Highly Active Gold and Gold-Palladium Catalysts Prepared by Colloidal Methods in the Absence of Polymer Stabilizers

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Abstract: Supported gold and gold-palladium nanoparticles are effective catalysts for the selective oxidation of glycerol and benzyl alcohol. Catalytic properties and stability are often sensitive to factors such as the dimensions, shape and composition of the metal nanoparticles. Although colloidal methods provide an easy and quick way to synthesize supported metal catalysts, they typically involve using polymers such as polyvinyl alcohol (PVA) or polyvinylpyrrolidone (PVP) as steric stabilizers, which can sometimes be detrimental in subsequent catalytic reactions. Here we report the synthesis of supported gold and gold-palladium nanoparticles without the addition of stabilizing polymers. The catalysts prepared with and without the addition of polymers performed very similarly in the selective oxidation of glycerol and benzyl alcohol suggesting that polymers are not essential to make active catalysts for these reactions. Thus, this new stabilizer free method provides a facile and highly effective way of circumventing the inherent problems of polymer stabilizers when preparing gold and gold palladium catalysts.

Supported gold and gold-palladium nanoparticles are exceptionally effective catalysts for selective oxidation.[1-5] Structural properties of these catalysts (*i.e.,* particle size, composition, oxidation state) have a significant influence on catalytic activity, selectivity and stability.[6-10] Therefore, an important objective is to control these parameters in order to synthesise effective catalysts. The generation of colloidal metal sols typically involves polymer additives as particle stabilizers.[10-13] It is well recognised that ligand stabilization of the colloidal metal sol is a crucial step in order to produce small metal nanoparticles with a narrow particle size distribution.[11] In many examples, the presence of polymer ligands such as polyvinylpyrrolydone (PVP) or polyvinylalcohol (PVA) are necessary to prevent agglomeration of particles, and hence an overall increase in mean particle size, during the preparation procedure.[14] However, the presence of these polymer ligands can lead to several disadvantages in catalytic applications, since they can partially or completely block the access of reactant molecules to the metal surface, thereby decreasing the catalyst activity.[15] Refluxing the catalysts in water to remove water soluble polymers has been shown to be an effective way to increase catalytic activity for gas phase reactions, while calcination treatments to combust the protective polymer ligands can result in an increase in the mean particle size and carbon deposition.[10, 16] It has recently been reported by Deradet *et al.* that it is possible to prepare dilute stable colloidal solutions of Au with a mean particle diameter of 3.2 nm without the addition of

polymers.[17] The stabilization effect is provided by anionic $(BR_4)^-$ species (where R = H or OH) that originate from the hydrolysis of the reducing agent $(NaBH_4)$ present in the solution, in addition to chloride anions from the metal precursors. These anions when adsorbed onto the Au surface provide a degree of electrostatic stabilization to the nanoparticles.[18] The resultant colloidal gold sol was reported to be an active homogeneous catalyst for the reduction of 4-nitrophenol to 4-nitroaniline. However, the main issue of synthesising and utilising metal colloids without stabilizers is their long-term stability and resistance to sintering. Herein we describe the synthesis of TiO_2 supported Au and Au-Pd nanoparticles by a variant of the sol-immobilisation method previously reported in the literature, in which polymers were not added to act as steric stabilizers. The catalysts were investigated for the selective oxidation of glycerol and benzyl alcohol, as they have been previously shown to be active for these reactions.[19-21] The catalytic activities, selectivities and physical characteristics of the stabilizer free (SF) materials are compared to those of catalysts prepared by conventional methods using PVA and PVP.

Colloidal solutions were prepared by reducing aqueous solutions of Au or Au-Pd precursors with $NaBH_4$ either in the presence of PVA, PVP or under stabilizer free (SF) conditions. After 30 min of colloid generation the nanoparticles were immobilised by the addition of TiO_2 and acidification with H_2SO_4 before being filtered, washed and dried. Glycerol oxidation was studied in the presence of base for the monometallic stabilizer free (SF) 1% wt Au/TiO_2 material and the counterpart catalysts that use either PVA or PVP as a polymer stabilizer.
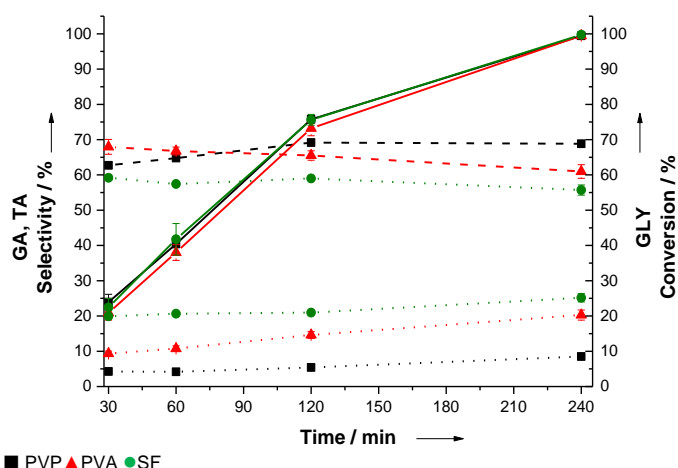

Figure 1. Comparison of the glycerol oxidation activity for sol-immobilised monometallic 1% Au / TiO_2 catalysts prepared either stabilizer free (SF), or in the presence of PVA or PVP ligands. *Key*: Bold lines - glycerol (GLY) conversion; dotted lines - tartronate (TA) selectivity; dashed lines - glycerate (GA) selectivity. *Reaction conditions*: 110 mg catalyst, 60 °C, 3 bar O2, 1200 rpm, GLY/Au=500:1(mol), NaOH/GLY=2:1 (mol), total volume 10 mL.

Figure 1 shows that complete glycerol conversion was achieved after 4 h for all the three variants (PVA, PVP and SF) of monometallic Au/TiO_2 catalysts with similar conversion versus

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time-on-line profiles. The main products obtained were glycerate (GA) and tartronate (TA) with a combined selectivity typically above 70%. The remaining 30% comprised minor products such as oxalate, lactate, glycolate, formate and acetate. Overall, the product distribution was broadly similar for all three catalysts. During the course of the reaction, the selectivity towards GA and TA remained constant for all three catalysts tested, indicating that they were relatively stable to further oxidation under the reaction conditions employed in the presence of glycerol. This also suggests that GA and TA are both produced as primary oxidation products and that TA is not predominantly generated via a consecutive oxidation pathway. This hypothesis was confirmed by performing experiments under identical conditions, but with GA as the starting material, using the Au/TiO$_2$ catalysts prepared with PVA and SF (Figure S1). These experiments show that GA oxidation was three-to-four times slower than glycerol oxidation, indicating that the relative stability of GA and TA in the glycerol oxidation reaction is due either to lower relative reaction rates or competitive adsorption of glycerol and GA. A comparison of the activity for glycerol oxidation of the monometallic catalysts synthesized with and without polymeric stabilizing ligands showed no significant difference in conversion, implying that polymer stabilizers are not necessary to produce highly active catalysts. Comparing the selectivity towards the major products, a 10-15% difference in the selectivity towards TA and GA was observed between the SF and the PVA/PVP stabilized catalysts. The selectivity at iso-conversion throughout the reaction towards TA followed the order SF > PVA > PVP, while the opposite trend was observed for selectivity towards GA. This suggests that the nature and presence of the polymer can alter reaction selectivity through either particle size effects or by partial ligand coverage of the active surface of the nanoparticles.

Figure 2 presents catalytic results from the comparable set of bimetallic 1% wt Au-Pd/TiO$_2$ sol-immobilised materials for glycerol oxidation. Again, all three catalyst variants (PVA, PVP and SF) showed similar reaction profiles in terms of glycerol conversion indicating that the presence of a polymer during the preparation of the catalyst is not required to achieve high catalytic activity, with full conversion being reached after 2 h of reaction. The trends in selectivity were not as pronounced as those observed for the corresponding monometallic Au catalysts at short reaction times. At reaction times exceeding 120 min, GA selectivity decreased with a concurrent increase in TA selectivity. It is also worth noting that in this case, further oxidation of GA could occur when glycerol was no longer available in the reaction mixture, in contrast to the situation found for monometallic Au catalysts. Figure S1 also contains results of GA oxidation with Au-Pd/TiO$_2$ samples prepared with PVA and SF. These bimetallic materials showed higher reaction rates towards GA oxidation than the corresponding monometallic counterparts. In common with the monometallic Au catalysts, no further oxidation of GA was observed during glycerol oxidation while non reacted glycerol is still present in the reaction mixture; however, in the case of both Au-Pd materials, further oxidation did occur when 100% glycerol conversion was reached with the Au-Pd (SF)/TiO$_2$ catalyst having a higher GA oxidation activity than the Au (PVA)/TiO$_2$ variant. These results suggest that the

preparation of Au-Pd catalysts without the addition of stabilizing polymers ligands results in materials with similar catalytic performance to those prepared in the presence of PVA or PVP for the selective oxidation of glycerol. To further confirm the similarity of the PVA and SF variants of the bimetallic materials, the catalytic activity for benzyl alcohol oxidation was also investigated. Figure 3 demonstrates that the PVA and SF variants of the Au-Pd catalysts had very similar reaction profiles in terms of benzyl alcohol conversion and selectivity towards benzaldehyde and toluene. Once again, there was no substantial difference in the catalytic activity and selectivity performance for the two catalysts implying that the materials are similar irrespective of the presence or absence of the polymer stabilizer during the initial colloid preparation.
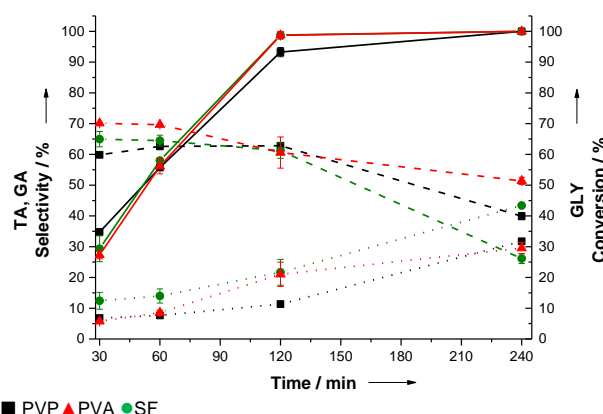

Figure 2. Comparison of the glycerol oxidation activity for sol-immobilised bimetallic 1% Au-Pd/TiO$_2$ catalysts samples synthesized either with PVA/PVP stabilizer addition or under stabilizer-free conditions. *Key*: Bold lines - glycerol (GLY) conversion; dotted lines - tartronate (TA) selectivity; dashed lines - glycerate (GA) selectivity. *Reaction conditions*: 110 mg catalyst, 60 °C, 3 bar O2, 1200 rpm, GLY/Au=500:1(mol), NaOH/GLY=2:1 (mol), total volume 10 mL.
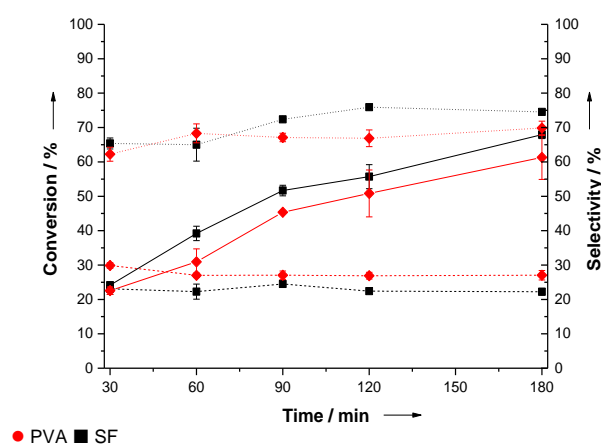

Figure 3 – Comparison of PVA and stabilizer free (SF) 1% Au-Pd / TiO$_2$ catalysts for the solvent-free oxidation of benzyl alcohol. *Key:* Bold lines - benzyl alcohol (BnOH) conversion; dotted lines - benzaldehyde (BnCHO) selectivity; dashed lines - =toluene (Tol) selectivity. *Reaction conditions*: 20 mg catalyst, BnOH/metals= 28000 (mol), 120 °C, 1 bar O2, 1000 rpm. To

elucidate any structural differences of the SF materials with their PVA or PVP variants, electron microscopy studies were performed on the unused materials. The particle size distributions, after immobilisation on the TiO_2 support, as determined from bright field TEM micrographs of the monometallic Au catalysts prepared by the SF, PVA and PVP methods are shown in Figures 4 and S2. Comparisons of the particle size distributions in Figure 4 show that materials prepared with polymer addition tend to have a narrower particle size distribution and lower mean particle size (PVA: 2.7 ± 0.6 nm; PVP: 3.5 ± 1 nm) than the stabilizer free sample (5.4 ± 1.6 nm). Analysis of the particle size distributions of the bimetallic Au-Pd catalysts prepared by the SF, PVA and PVP methods (also shown in Figure 4) indicate a similar trend in particle size distributions and mean particle size (PVA: 3.2 ± 1 nm; PVP: 3.0 ± 1.2 nm; SF: 3.9 ± 1.3 nm). The structures of supported nanoparticles in the 1% Au/TiO_2 (Figure 5 (a, b)) and 1% Au-Pd/TiO_2 (Figure 5 (c, d)) catalysts prepared by SF methods were also studied using aberration corrected scanning transmission electron microscopy (AC-STEM). The results did not show any significant variations in metal particle morphology or metal support interaction compared to catalysts prepared with PVA and PVP polymers as reported in our previous studies.[22] For the bimetallic 1% Au-Pd/TiO_2 SF catalyst, the nanoparticles were found to be alloyed as expected, as confirmed by X-ray energy dispersive spectroscopy (X-EDS) (Figure 5(d)).
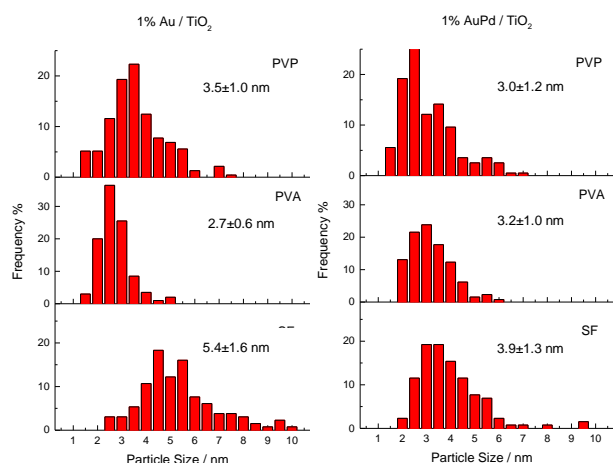

Figure 4 – Particle size distributions derived from bright field TEM images of more than 100 monometallic Au or bimetallic Au-Pd particles prepared either stabilizer free, or with PVA and PVP ligands present.

Although having a slightly larger mean size and a broader particle size distribution, the catalysts prepared using the SF route perform in a very similar manner to their counterparts prepared with PVA or PVP. This suggests that while the catalysts prepared with stabilisers have a higher number of surface Au or Pd atoms the glycerol oxidation reaction rate is not proportional to this alone. In fact the activity of these catalysts is determined by the balance between optimum particle size and the availability of the nanoparticles to carry out the reaction. Previous studies[23] have demonstrated that catalysts with particle size around 5 nm were in fact more active than analogous catalysts with smaller mean particle

size despite lower amounts of surface Au which could suggest that the smaller particles formed when using PVA are not as effective in this reaction despite the increase in surface Au or Pd. The higher overall selectivity towards TA displayed by the SF-type materials also does not correlate with the measured mean particle size, suggesting that the stabilizing ligands in these catalysts do play some role in determining the selectivity to specific products.
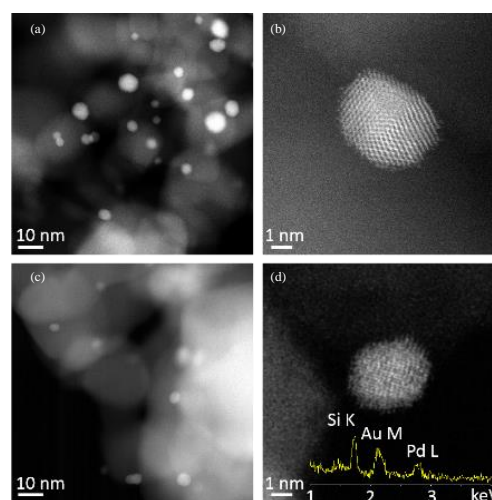

Figure 5 – Representative high angle annular dark field (HAADF) STEM images of (a, b) 1% Au/TiO_2 and (c, d) 1% Au-Pd/TiO_2 materials prepared via the stabilizer-free route. The inset in *(d)* shows the corresponding X-ray energy dispersive spectrum (XEDS) obtained from the particle imaged, indicating that it is a bimetallic alloy. The Si K signal is an artefact arising from internal fluorescence of the detector.

For the bimetallic 1% Au-Pd/TiO_2 catalysts, the results obtained for glycerol and benzyl alcohol oxidation reactions demonstrate that stabilizing ligands are not necessary in the sol-immobilisation synthesis method to produce materials that achieve high catalytic activity. For glycerol oxidation, selectivity profiles for the sol-immobilised Au-Pd catalysts operating at similar conversion levels, while not as pronounced as the monometallic Au catalysts, do still show that the SF variant has higher selectivity towards TA, in addition to an enhanced oxidation of the GA to TA after the glycerol has been consumed.

X-ray photoelectron spectroscopy (XPS) (Table 1) was carried out on all samples and confirmed the similarity of the sol-immobilised materials produced with and without the addition of polymer stabilizers. The binding energy of the Au (84.2-83.9 eV) indicates the presence of metallic Au in all of the monometallic samples as expected.[24] Analysis of the bimetallic catalysts indicated a similar Au : Pd surface ratio in all samples with the Pd being present in the metallic state as indicated by its binding energy (335.0 - 335.5 eV). To evaluate the effect of the polymer on the stability of the catalysts during reaction, both the monometallic and the bimetallic catalysts were re-used for glycerol oxidation and the catalytic results are shown in Table 1. Both monometallic and bimetallic catalysts prepared with PVP were shown to be

Table 1. Summary of physical characteristics determined by XPS and TEM analysis of monometallic Au and bimetallic Au-Pd sol-immobilised catalysts supported on TiO_2 prepared either under stabilizer free (SF) conditions, or in the presence of PVA or PVP ligands. Also presented are the corresponding catalyst re-usability measurements determined from repeated glycerol oxidation testing. The standard error in the glycerol oxidation conversion results is ± 3%.

Catalyst	Stabilizer Identity	Mean Particle Size (nm)	Au 4f binding energy. (eV)	Pd 3d binding energy (eV)	Au:Pd atomic ratio	Glycerol Conversion at 60 min 1st use (%)	Glycerol Conversion at 60 min 2nd use (%)
1% Au / TiO_2	SF	5.4	84.2	-	-	58	48
	PVA	2.7	84.2	-	-	52	45
	PVP	3.5	84.2	-	-	42	40
1% Au-Pd / TiO_2	SF	3.9	84.0	335.0	1.5	94	87
	PVA	3.0	84.0	335.5	1.4	95	89
	PVP	3.2	83.9	335.4	1.4	91	94

Reaction conditions for 1st test: 110 mg catalyst, 60 °C, 3 bar O_2, 1200 rpm, GLY/Au=500:1(mol), NaOH/GLY=2:1 (mol), total volume 10 mL. *Reaction conditions for re-usability test*: 60 mg catalyst, 60 °C, 3 bar O_2, 1200 rpm, GLY/Au=500:1(mol), NaOH/GLY=2:1 (mol), total volume 10 mL.

stable to re-use within experimental error. In contrast, catalysts prepared with PVA, which is known to be prone to removal from the metal surface in aqueous solutions at elevated temperatures[19], showed a decrease in conversion of around 6% for both the mono- and bi-metallic catalyst systems. Catalysts prepared via SF methods also showed a deactivation on re-use of around 10 % conversion in the monometallic case and 7% in the bimetallic case. While the degree of deactivation of the SF materials is greater than that observed for the catalysts prepared with stabilizers, their absence do not lead to excessive leaching of the metals from the TiO_2 as evidenced through analysis of the reaction mixture by MP-AES (Table S2).

In conclusion, we have shown that colloidal Au and Au-Pd sols can be stabilized on TiO_2 without the need for polymer additives and produce highly active supported catalysts for selective alcohol oxidation. It is, however, important that they are deposited onto a support within 30 min of their synthesis due to the particles being unstable in solution for extended times, as they typically precipitate out after 24 h. The materials that result from these SF preparations are very similar in activity and physical characteristics to those prepared with PVA or PVP polymer additives; however, they have a slightly larger mean particle size. Nevertheless, the absence of the polymer additives removes complications in terms of subsequent dissolution of the protective polymer into the reaction media and the blocking of potentially active surface sites to substrates during reactions. The results also suggest that the presence of the stabilizing ligands can also affect the selectivity to certain products in selective alcohol oxidation reactions while not markedly effecting the overall conversion levels.

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COMMUNICATION

Catalysis : Au Naturale – We show that the presence of polymer stabilisers is not necessary to produce catalysts that are highly active for the selective oxidation of glycerol and benzyl alcohol. Gold and gold palladium nanoparticles prepared in the absence of PVA and PVP stabilisers show identical activity to those prepared with stabilisers but crucially the polymer additives alter the reaction selectivity.

Stabiliser Free Catalysts
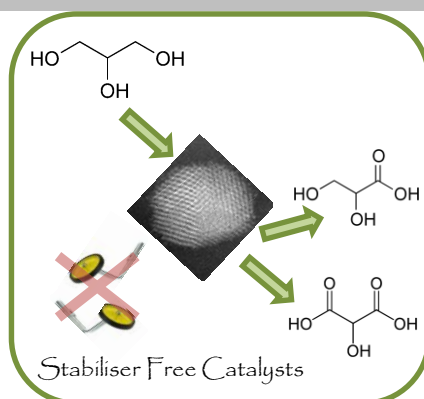
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