction

Benzaldehyde is one of the most valuable aromatic aldehydes due to its application in perfumery, pharmaceuticals, cosmetics, dyestuff and agrochemical industry. Commercially, it is mainly produced via the toluene chlorination/hydrolysis process, which generates large amounts of toxic acidic waste, leading to equipment corrosion and costly separation processes [1]. The high demand for green processes and in particular, the need for chlorine-free

benzaldehyde production has promoted the development of novel, environmental benign and alternative production routes.

Selective oxidation of benzyl alcohol to benzaldehyde in liquid phase has shown advantages in terms of easy recovery, reusability and high catalytic activity [1]. Among heterogeneous catalysts, bimetallic catalysts integrating Au with other noble metals (Pd and Pt) have exhibited higher catalytic activity than monometallic catalysts for the selective oxidation of benzyl alcohol [2–11]. In particular, Au-Pd nanoparticles supported on different kinds of supports have demonstrated promising results [2–11].

Even though selective oxidation of benzyl alcohol on Au-Pd catalysts is a well-studied process in the literature, the detailed nature of the interaction between the two metals at atomic level has not

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been considered in full details, in spite of its relevance to understand their performance. Recent reports on gold-based bimetallic catalysts, prepared by different approaches have pointed out that a complex nanostructure in this kind of materials forms [12,13].

On the other hand, the support plays an important role in the oxidation of benzyl alcohol. Thus, bimetallic Au and Pd nanoparticles have been deposited on different kinds of materials, such as activated carbon, carbon nanotubes, TiO₂, Mg–Al mixed oxide, ceria, ZnO, Nb₂O₅, SiO₂, Al₂O₃, SBA-15, zirconia, polyaniline or MgO, among others [2–11,14–25]. It has been reported that gold and palladium nanoparticles supported on reducible oxides, such as CeO₂, exhibit better catalytic behavior due to the ability of these materials to activate the O₂ molecule [14,26]. In particular, CeO₂ is a very reactive support due to its unique redox properties, related to its capacity to reversibly exchange lattice oxygen with its surroundings in response to changes in the oxidation state of cerium atoms between Ce⁴⁺ and Ce³⁺, which is usually referred as oxygen storage capacity (OSC). Furthermore, the introduction of Zr⁴⁺ ions into the CeO₂ fluorite lattice improves the OSC, the formation of oxygen vacancies [27] and the thermal stability with respect to the pure oxide [28,29]. Only a few works have studied ceria-zirconia mixed oxides as supports for bimetallic Au–Pd catalysts. A previous contribution from our lab has reported that no synergistic effect was found on bimetallic Au–Pd catalysts supported on ceria-zirconia prepared by deposition-precipitation (DP) of Au followed by impregnation of Pd method for CO oxidation reaction [30]. In contrast, synergistic effects were observed on both bimetallic Au–Pd and Au–Ru supported on ceria-zirconia mixed oxide catalysts for selective oxidation of glycerol [12,31].

Taking all this into consideration, in this work, bimetallic Au–Pd catalysts supported on a Ce_{0.62}Zr_{0.38}O₂ oxide have been prepared by sol-immobilization method and a detailed characterization work has been performed in order to determine the extent of Au–Pd interaction reached using this particular type of synthetic approach. Their catalytic performance in the selective oxidation of benzyl alcohol has been evaluated. In particular, the effect of the redox nature of the activation pretreatment atmosphere has been studied in order to optimize the synthesis method of bimetallic Au–Pd catalysts supported on Ce_{0.62}Zr_{0.38}O₂. Thus, pretreatments under hydrogen, nitrogen and oxygen have been investigated as representative of activation of the catalysts under reducing, inert and oxidizing conditions.

2. Experimental

2.1. Catalyst preparation

The support used in all the preparations described below was a Ce_{0.62}Zr_{0.38}O₂ (CZ) mixed oxide kindly donated by Grace Davison. The BET surface area of this commercial material was 67 m² g⁻¹.

2.1.1. Monometallic catalysts

The monometallic and bimetallic catalysts have been prepared by the sol-immobilization method. The nominal loadings of the monometallic catalysts were 1 wt.%. 2 mL of Na₂PdCl₄ (10 mg Pd mL⁻¹) solution and 2 mL of polyvinylpyrrolidone aqueous solution (PVP, 1%, w/w) were added to 200 mL of deionized water, stirring for 2 min. Then 4 mL of 0.1 M NaBH₄ solution was put into the mixture of the Pd precursor and PVP under magnetic stirring for sol generation. A brown Pd sol immediately formed. An UV–vis spectrum of the Pd sol was recorded for ensuring the complete reduction of Pd(II).

The Au sol was prepared with the same method using NaAuCl₄·2H₂O as precursor. A ruby red Au sol immediately formed after addition of NaBH₄ solution to the mixture of NaAuCl₄ and

PVP. The UV–vis spectrum of the gold sol also confirmed complete reduction of Au (III) species.

Within 3 min from their generation, the colloids (acidified to pH = 2 by addition of sulfuric acid) were immobilized by adding 2 g of Ce_{0.62}Zr_{0.38}O₂ mixed oxide support under vigorous stirring for 1 h. The slurry was further filtered, washed with distilled water and dried at 80 °C for 2 h. The dried catalysts were oxidized in a flow of O₂ for 1 h at 250 °C with a heating rate of 10 °C min⁻¹. Then, the treatment atmosphere was changed at the same temperature to a flow of nitrogen. After 1 h under this environment, the catalyst was cooled down to room temperature, also under the nitrogen flow. The monometallic catalysts were coded as 0.82%PdCZ and 0.86%AuCZ, in which 0.82% and 0.86% stand for the actual Pd and Au loadings as determined from ICP–AES analysis.

Another monometallic reference 2.5 wt.% Au/Ce_{0.62}Zr_{0.38}O₂ catalyst was prepared by DP method using sodium carbonate as precipitating agent [12,30]. This DP sample was filtered and washed several times with deionized water at room temperature until no chloride ions could be detected with AgNO₃. It was dried overnight in an oven at 100 °C. Finally the sample was oxidized at 250 °C in 5% O₂/He for 1 h and purged with a flow of helium at the same temperature for 1 h. Cooling down to room temperatures was also performed under the inert gas flow. This catalyst is coded as 2.5%AuCZ. As described in our previous work [12,30], the size of the Au metal particles of this 2.5%AuCZ catalyst ranges from 1 to 8 nm, with an average value of 1.7 nm. The metal dispersion of this catalyst is 39%.

2.1.2. Bimetallic Au–Pd catalysts

In order to synthesize bimetallic Au–Pd supported on ceria-zirconia catalysts with total metal loading around 1 wt.%, a Au sol was firstly prepared using the same method described for the 0.86%AuCZ catalyst. 2.19 mL of NaAuCl₄·2H₂O (10 mg Au mL⁻¹) solution and 2.19 mL PVP solution (1%, w/w) were added in 219 mL of H₂O. After stirring for 2 min, 0.1 M NaBH₄ (4.38 mL) was added under vigorous magnetic stirring. The ruby red Au sol immediately formed. After 3 min of sol generation, 3 g of Ce_{0.62}Zr_{0.38}O₂ support was added to the Au sol under vigorous stirring. After 1 h of stirring, the slurry was filtered and washed with distilled water and dried during 15 min at 80 °C.

The second step of the preparation was deposition of Pd on the Au/Ce_{0.62}Zr_{0.38}O₂ sample. For this purpose, the monometallic Au sample previously prepared was dispersed in 250 mL of water at room temperature. To guarantee saturation, H₂ was bubbled for 1 h (50 mL min⁻¹) into the suspension under atmospheric pressure and room temperature. Then, 0.81 mL of Na₂PdCl₄ (10 mg Pd mL⁻¹) solution and 0.81 mL of PVP solution (1%, w/w) were added under vigorous magnetic stirring. After additional 1 h of stirring, the resulting slurry was filtered and washed with distilled water and dried in air at 80 °C for 2 h. The catalyst obtained this way was coded as 1.4AuPd-F. Subsequently the 1.4AuPd-F catalyst was activated using three different pretreatments: (1) under nitrogen at 250 °C for 2 h (1.4AuPd-I); (2) under oxygen for 1 h followed by nitrogen 1 h also at 250 °C (1.4AuPd-O); (3) a portion of the 1.4AuPd-O sample was reduced bubbling H₂ at room temperature into a vigorously stirred aqueous suspension of this catalyst during 1 h (1.4AuPd-R).

2.2. Catalyst characterization

The gold and palladium loadings of the catalysts were determined by ICP–AES. X-ray diffraction (XRD) patterns of the catalysts were recorded using a Bruker diffractometer AXS, Model D8 Advance, employing Cu K α radiation source (1.5418 Å) operated at 40 kV and 40 mA. Scans were collected from 10 to 100 ° with a 0.05 ° step size and step time of 30 s. The BET specific surface areas

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