Gold-Nanoparticle-Based Catalysts for the Oxidative Esterification of 1,4-Butanediol into Dimethyl Succinate
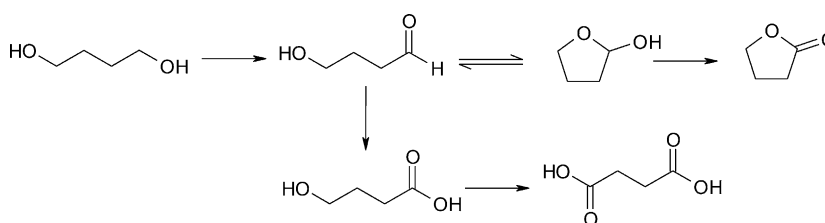
Gemma L. Brett,[a] Peter J. Miedziak,[a] Qian He,[b] David W. Knight,[a] Jennifer K. Edwards,[a] Stuart H. Taylor,[a] Christopher J. Kiely,[b] and Graham J. Hutchings*[a]

The oxidation of 1,4-butanediol and butyrolactone have been investigated by using supported gold, palladium and gold–palladium nanoparticles. The products of such reactions are valuable chemical intermediates and, for example, can present a viable pathway for the sustainable production of polymers. If both gold and palladium were present, a significant synergistic effect on the selective formation of dimethyl succinate was observed. The support played a significant role in the reaction, with magnesium hydroxide leading to the highest yield of dimethyl succinate. Based on structural characterisation of the fresh and used catalysts, it was determined that small gold–palladium nanoalloys supported on a basic $Mg(OH)_2$ support provided the best catalysts for this reaction.

Introduction

Recently, there has been considerable scientific interest in the liquid-phase oxidation of 1,4-butanediol into lactones. The primary use of these lactones is as intermediates in the synthesis of a variety of polymers, including *N*-methylpyrrolidone (NMP).[1] The product, γ-butyrolactone, is widely used in agriculture, in the synthesis of resins and fibres,[2] and in the petroleum industry, as well as a solvent.[3] The dehydrogenation of 1,4-butanediol is the traditional route to butyrolactone, and this transformation can be achieved by using copper-based catalysts at high temperatures.[4] Other methods for its production include the hydrogenation of maleic anhydride over nickel catalysts[5] and its isolation as an intermediate product in the hydrogenation of maleic esters. Huang et al. have suggested that the oxidation of 1,4-butanediol first proceeds through the formation of 4-hydroxybutanal and then through two alternative pathways: 1) through tetrahydrofuran-2-ol to afford γ-butyrolactone or 2) through 4-hydroxybutanoic acid to afford suc-

Scheme 1. Reaction pathway for the oxidation of 1,4-butanediol as reported by Huang et al.[3a]

cinic acid,[3a] as shown in Scheme 1. They showed that a range of gold-nanoparticle-based catalysts that were prepared by the deposition/precipitation method supported on iron oxide or titania displayed high conversions of 1,4-butanediol at 140 °C.[3b] However, disappointingly, these catalysts required very high gold loadings of 6–8%. Hence, there is a need to design improved catalysts with lower precious-metal content, which will enable a more-sustainable approach to making these important molecules.

Gold catalysts have been shown to be extremely active for oxidation reactions, in particular for hydrocarbons[6] and alcohols.[7] A number of preparation methods have been investigated, including impregnation,[8] deposition precipitation,[7b] physical mixing[9] and sol-immobilisation.[10] In general, sol-immobilisation methods lead to catalysts that are more active than other methods for the oxidation of alcohols, owing to the formation of small metal nanoparticles with a very narrow particle-size distribution.[11] Improvements in the activity and selectivity of gold catalysts for oxidation reactions can also be achieved by the addition of a second metal, such as palladium,[12] and this is an approach that we have exploited in this study.

The oxidation of alcohols in methanol with catalytic amounts of base represents a new route to value-added products from biomass. Industrially significant chemicals can be synthesised by using this method, in which the use of stoichiometric amounts of base are not required,[13] as is the case in

[a] Dr. G. L. Brett, Dr. P. J. Miedziak, Prof. D. W. Knight, Dr. J. K. Edwards,
    Dr. S. H. Taylor, Prof. G. J. Hutchings
    Cardiff Catalysis Institute, School of Chemistry
    Cardiff University
    Main Building, Park Place, Cardiff, CF10 3AT (UK)
    E-mail: hutch@cardiff.ac.uk

[b] Dr. Q. He, Prof. C. J. Kiely
    Department of Materials Science and Engineering
    Lehigh University
    5 East Packer Avenue, Bethlehem, PA 18015-3195 (USA)

some aqueous-phase oxidation reactions.[14] Hayashi et al.[15] performed the oxidations of ethanol, 1-propanol, 1-butanol, allyl alcohol, diethylene glycol, methallyl alcohol, ethylene glycol and 1,3-propanediol by using methanol as the solvent to produce various esters. They compared metal-oxide-supported (Al/SiO$_2$[16] and alumina[17]) gold, palladium and ruthenium catalysts for the oxidative esterification of ethylene glycol. The reaction products were methyl glycolate and methyl formate. The gold catalyst was superior to the other catalysts that were studied, displaying both the highest conversion of ethylene glycol and the highest selectivity for methyl glycolate. Interestingly, for the diols of ethylene glycol and 1,3-propanediol, only one hydroxyl group was reactive towards oxidative esterification. It was hypothesised that the reaction proceeded through a hemiacetal and that the rate-determining step, as in aqueous-phase oxidation reactions, was the removal of a hydrogen atom from a hydroxy group. This effect was also observed by Taarning et al.[18] Nielsen et al.[19] investigated the oxidation of primary alcohols in methanol. A gold catalyst was chosen, and the effect of pH value was studied. They found that the addition of acid was detrimental to the conversion of 1-hexanol, whereas the addition of a base, NaOCH$_3$, increased the rate of conversion of 1-hexanol and, hence, the yield of methyl hexanoate. Further work on the oxidative esterification of glycerol indicated that the reaction could be performed under base-free conditions and that the nature of the support played a critical role in the reaction selectivity.[20] Although the oxidation of 1,3-propanediol was very selective, as observed by Hayashi et al.,[15] only one hydroxy group was oxidised into methyl-3-hydroxypropionate with 90% selectivity. The other observed products were dimethyl malonate and methyl acrylate. Again, the first step in the reaction was the formation of an aldehyde, in this case 3-hydroxypropanal. Homogeneous catalysts have been successfully employed for oxidising both hydroxy groups of 1,8-octanediol, 1,9-nonanediol and 1,12-dodecandiol.[21] An iridium complex and 2-(methylamino)ethanol (MAE) were utilised to achieve 55% selectivity for the monoesters and 45% selectivity for the diesters of these diols. The diols were reacted with catalysts [(CpIrCl$_2$)$_2$] (Cp=cyclopentadiene) and MAE in acetone and methanol at room temperature for 24 h.

Herein, we report the utilisation of gold-containing supported catalysts, which were synthesised by both impregnation and sol-immobilisation methods, for the oxidative esterification of 1,4-butanediol and butyrolactone into dimethyl succinate at significantly lower catalyst loadings than previously reported. This product has important applications in the synthesis of pharmaceuticals, agrochemicals and perfumes. A major aim of this study was to further probe the behaviour of α,γ-diols, shorter-chained analogues (C$_2$ and C$_3$) which have been shown to be inactive for the oxidation of the second hydroxy group. The role of the support, the catalyst-preparation method and the Au/Pd ratio were investigated in detail. The use of a Mg(OH)$_2$ support for the nanoparticles facilitated the

esterification of both hydroxy functional groups of 1,4-butanediol, which represents a significant advance in this type of catalysis. We further discuss the stability of these catalysts under the optimised reaction conditions.

Results and Discussion

Supported gold catalysts were tested in the oxidative esterification of 1,4-butanediol in methanol at 40–60 °C in a low-pressure glass reactor. Under our reaction conditions, the oxidation of 1,4-butanediol in methanol was observed to proceed following the sequential pathway outlined in Scheme 2. In this process, the primary product is either formed by the intramolecular dehydration of 4-hydroxybutanoic acid or, as stated above, from the very first oxidation product, 4-hydroxybutanal; 4-hydroxybutanal is in equilibrium with its cyclic hemiacetal form, 2-hydroxytetrahydrofuran, which could be oxidised directly into butyrolactone (GBL). Subsequently, butyrolactone reacts through a ring-opening esterification reaction with methanol to afford methyl-4-hydroxybutyrate (MHB), which is further oxidised into dimethyl succinate (DMS). The role of base in other alcohol-oxidation reactions is to activate the primary hydroxy group to facilitate oxidation.

The effect of the support on activity has been discussed in many gold-catalysed reactions, and carbon and titania supports in particular have been shown to be highly active and selective for oxidation reactions under aqueous conditions.[14, 15, 22] Ceria-supported gold catalysts have also been shown to be the most selective for the oxidative esterification of 1,2-propanediol[13] and they are also active for other alcohol-oxidation reactions.[23] Thus, gold supported on carbon, titania and ceria were prepared by using the sol-immobilisation method. This synthesis route was selected because it has previously been shown to give excellent size control of the gold nanoparticles.[11c] The catalysts were tested in the oxidative esterification of 1,4-butanediol under mild conditions of 40 °C in a glass reactor at 3 bar O$_2$ (Table 1). Under these conditions, the ceria-supported catalyst was more active, with 36% conversion after 24 h compared to about 16% on both carbon and titania. Of all the supports that we investigated, ceria was also the most selective for succinate; however, all of the catalysts tested showed relatively low selectivities for succinate. The reaction temperature was increased to 60 °C for the gold on a titania catalyst, which led to an approximate doubling of the conversion of 1,4-butanediol, but did not significantly increase the selectivity for succinate.

Owing to the low selectivities for succinate in the initial reactions with 1,4-butanediol, a series of additional experiments were performed that focused on the reactivity of the intermediate product, butyrolactone. The conversion of butyrolactone into methyl-4-hydroxybutyrate and, subsequently, di-
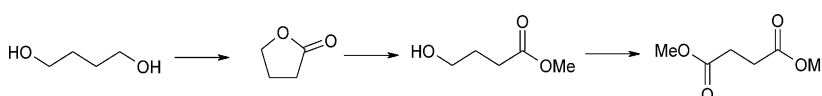
Scheme 2. Proposed reaction pathway for the oxidation of 1,4-butanediol in methanol.

Table 1. Effect of the catalyst support on the oxidative esterification of 1,4-butanediol by Au nanoparticles that were prepared by using the sol-immobilisation method.[a]

Catalyst	t [h]	T [°C]	Conversion [%]	Selectivity [%]		
				GBL	MHB	DMS
1%Au/C	24	40	17.6	93.1	5.3	1.6
1%Au/C	48	40	29.3	95.2	3.0	1.8
1%Au/CeO$_2$	24	40	35.9	93.6	4.4	2.0
1%Au/CeO$_2$	48	40	42.4	93.7	4.2	2.1
1%Au/TiO$_2$	24	40	15.8	97.3	1.6	1.1
1%Au/TiO$_2$	48	40	21.5	96.6	2.0	1.3
1%Au/TiO$_2$	24	60	28.0	92.8	5.8	1.5
1%Au/TiO$_2$	48	60	41.7	90.5	7.4	2.1

[a] Substrate/metal = 500:1, substrate/NaOMe = 5:1, 100 °C, $P(O_2)$ = 3 bar, 24 h.

methyl succinate should be feasible because the initial conversion into methyl-4-hydroxybutyrate proceeds through a facile ring-opening esterification reaction. The temperature of the reaction was selected to be 60 °C because the conversion of 1,4-butanediol was significantly higher at this temperature. Mg(OH)$_2$ was also included as a support because it has previously been demonstrated to be active for alcohol oxidation under base-free conditions.[24] In this case, MgO was used as the support, but this would undoubtedly become hydrated under the catalyst-preparation conditions to form Mg(OH)$_2$, as determined by XRD (see the Supporting Information, Figure S1). The results of these tests are summarised in Table 2.

Increasing the reaction temperature and changing the substrate did not lead to significant increases in terms of succinate selectivity on most of the supports; however, there was an increase in succinate selectivity on the ceria-supported catalyst. Monometallic palladium catalysts have previously been shown to be active for the oxidation of diols;[22c] thus, a series of analogous palladium catalysts were prepared and tested under the same conditions (Table 2). In general, the conversions were

higher than those with the gold catalysts and there was a significant increase in the selectivity for the succinate on the titania- and magnesium-hydroxide-supported catalysts (about 6% and 16%, respectively). The addition of palladium to gold to form alloy catalysts has also been reported to afford considerably enhanced activity;[11b,c] therefore, we also synthesised bimetallic catalysts. Although there was no observable synergistic effect from combining these metals on the reaction conversion, there was a considerable enhancement in the succinate selectivity (Table 2). The only exception to this trend was the ceria-supported catalyst, which showed almost-identical performance to the monometallic palladium catalyst.

Because the magnesium-hydroxide-supported catalyst showed the highest selectivity for succinate of all the catalysts that were tested, the Au/Pd ratio was systematically investigated to identify the optimum catalyst composition (Table 3).

Table 3. Effect of the metal/support combination on the oxidation of butyrolactone with catalysts that were prepared by using the sol-immobilisation method.[a]

Au/Pd ratio	Conversion [%]	Selectivity [%]	
		MHB	DMS
1:0	19.0	96.7	0.6
3:1	24.0	94.4	5.5
2:1	27.6	84.7	15.2
1:1	39.9	66.2	33.7
1:2	39.5	69.0	26.0
1:3	36.5	87.3	12.1
0:1	31.5	94.4	4.4

[a] Substrate/metal = 500:1, substrate/NaOMe = 5:1, 100 °C, $P(O_2)$ = 3 bar, 60 °C, 24 h, 1 wt.% metal/Mg(OH)$_2$.

Following the observed pattern of activity for the monometallic catalysts, the more-gold-rich catalyst formulations showed lower conversions than the more-palladium-rich materials. The highest conversion of butyrolactone and selectivity for succinate were achieved by using a Au/Pd catalyst with a 1:1 molar ratio.

This same general trend in conversion with composition has previously been shown for the oxidation of octan-1-ol in methanol[26] and the solvent-free oxidation of benzyl alcohol.[12d] The MgO support itself facilitated the ring-opening of butyrolactone in 18% conversion after 0.5 h; however, no dimethyl succinate was observed. The blank reaction showed less than 1% conversion under the same conditions.

The optimised magnesium-oxide-supported AuPd catalyst (1:1 molar ratio) was also tested for its reusability. The catalyst was used once for either 2 or 4 h at 60 °C, recovered and retested under the same conditions. Interestingly, as shown in Table 4, the re-use of the catalysts had almost no effect on the conversion, but the selectivity for succinate significantly decreased. This result implies that the different steps in the reaction are catalysed by different active species and that these different species have different stabilities under the reaction conditions employed.

Table 2. Effect of the metal/support combination on the oxidation of butyrolactone with catalysts that were prepared by using the sol-immobilisation method.[a]

Catalyst	Conversion [%]	Selectivity [%]	
		MHB	DMS
1%Au/C	24.6	97.1	0.5
1%Au/CeO$_2$	28.8	94.9	3.1
1%Au/Mg(OH)$_2$	24.0	96.0	0.8
1%Au/TiO$_2$	19.0	96.5	0.6
1%Pd/C	32.0	98.0	2.0
1%Pd/CeO$_2$	43.3	98.6	0.3
1%Pd/Mg(OH)$_2$	36.0	89.9	6.0
1%Pd/TiO$_2$	42.2	83.9	15.7
0.5%Au0.5%Pd/CeO$_2$	42.9	98.0	0.3
0.5%Au0.5%Pd/Mg(OH)$_2$	38.1	68.6	27.2
0.5%Au0.5%Pd/TiO$_2$	49.3	77.1	20.7

[a] Substrate/metal = 500:1, substrate/NaOMe = 5:1, 100 °C, $P(O_2)$ = 3 bar, 60 °C, 24 h.

Table 4. Reusability of AuPd/Mg(OH)₂ in the oxidation of butyrolactone.[a]				
AuPd/MgO	t [h]	Conversion [%]	Selectivity [%] MHB	DMS
fresh	2	34.8	66.2	33.7
fresh	4	39.9	56.6	43.3
used once	2	35.5	93.6	6.1
used once	4	40.3	90.6	9.1

[a] Substrate/metal = 500:1, substrate/NaOMe = 5:1, 100 °C, $P(O_2)$ = 3 bar, 60 °C, 24 h. The catalysts were prepared by using the sol-immobilisation method with a 1:1 molar ratio of Au/Pd.

To try to elucidate the origin of this effect on the selectivity, we characterised the optimised MgO-supported sol immobilisation catalysts. Disappointingly, analysis of the surface compositions of the fresh and used catalysts by X-ray photoelectron spectroscopy was not feasible in this case because the binding energy for the dominant magnesium peak masked the signals from the supported AuPd nanoparticles. Therefore, we concentrated on STEM analysis on the fresh and used AuPd/MgO catalyst samples.

Figure 1a and b show a high-angle annular dark field (HAADF) image and the corresponding particle-size distribution of the fresh catalyst. The mean particle size was 3.1 nm, and almost no particles larger than 8 nm were observed. STEM-XEDS (X-ray energy dispersive spectroscopy) analysis of individual particles showed that they were AuPd alloys (Figures 1c and d), with the smallest ones tending to be gold-rich. A STEM-HAADF image of the same catalyst material in a subsequent reaction is shown in Figure 2a.

It is clear that considerable sintering of the metal particles occurred during the reaction. However, despite this extensive

Figure 2. STEM-HAADF images of the used catalyst that was prepared through sol-immobilisation: a) Representative lower-magnification HAADF image, which shows that significant particle coarsening had occurred after 4 h of use. b) Representative higher-magnification HAADF image of a residual un-sintered nanoparticle and c) the corresponding XEDS spectrum.

restructuring, some small, gold-rich bimetallic AuPd particles remained (Figures 2b, and c). When these microstructural data are considered in conjunction with the activity data in Table 4, it is possible to draw a correlation between the number of small bimetallic AuPd particles that are present and the amount of succinate that is formed. We have previously shown that there was a size/composition dependence of the AuPd catalysts that were prepared through sol-immobilisation; the smallest particles tended to be more gold-rich, whereas the larger ones were consistently more palladium rich.[27]

This result suggests that the smaller gold-rich alloy particles are more active for the conversion of methyl-4-hydroxybutyrate into dimethyl succinate. However, because these nanoparticles did not seem to be particularly stable under our reaction conditions, we also prepared catalysts by using the impregnation and modified-impregnation methods. The results of testing these catalyst materials in the oxidation of butyrolactone are listed in Table 5.

The catalyst prepared through sol-immobilisation showed considerably higher selectivity for dimethyl succinate than either of the catalysts that were prepared by using the impregnation route. The standard catalyst prepared through impregnation showed the lowest activity, with a turn-over frequency (TOF) of 225 h⁻¹, compared with TOFs of 295 and 312 h⁻¹ for the catalysts prepared through sol-immobilisation and modified impregnation, respectively. It has previously been shown that catalysts that were prepared through impregnation were less active than those that were prepared through sol-immobilisation[11b,c] because catalysts prepared through impregnation tended to contain a significant population of larger metal particles (> 20 nm in size), which were thought to be less active
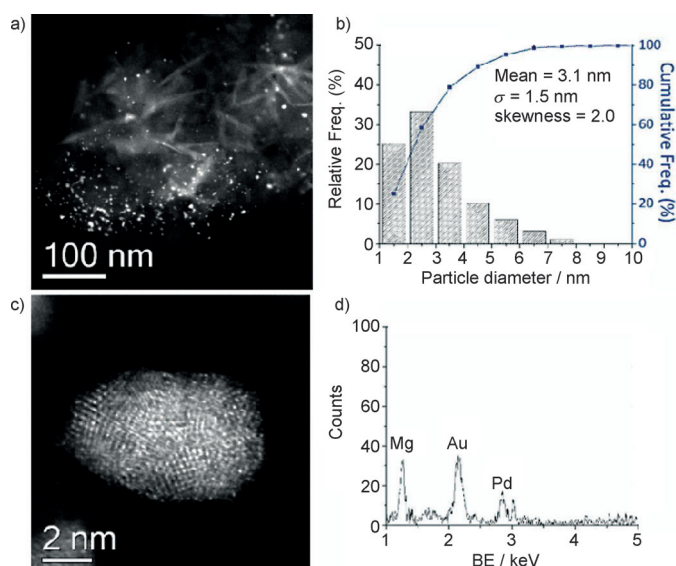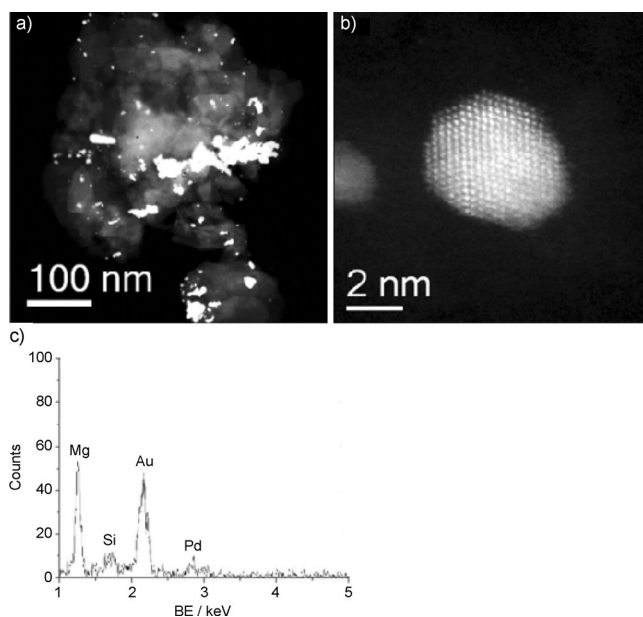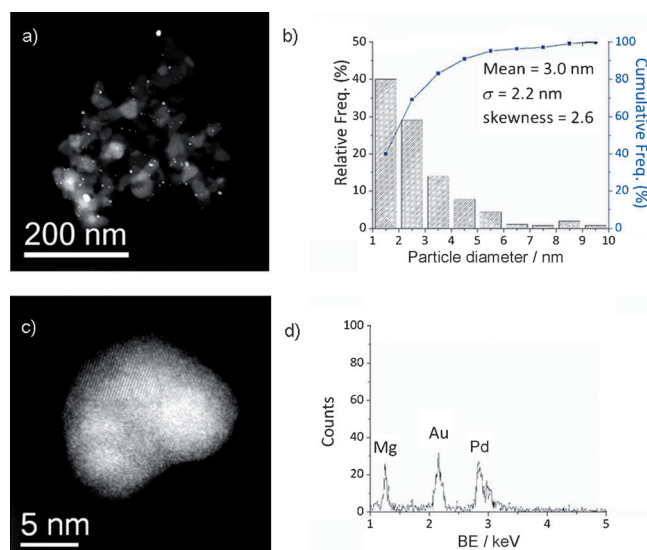

Figure 1. STEM-HAADF images of the fresh catalyst that was prepared through sol-immobilisation: a) Representative lower-magnification HAADF image and b) the corresponding particle-size distribution. c) Representative higher-magnification HAADF image of an individual nanoparticle and d) the corresponding XEDS spectrum.

Table 5. Effect of the preparation method on the oxidation of butyrolactone for various AuPd/Mg(OH)$_2$ and AuPd/MgO catalysts.[a]

Catalyst (molar ratio)	t [h]	Conversion [%]	Selectivity [%]		TOF [h^{-1}]
			MHB	DMS	
AuPd/MgO (1:1, I$_m$)	0.5	22.5	99.8	0.2	225
AuPd/MgO (1:1, I$_m$)	1.0	23.1	99.8	0.1	
AuPd/MgO (1:1, I$_m$)	2.0	26.6	99.8	0.1	
AuPd/MgO (1:1, I$_m$)	4.0	28.5	99.6	0.2	
AuPd/MgO (MI$_m$)	0.5	31.2	98.4	1.5	312
AuPd/MgO (MI$_m$)	1.0	34.3	97.4	2.2	
AuPd/MgO (MI$_m$)	2.0	36.8	97.2	2.5	
AuPd/MgO (MI$_m$)	4.0	37.6	96.4	3.3	
AuPd/Mg(OH)$_2$ (SI$_m$)	0.5	29.6	77.9	22.0	295
AuPd/Mg(OH)$_2$ (SI$_m$)	1.0	32.7	72.0	27.0	
AuPd/Mg(OH)$_2$ (SI$_m$)	2.0	34.8	66.2	33.7	
AuPd/Mg(OH)$_2$ (SI$_m$)	4.0	39.9	56.6	43.3	

[a] Substrate/metal = 500:1, substrate/NaOMe = 5:1, 100 °C, $P(O_2)$ = 3 bar, 60 °C, 24 h.

for oxidation reactions than the smaller alloy particles. STEM-HAADF imaging of the AuPd/MgO catalyst prepared by performing a modified impregnation (Figure 3 a and b) showed that it contained similar-sized bimetallic particles compared to the corresponding SI$_m$ material (mean sizes of 3.0 and 3.1 nm, respectively). STEM-XEDS analysis of individual particles in the catalysts that were prepared by performing modified impregnation also showed them to be AuPd alloys (Figures 3 c and d), but with compositions that were close to the nominally expected values. However, we have previously reported that the bimetallic nanoparticles present in the catalyst that was prepared through modified impregnation did not exhibit the same systematic size/composition variations that were inherent to the sol-immobilisation method.[8]

Figure 3. STEM-HAADF images of the fresh catalyst prepared by the modified impregnation method. a) Representative lower magnification HAADF image and b) the corresponding particle size distribution over the 1–10 nm range. c) Representative higher magnification HAADF image of an individual nanoparticle and d) its corresponding XEDS spectrum.

With this result in mind, it is interesting to note from the catalytic data shown in Table 5 that, despite the similar mean particle sizes, there are very significant differences between the selectivities for succinate, thus suggesting that not only are small particles required to perform the oxidation reaction, but also that these particles need to have a gold-rich composition. The catalysts prepared by using the conventional impregnation method had both the lowest activities and selectivities for succinate. The materials that were prepared through the conventional impregnation method have been extensively characterised elsewhere.[28] This synthesis route is known to generate catalysts with a bimodal particle-size distribution, with small Pd-rich particles within the range 2–10 nm and larger Au-rich particles (> 20 nm). Therefore, in this case, smaller alloy particles do not have the optimal Au-rich character that is needed to effectively catalyse this reaction.

Conclusions

We have performed a systematic investigation into the oxidations of 1,4-butanediol and butyrolactone and have shown that there is a significant synergistic effect to be gained in terms of the selectivity for dimethyl succinate by alloying gold and palladium. We have also shown that the support plays a significant role in the reaction, with magnesium oxide leading to the highest yield of dimethyl succinate.

This particular reaction nicely demonstrates the sensitivity of oxidation reactions towards the size and composition of the metal nanoparticles. The sol-immobilisation method produced the most-active catalyst for the oxidation of butyrolactone into dimethyl succinate; however, upon re-use, the selectivity profile of the products dramatically changed. STEM analysis revealed that significant sintering of the metal nanoparticles occurred under the reaction conditions for the sol-immobilisation-derived materials. Despite having a similar particle-size distribution to the sol-immobilisation-prepared catalyst, the catalysts synthesised by using the modified impregnation method did not have the same activity, possibly owing to the difference between the compositions of the smallest particles caused by the two different preparation methods.

To achieve high selectivity for succinate, we need to be able to prepare stable 3–5 nm bimetallic particles with a narrow particle-size distribution and precisely controlled composition, which we consider needs to be significantly gold-rich. We conclude that such catalysts would be significantly advantageous for oxidation reactions; however, at this stage, none of the preparation methods that we have investigated so far can provide all of three requirements simultaneously. Nevertheless, our work points out the direction that the alloy nanostructure/composition needs to be modified to design more-active catalysts for this type of reaction.

Experimental Section

Materials

1,4-butanediol (99%), methanol, sodium methoxide (30 wt.% in methanol) and all of the intermediates were purchased from Sigma–Aldrich. $NaBH_4$ (96%), polyvinyl alcohol (PVA; $M_W = 10\,000$, 98% hydrolysed), tetrakis(hydroxymethyl)phosphonium chloride (THPC, 80% aqueous solution) were purchased from Sigma–Aldrich. TiO_2 (P25) was purchased from Degussa; activated carbon Darco G60 and sodium hydroxide were purchased from Sigma–Aldrich. MgO was obtained from the Nanoscale Corporation. $PdCl_2$ and $HAuCl_4 \cdot 3 H_2O$ were purchased from Johnson Matthey. Pure oxygen (99.9%) was obtained from BOC. In addition, we contrasted the reactivity of our materials with those of standard gold catalysts prepared by the World Gold Council, which were comprised of 4.5%Au/Fe_2O_3 (Lot No. 02–04) and 1.5%Au/TiO_2 (Lot No. 02–9). The surface areas of the supports were as follows: CeO_2 (50 $m^2 g^{-1}$), activated carbon G60 (600 $m^2 g^{-1}$), MgO (600 $m^2 g^{-1}$) and P25 TiO_2 (35–65 $m^2 g^{-1}$).

Catalyst preparation

Gold, palladium and gold–palladium catalysts supported on carbon or titania were prepared by using a sol-immobilisation process (denoted SI_m) based on a $NaBH_4$/PVA colloidal method. The detailed experimental procedure for the synthesis of monometallic gold- and palladium-supported catalysts was described previously.[20] Briefly, for the bimetallic gold/palladium-supported catalyst, the following procedure was used: An aqueous solution of $PdCl_2$ and $HAuCl_4 \cdot 3 H_2O$ with the desired concentration was prepared and PVA (1 wt% solution) was added (PVA/metal = 1:2 w/w). Then, a freshly prepared 0.1 M solution of $NaBH_4$ ($NaBH_4$/metal, 5:1 mol/mol) was added to form a dark-brown sol. After 30 min of sol generation, the colloid was immobilised by adding activated carbon (acidified to pH 1 with sulfuric acid) under vigorous stirring. The amount of support material required was calculated to yield a total final-metal loading of 1 wt%. After 2 h, the slurry was filtered and the catalyst washed thoroughly with distilled water and dried at 120 °C for 16 h.

Impregnation methods

AuPd catalysts were prepared by using two different impregnation techniques: Method 1 utilised wet impregnation (denoted I_m). Palladium chloride (41.66 mg) was dissolved in an aqueous solution of chloroauric acid (4.08 mL of a 12.25 mg mL^{-1} solution). Then, the support (0.95 g) was added and the mixture was stirred and heated until a paste was formed. The catalyst was dried at 110 °C for 16 h. After this time, the catalyst was ground and calcined (400 °C, 3 h) at a ramp rate of 20 °C min^{-1}.

Method 2 was termed a modified impregnation process (denoted MI_m).[8] A bimetallic 0.5 mol%Au0.5 mol%Pd/MgO catalyst was prepared by using the following method. A round-bottomed flask (50 mL) was fitted with a magnetic stirrer bar and charged with chloroauric acid (5.6 mL of an 8.9 mg mL^{-1} solution) and an acidic solution of $PdCl_2$ (8.3 mL of a 6 mg mL^{-1} solution in a 0.58 M aqueous solution of HCl). The volume of the solution was adjusted by adding deionised water to a total volume of 16 mL. The solution was stirred vigorously (1000 rpm) and the temperature of the oil bath was raised from 27 to 60 °C over a period of 10 min. After this time, the MgO support was added (0.99 g) over a period of 8–10 min with constant stirring. After completion of the addition, the slurry was stirred at 60 °C for an additional 15 min. Then, the temperature of the oil bath was raised to 95 °C and the slurry was stirred at that temperature for 16 h. Subsequently, the solid powder was transferred into a mortar and was ground with a pestle thoroughly to form a uniform mixture. The catalyst was treated at 400 °C for 3 h under a steady flow of 5% H_2 in Ar at a ramp rate of 10 °C min^{-1}.

Catalyst characterisation

Samples for scanning transmission electron microscopy (STEM) analysis were prepared by dipping a holey carbon-coated copper TEM grid directly into the finely ground dry catalyst powder. HAADF imaging and XEDS were performed on an aberration-corrected JEOL 2200FS STEM operating at 200 kV.

Powder X-ray diffraction (XRD) patterns were acquired on an X'Pert PanAlytical diffractometer operating at 40 kV and 30 mA with CuK_α radiation. Analysis of the patterns was performed by using X'Pert HighScore Plus software for the full-pattern analysis and Specview software for the line-broadening analysis. Phases were identified by matching experimental patterns against those in the standard JCPDS database.

Catalyst testing

A Colover glass reactor (50 mL) was charged with the chosen alcohol (3 mM), methanol (0.37 M), sodium methoxide (0.6 mM) and catalyst (substrate/metal, 500:1 molar ratio). Then, the reactor was sealed, pressurised (3 bar O_2) and purged three times. The oxygen inlet was left open so that oxygen could be replenished as soon as it was consumed. Then, the reactor was heated to the required temperature and the stirrer speed was set to 1000 rpm. The reaction duration was 24 h. Samples were removed periodically and analysed by gas chromatography on a CP-wax column.

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