

Selective suppression of disproportionation reaction in solvent-less benzyl alcohol oxidation catalysed by supported Au-Pd nanoparticles

Meenakshisundaram Sankar,¹ Ewa Nowicka,¹ Qian He,² Stuart H. Taylor,¹ Donald Bethell, David W. Knight,¹ Christopher J. Kiely² and Graham J. Hutchings*¹

¹ Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, UK

² Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, PA 18015-3195, USA

³ Department of Chemistry, University of Liverpool, Crown Street, Liverpool, L69 7ZD United Kingdom

* Corresponding author: Hutch@cardiff.ac.uk

Introduction

Oxidation is a fundamental functional group transformation in general organic synthesis. It often shows a number of undesirable features, such as the requirement for relatively expensive and toxic stoichiometric reagents, less than perfect yields, and sometimes complicated product separation procedures. Recently supported Au and Au-Pd nanoparticulate catalysts have been reported to be extremely active for the oxidation of CO, alcohols and alkanes. In the solvent-less oxidation of benzyl alcohol, toluene is found to be a major by product. Here, we report the selective “switching-off” of toluene formation by careful catalyst design, without compromising the catalytic activity.

Experimental

Supported AuPd nanoparticulate catalysts were prepared using a sol-immobilization method, where the AuPd nanoalloys are preformed and then supported on to a metal oxide support.^[1] In a typical solvent-less, aerobic oxidation of benzyl alcohol, the requisite amount of catalyst and substrate were charged into the reactor which was then purged with gas (He or O₂ as the case may be) three times before closing and the pressure was maintained at 1 bar (relative pressure) and then heated to the desired temperature. The samples were taken at regular intervals analysed by GC-MS, GC and NMR. For the quantification of the amounts of reactants consumed and products generated, an external calibration method was used. It was established that no reaction occurred in the absence of the Au-Pd catalyst or in the presence of the catalyst support alone. The catalysts were characterized using a JEOL 2000FX TEM operating at 200kV. STEM high angle annular dark field (HAADF) images of the bimetallic particles were obtained using an aberration corrected JEOL 2200FS TEM operating at 200kV.

Results/Discussion

In the solvent free oxidation of benzyl alcohol to benzaldehyde using supported gold palladium nanoparticles as catalysts, two pathways have been identified as the sources of the principal product, benzaldehyde.^[1] One is the direct catalytic oxidation of benzyl alcohol to benzaldehyde by O₂, while the second is the disproportionation of two molecules of benzyl alcohol to give equal amounts of benzaldehyde and toluene.^[1] Here we report that, by changing the metal oxide used to support the metal nanoparticles catalyst from titania to magnesium oxide or zinc oxide, it is possible to switch off the disproportionation reaction and thereby completely stop the toluene formation (Table-1). It has been observed that the presence of O₂ increases the turn-over number of this disproportionation reaction as compared to reaction in a helium atmosphere, implying that there are two catalytic pathways leading to toluene.^[2]

Table-1: Aerobic oxidation of benzyl alcohol using supported AuPd nanocrystals

Catalyst	Conversion(%)	Benzaldehyde(%)	Toluene(%)
1% AuPd/TiO ₂	65	79	21
1% AuPd/MgO	26	99	0.4
1% AuPd/ZnO	39	99	0.5

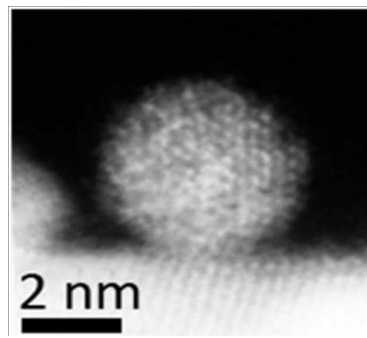


Figure-1: STEM image of 1% AuPd supported on MgO catalyst.

To investigate if the difference in the support materials affect the Au-Pd particle size distribution or the mode of attachment of the metal nanoparticle to the metal oxide support, the catalysts were characterized, initially by TEM and then by STEM. A representative STEM image of 1% AuPd/MgO is given in Figure-1. From the particle size distribution data, it is clear that there is no major difference between the primary Au-Pd bimetallic particle sizes on different supports, which mainly fall in the 3.0nm to 6.0nm size range. This is to be expected as all the metal particles were derived from the same AuPd colloid preparation. Thus, the difference in the reactivity is because of the acidity/basicity of the support and not because of any particle size differences of the catalysts tested. A mechanistic proposal will also be presented.

References.

1. S. Meenakshisundaram, E. Nowicka, P. J. Miedziak, G. L. Brett, R. L. Jenkins, N. Dimitratos, S. H. Taylor, D. W. Knight, D. Bethell and G. J. Hutchings, *Faraday Discussion*, **145**, 341 (2010)
2. M. Sankar, E. Nowicka, R. Tiruvalam, Q. He, S. H. Taylor, C. J. Kiely, D. Bethell, D. W. Knight, and G. J. Hutchings, *Chemistry A European Journal*, **In press** (2011).