

# Effect of support morphology and catalyst preparation on the selective oxidation activity of Au-Pd supported on nanostructured ceria

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## Abstract

*Au-Pd nanoparticles supported on different ceria nanostructures were prepared by colloidal synthesis and immobilization, and by conventional impregnation. The catalysts were tested in the selective oxidation of benzyl alcohol. Au-Pd supported on ceria nanorods and prepared by sol-immobilization exhibited high catalytic activity ( $TOF > 36,000 \text{ h}^{-1}$ ), and was found to be considerably more active than all the other catalysts investigated in the study and similar Au-Pd catalysts reported in literature.*

**Keywords:** Selective oxidation, Ceria, Gold-palladium.

## 1. Introduction

The catalytic activity of supported gold catalysts is highly dependent on the nature of the support and its physiochemical properties, the metal particle size, and the catalyst preparation method. Gold catalysts are typically more active when deposited on reducible metal oxides such as  $\text{CeO}_2$  and  $\text{TiO}_2$ , which has been ascribed to the metal-support interaction and the ability of these materials to activate oxygen molecules<sup>1,2</sup>. In particular, nanostructured ceria is a very reactive support due to its distinctive redox properties, and ability to reversibly exchange lattice oxygen in response to changes in the oxidation state between  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$ . The catalyst preparation method is also an important factor that can significantly influence the catalytic performance of Au and Au-Pd catalysts. In the present work, Au-Pd NPs prepared by colloidal synthesis and immobilized on ceria nanorods (Ce-NR) and on ceria nanopowder have been studied for the selective oxidation of benzyl alcohol. The Au-Pd/Ce-NR catalyst is shown to be considerably more active than the equivalent catalyst supported on ceria nanopowder. For comparison purposes, we also show that catalysts prepared by sol-immobilization are significantly more active than the catalysts prepared by dry impregnation.

## 2. Experimental

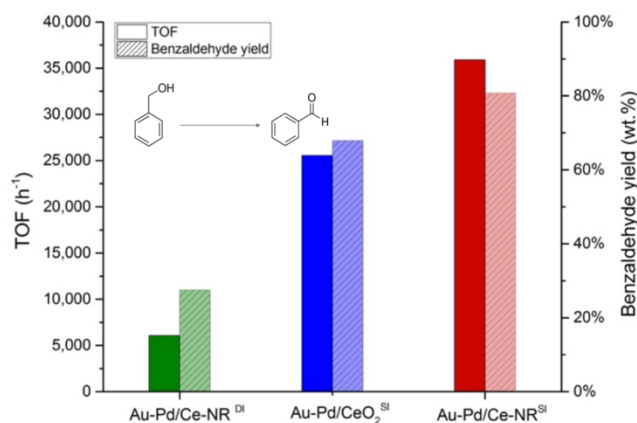
Ceria nanorods were prepared by the alkaline hydrothermal treatment method reported previously<sup>3</sup>. The Au-Pd colloid was prepared according to previously reported procedures<sup>4</sup>. Catalysts were characterized with XRD, ICP, TEM, STEM, EDX, XPS, zeta potential and nitrogen-adsorption desorption measurements. The catalytic activity was evaluated in the solvent-less selective oxidation of benzyl alcohol, which is widely used as a model selective oxidation reaction for the study of supported Au-Pd catalysts.

## 3. Results and discussion

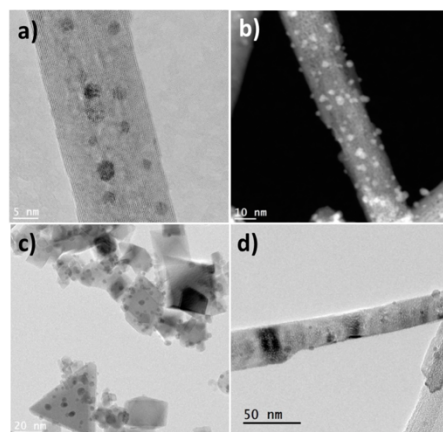
In this study, we investigated the solvent-less selective oxidation performance of the prepared Au-Pd catalysts, and examined the influence of the support material morphology and the catalyst preparation method on the activity and selectivity. Figure 1 shows the turnover frequency (TOF), and the total benzaldehyde yield. The catalyst prepared by sol-immobilization on ceria nanorods (Au-Pd/Ce-NR<sup>SI</sup>) exhibited the highest catalytic activity with  $TOF > 36,000 \text{ h}^{-1}$ , and the highest benzaldehyde yield (ca. 80%). On the other hand, Au-Pd supported on commercial  $\text{CeO}_2$  nanopowder (Au-Pd/ $\text{CeO}_2$ <sup>SI</sup>) displayed a lower activity ( $TOF \sim 25,500 \text{ h}^{-1}$ ) and a lower benzaldehyde yield of 68%. Au-Pd supported on Ce-NR and prepared by traditional dry impregnation (Au-Pd/Ce-NR<sup>DI</sup>) was less active than the catalysts prepared by sol-immobilization displaying a TOF of  $>6,000 \text{ h}^{-1}$ , and benzaldehyde yield of only ca. 27%.

The synergic effect of Au-Pd alloying in the selective oxidation of benzyl alcohol was confirmed in the present study whereby Au/Ce-NR and Pd/Ce-NR catalysts were tested under the same reaction conditions as in Figure 1, and exhibited TOF of 1,664 and 12,300 h<sup>-1</sup>, respectively. The TOF observed for Au-Pd/Ce-NR<sup>SI</sup> is markedly higher than the TOF of similar Au-Pd catalysts reported in literature<sup>5,6</sup>.

The superior catalytic activity of Au-Pd/Ce-NR is due to its unique physicochemical and morphological properties. Characterization of the catalysts by XPS revealed that Au-Pd/Ce-NR<sup>SI</sup> display more than three times the Au and Pd surface concentration in comparison with Au-Pd/CeO<sub>2</sub><sup>SI</sup>, which implies that the high catalytic activity of Au-Pd/Ce-NR is in part associated with the high Au-Pd surface concentration, and the ability of the reactants to easily access the highly dispersed active metal sites on the external surfaces of the support, and products to leave. XPS also showed a high surface concentration of Ce<sup>3+</sup>, and it is likely that this and the presence a large number of oxygen vacancies and surface defects leads to the stabilization of the Au-Pd NPs facilitating the observed high and uniform metal dispersion on Ce-NR as shown in Figure 2. Furthermore, surface oxygen vacancies on the Ce-NRs likely play an important role in contributing to the activation of oxygen.



**Figure 1.** Initial TOF (h<sup>-1</sup>) at 0.5 hour and benzaldehyde yield after 3 hours for the different catalysts investigated in the study. Reaction conditions: T= 120°C, pO<sub>2</sub>= 2 bar, stirring rate=1,000 rpm, molar ratio of benzyl alcohol/metal = 50,000.



**Figure 2.** HRTEM and HAADF-STEM images of catalyst sample Au-Pd/Ce-NR<sup>SI</sup> (a,b), Au-Pd/CeO<sub>2</sub><sup>SI</sup> (c), and Au-Pd/Ce-NR<sup>DI</sup> (d).

#### 4. Conclusions

The superior catalytic activity of Au-Pd/Ce-NR<sup>SI</sup> is attributed to a combination of the physicochemical properties of the ceria nanorods support and the preparation method, which allows a high degree of control of the Au-Pd particle size, and facilitates high metal dispersion, and a high concentration of Au-Pd over the exterior surface of the nanorods. In particular, the unique redox properties and abundance of oxygen vacancies on the surface of Ce-NR contribute to the outstanding catalytic activity of Au-Pd/Ce-NR<sup>SI</sup> for selective oxidation.

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