

## Applying tri-metallic catalysts to improve oxidation reactions

Peter J Miedziak<sup>1\*</sup>, Qian He<sup>2\*</sup>, Nikolaos Dimitratos<sup>1</sup>, Jennifer K. Edwards<sup>1</sup>, Stuart H. Taylor<sup>1</sup>, Christopher J. Kiely<sup>2</sup> and Graham J. Hutchings<sup>1</sup>

<sup>1</sup> Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Main Building, Park Place, Cardiff, CF10 3AT, UK

<sup>2</sup> Department of Materials Science and Engineering, Lehigh University, 5 East Packer Avenue, Bethlehem, Pennsylvania, PA 18015, USA.

\*corresponding author: miedziakpj@cf.ac.uk

### Introduction

The oxidation of alcohols to aldehydes is an industrially important process. Conventionally these reactions are carried out using expensive and toxic oxidants such as chromate or permanganate, causing serious environmental and economic concerns. The catalytic oxidation of alcohols to aldehydes and acids using molecular oxygen/air is an attractive alternative. We have previously demonstrated that Au-Pd bimetallic nanoparticles can be very active for the alcohol oxidation reaction, and provide high selectivity toward aldehydes even under solvent-free reaction conditions[1]. In this report to achieve high selectivity towards aldehyde, either a low reaction temperature approach was chosen, resulting in a low turnover frequency (TOF), or the conversion was kept at a low level. We now demonstrate that by adding a small amount of Pt to these Au-Pd catalysts we can improve the selectivity in benzyl alcohol oxidation and improve the activity for both glycerol oxidation and the direct synthesis of hydrogen peroxide.

### Materials and Methods

The Au-Pd and Au-Pd-Pt catalysts were prepared using the sol immobilization method[2]. Benzyl alcohol oxidation was carried out in a stirred reactor (100 mL, Parr reactor). The vessel was charged with alcohol (40 mL) and catalyst (0.05 g). The autoclave was then purged 5 times with oxygen leaving the vessel at 10 bar gauge. The stirrer was set at 1500 r.p.m. and the reaction mixture was raised to the required temperature. Samples from the reactor were taken periodically *via* a sampling system. Analysis of the products was carried out by GC (Varian star 3400 cx with a 30 m CP-Wax 52 CB column)

### Results and Discussion

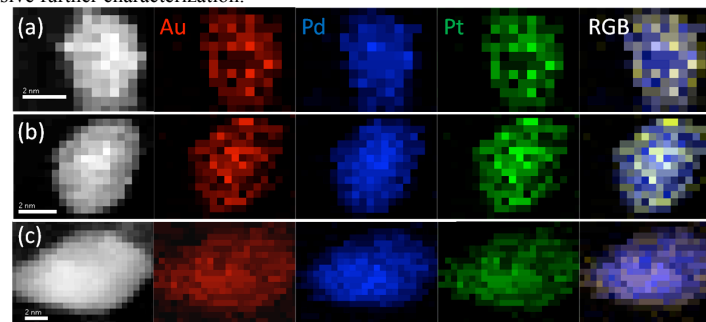
Benzyl alcohol conversion and product selectivity is given in **Table 1**.

**Table 1.** Activity and selectivity for various bi and tri-metallic catalysts.

Catalyst	C (%)	Selectivity (%)				
		Tol	Ald	Acid	Ate	TOF /h <sup>-1</sup> <sup>b</sup>
1wt% (0.5Au+0.5Pd)/C	80.7	3.4	67.0	23.1	6.5	63800
1wt% (0.3Au+0.4Pd+0.3Pt)/C	35.4	0.9	83.3	7.9	7.9	16000
1wt% (0.4Au+0.4Pd+0.2Pt)/C	36.7	0.6	81.7	8.0	9.7	22100
1wt% (0.45Au+0.45Pd+0.1Pt)/C	53.9	0.1	80.2	13.1	6.6	31900

Tol=Toluene, Ald = Benzaldehyde, Acid = Benzoic Acid, Ate = benzylbenzoate

The data shows that the addition of a small amount of Pt can significantly enhance the selectivity of benzaldehyde in the solvent-free oxidation of benzyl alcohol reaction, while still maintaining a high alcohol conversion. Hydrogen peroxide synthesis data shows a large improvement in the rate of formation whilst glycerol oxidation data shows that the platinum containing catalysts can facilitate the removal of sacrificial base from the reaction. This data in combination with the benzyl alcohol oxidation results indicates that the platinum is having an effect similar to the use of basic supports such as MgO that we have previously reported for these reactions[3]. STEM analysis of the 0.3Au-0.4Pd-0.3Pt sample is shown in **Figure 1**, this indicates that the metals are present as homogeneous alloys at this ratio which is supported by extensive further characterization.



**Figure 1.** STEM-XEDS spectrum image analysis of the 1wt% (0.3Au-0.4Pd-0.3Pt)/C. The first column shows HAADF images from representative particles that are (a) ~3 nm, (b) ~5 nm, and (c) ~10 nm in size. The scale bar represents 2 nm. Significance

### Significance

The addition of platinum to gold-palladium catalysts can lead to a significant improvement in either the selectivity or activity, dependent on the reaction system studied. Beneficial effects are reported for the oxidation of benzyl alcohol, the oxidation of glycerol and the direct synthesis of hydrogen peroxide. The exact nature of the metal nanoparticles is not fully understood due to the difficulty distinguishing between gold and platinum however various characterization techniques suggest they are homogeneous alloys.

### References

- [1] D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzing, M. Watanabe, C.J. Kiely, D.W. Knight, G.J. Hutchings, *Science (Washington, DC, U. S.)* **2006**, *311*, 362.
- [2] J.A. Lopez-Sanchez, N. Dimitratos, P. Miedziak, E. Ntainjua, J.K. Edwards, D. Morgan, A.F. Carley, R. Tiruvalam, C.J. Kiely, G.J. Hutchings, *Physical Chemistry Chemical Physics* **2008**, *10*, 1921.
- [3] G.L. Brett, Q. He, C. Hammond, P.J. Miedziak, N. Dimitratos, M. Sankar, A.A. Herzing, M. Conte, J.A. Lopez-Sanchez, C.J. Kiely, D.W. Knight, S.H. Taylor, G.J. Hutchings, *Angewandte Chemie - International Edition*, **2011**, *50*, 10136.