Gold-palladium supported on titanate nanotubes and the influence of the catalyst preparation method on the catalytic activity for selective oxidation

Motaz Khawaji, **David Chadwick***

Department of Chemical Engineering, Imperial College London, London, SW7 2AZ, United Kingdom

**Corresponding author: d.chadwick@imperial.ac.uk*

The catalytic activity of gold catalysts is highly dependent on the catalyst preparation method and nature of the support, which both influence the metal dispersion and particle size. We have recently reported on the preparation of highly active Au-Pd/Ti-NT catalyst using colloidal synthesis and immobilization. This new catalyst showed a markedly superior catalytic activity for the selective oxidation of benzyl alcohol compared to similar catalysts reported in literature, and to other Au-Pd catalysts supported on Ti-NTs and prepared by deposition-precipitation, adsorption, and dry and wet impregnation methods. The superior catalytic activity of this new catalyst is attributed to the high metal dispersion on the external surfaces of Ti-NTs, the narrow particle size distribution, and the high degree of Au-Pd alloying in each individual nanoparticle.

Keywords: Selective oxidation, Gold-palladium, Titanate nanotubes.

1. Introduction

The catalytic activity of gold is highly dependent on Au particle size and the dispersion of Au nanoparticles (NPs), which both are influenced by the catalyst preparation method and the nature of the support. Usually, well-dispersed Au NPs of ≤5 nm in size display the highest catalytic activity [1]. It has been shown that different preparation methods produce different attachments of Au NPs on the support [2]. Hence, good catalytic performance can be achieved by judicious selection of the preparation method and support material. The catalytic activity of gold is enhanced by several folds by alloying gold with palladium. In the selective oxidation of alcohols to aldehydes, for instance, alloying Au with Pd results in up to twenty-five-fold enhancement in the activity while retaining the selectivity [1].

Titanate nanotubes possess several advantages over conventional titania. In the present work, we show that Au-Pd NPs can be prepared by colloidal synthesis and immobilized on the external surface of Ti-NTs to create a reproducible, stable, and highly active selective oxidation catalyst [3]. The present study also examined for comparison purposes the catalytic performance of Au–Pd/Ti-NT prepared by other common methods, namely deposition-precipitation, dry impregnation, wet impregnation, and adsorption. The present work demonstrates clearly that the catalytic activity of Au–Pd/Ti-NT is dependent on the preparation method, particle size, and the location of Au-Pd NPs and their dispersion on the surface of Ti-NTs, and that sol-immobilization is the more effective method of preparation.

2. Experimental

Titanate nanotubes were prepared by the alkaline hydrothermal treatment method reported previously[4]. The Au-Pd colloid was prepared according to previously reported procedures[3]. 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

Different catalyst preparation methods were used to prepare Au-Pd/Ti-NTs catalysts: dry impregnation, wet impregnation, adsorption, deposition-precipitation and sol-immobilization. All catalysts had a nominal metal loading of 2 wt.% with a Au:Pd weight ratio equivalent to 1:1. The catalysts were tested in the solvent-less selective oxidation of benzyl alcohol to benzaldehyde with molecular O_2. The selective oxidation of benzyl alcohol to benzaldehyde has been widely used as a model oxidation reaction for studying supported Au-Pd catalysts. The kinetics of adsorption of Au-Pd sols is largely dependent on the surface charge of the support and the metal NPs. Therefore, the surface charge of the Ti-NTs was investigated first, and the preparation conditions were tuned to favor the adsorption of the Au-Pd sol. The final metal loadings were found to be close to the nominal loading, which implies that most of metal NPs were efficiently adsorbed by the support. Figure 1 shows the catalytic performance of the catalysts prepared in our study. The catalyst prepared by sol-immobilization was found to be significantly more active than the catalysts prepared by all the other methods. HRTEM images revealed significant information about the structure and morphology of the catalysts, as well as the particle size distribution of Au-Pd NPs, (figure 2). The catalyst prepared by sol-immobilization (figures 2.a and b) exhibited the narrowest particle size distribution and smallest mean particle size. Catalysts prepared by adsorption (figure 2.c) had small mean particle size, but a wide particle size distribution. Deposition-precipitation, dry and wet impregnation resulted in a relatively wide particle size distribution and large mean particle size, with particles as large as 200 nm observed (figures 2.d , 2.e and 2.f). The use of colloidal synthesis in the synthesis of Au-Pd NPs allowed for a high degree of control over the particle size, and facilitated high metal dispersion on the surface of Ti-NTs, which in turn led to a highly active catalyst. In order to better understand the relationship between the catalyst preparation method and the catalytic activity, the catalysts were further characterised with STEM, EDX and XPS, which enabled determining the Au-Pd surface concentration and degree of alloying in each catalyst.

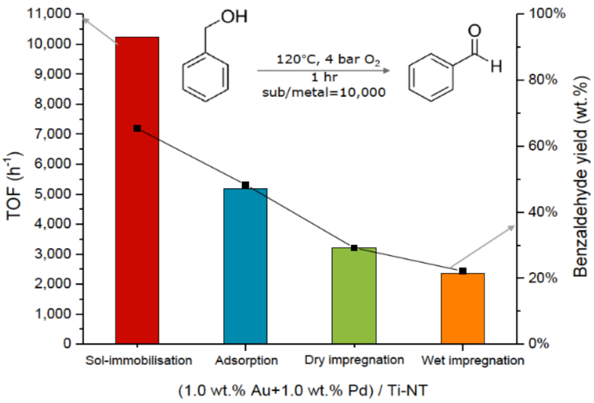

Figure 1. Benzyl aldehyde yield and TOFs for catalysts prepared by different methods. Reaction conditions: 120ºC, 4 bar O_2, 1 hour, molar ratio of substrate to metal =10,000.

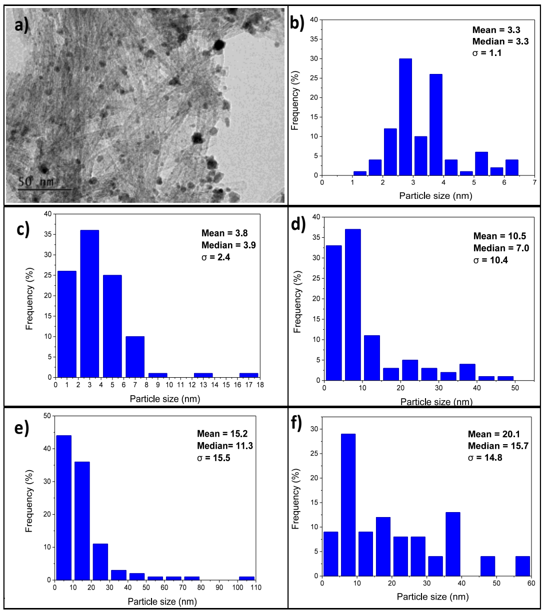

Figure 2. TEM images and the corresponding histograms of the particle size distributions for; a) and b) for Au-Pd/Ti-NTs prepared by sol-immobilisation, c) Au-Pd/Ti-NTs prepared by adsorption, d) Au-Pd/Ti-NT prepared by deposition-precipitation, e) Au-Pd/Ti-NTs prepared by dry impregnation, f) Au-Pd/Ti-NTs prepared by wet impregnation.

4. Conclusions

A highly active selective oxidation catalyst can be prepared by immobilizing Au-Pd NPs on the outer surface of Ti-NTs. The catalytic activity of Au–Pd/Ti-NTs is shown to be highly dependent on the catalyst preparation method, particle size, and dispersion of Au-Pd NPs on the surface of Ti-NTs. More importantly, this work clearly demonstrates the superior catalytic activity Au–Pd/Ti-NTs prepared by sol-immobilization, which can be attributed to the high metal dispersion, narrow particle size distribution, and the consistent formation of Au-Pd mixed alloy nanoparticles in close to a 1:1 wt. ratio.

References

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