Glycerol Oxidation Using Gold-Containing Catalysts

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CONSPECTUS: Glycerol is an important byproduct of biodiesel production, and it is produced in significant amounts by transesterification of triglycerides with methanol. Due to the highly functionalized nature of glycerol, it is an important biochemical that can be utilized as a platform chemical for the production of high-added-value products. At present, research groups in academia and industry are exploring potential direct processes for the synthesis of useful potential chemicals using catalytic processes. Over the last 10 years, there has been huge development of potential catalytic processes using glycerol as the platform chemical.

One of the most common processes investigated so far is the catalytic oxidation of glycerol at mild conditions for the formation of valuable oxygenated compounds used in the chemical and pharmaceutical industry. The major challenges associated with the selective oxidation of glycerol are (i) the control of selectivity to the desired products, (ii) high activity and resistance to poisoning, and (iii) minimizing the usage of alkaline conditions. To address these challenges, the most common catalysts used for the oxidation of glycerol are based on supported metal nanoparticles. The first significant breakthrough was the successful utilization of supported gold nanoparticles for improving the selectivity to specific products, and the second was the utilization of supported bimetallic nanoparticles based on gold, palladium, and platinum for improving activity and controlling the selectivity to the desired products. Moreover, the utilization of base-free reaction conditions for the catalytic oxidation of glycerol has unlocked new pathways for the production of free-base products, which facilitates potential industrial application.

The advantages of using gold-based catalysts are the improvement of the catalyst lifetime, stability, and reusability, which are key factors for potential commercialization. In this Account, we discuss the advantages of the using supported gold-based nanoparticles, preparation methods for achieving highly active gold-based catalysts, and parameters such as particle size, morphology of the bimetallic particle, and metal−support interactions, which can influence activity and selectivity to the desired products.
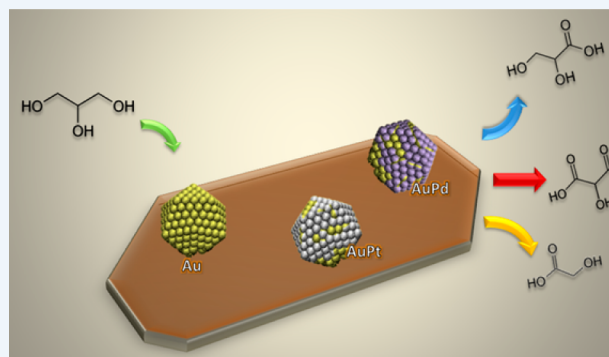
INTRODUCTION

Currently, the majority of important commodity chemicals and fuels are produced from fossil fuel resources, such as coal, petroleum, and natural gas.[1] The main disadvantage of fossil resource reserves is that they are nonrenewable, implying significant negative side effects for global economy and society, as well as enhancing global warming. Moreover, their rapid depletion leads to a significant increase of price of petrochemical products. In this respect, the search for alternative resources and the development of new processes for the production of fine chemicals and fuels become essential. One of the main alternative resources is biomass, which can be converted into fuel and fine chemicals. The main advantage of using biomass is its renewable nature: 75% of biomass consists of carbohydrates and 20% consists of lignins, with the remaining fraction consisting of fats, oils, proteins, terpens, and waxes.[2]

One of the main alternative biorenewable materials is triglycerides, which are the major component of animal fats, vegetable oils, waste grease, and oil-processing waste. These materials have recently been employed for the synthesis of biodiesel, one of the major alternatives to petroleum fuels. Its main advantages are that it is nonflammable and nontoxic, that it is safe for use in conventional diesel engines, and that it reduces emissions such as sulfur, smoke, and odors. Through improvements in fuel distribution infrastructure, together with some additional technological improvements for its production, biodiesel will soon be more economically viable and will therefore experience increased usage.

One of the main byproducts obtained during the production of biodiesel is glycerol, a highly functionalized biorenewable molecule.[3] The effective utilization of glycerol and its efficient conversion into various value added products will have a positive effect on the economics of biodiesel production, resulting in increased production and increased utilization of this alternative fuel resource. It is expected that the global demand for glycerol in terms of consumption volumes will increase from 2000 kt in 2011 to 3070 kt by 2018, with revenues expected to reach $2.1
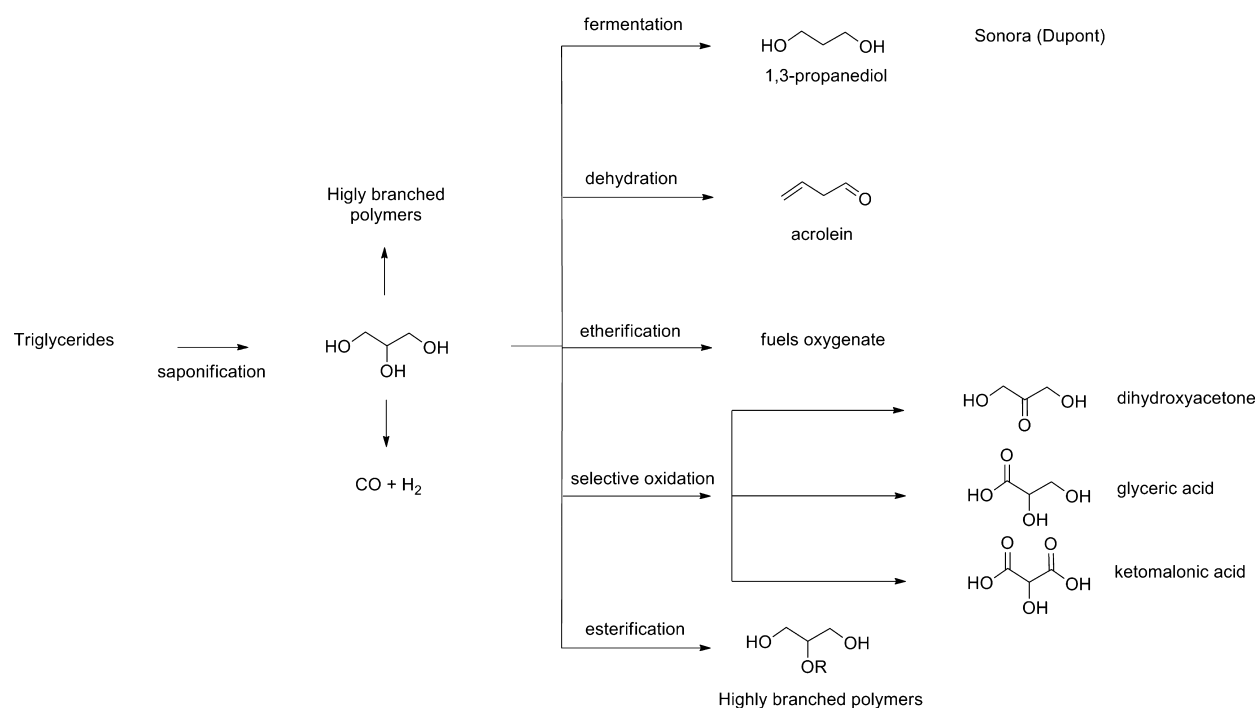
Figure 1. Main reaction pathways for the transformation of glycerol to commodity chemicals and fuels.
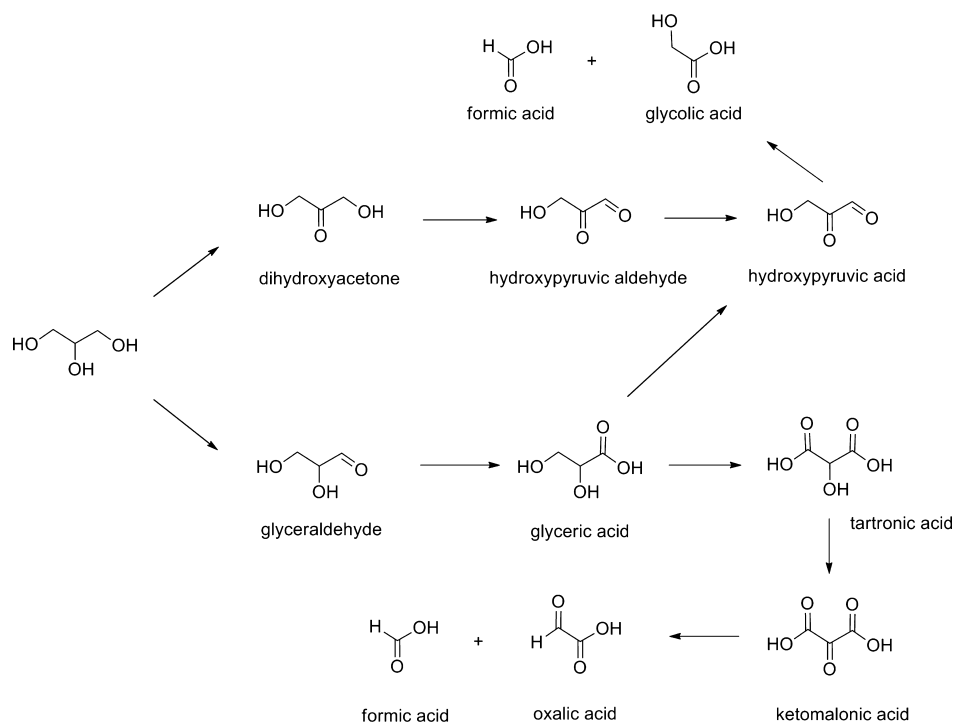
Figure 2. Reaction scheme for glycerol oxidation under basic conditions.

billion. Exploring new technological routes for the utilization of glycerol will clearly be beneficial for biodiesel production in the near future.

Glycerol could be expected to become one of the major renewable building block chemicals analogous to those from the petrochemical industry (methane, ethylene, methanol, etc.) in the near future. A number of potential products can be obtained by the selective transformation of glycerol using a range of processes, such as dehydration, hydrogenation, hydrogenolysis,

esterification, etherification, and oxidation (Figure 1). In this Account, we will focus on its catalytic oxidation using supported metal nanoparticles, as pioneered and developed by the groups of Hutchings and Prati together with their co-workers.

■ OXIDATION OF GLYCEROL USING SUPPORTED MONOMETALLIC NANOPARTICLES

The selective oxidation of glycerol follows a complex reaction pathway yielding different C_3 products (glyceric acid (GLYA),

Table 1. Oxidation of Glycerol Using Supported Au Nanoparticles

		reaction conditions						selectivity,[a] %			
catalyst	Au size (nm)	T (°C)	NaOH (equiv)	Gly/Au mol/mol	time (h)	conv (%)	TOF (h^{-1})	GLYA	GLYCA	TA	ref
1% Au/graph	b	60	6	540	3	43	b	80	0	20	7
5% Pt/graph	b	60	1	500	3	59	b	66	b	2	7
5% Pd/graph	b	60	1	500	3	53	b	50	b	8	7
1% Au/AC Cit-calc	30	60	1	500	20	99	b	89	b	b	11
1% Au/AC PVA	5	60	1	500	6	99	b	45	b	b	11
1% Au/CNF-PS	3.7	50	4	1000	4	64	948	56	22	b	18
1% Au/CNF-HT	3.5	50	4	1000	4	70	982	22	35	b	18
1% Au/TiO$_2$ PVA Au/PVA (1:1)	3.5	50	4	1000	4	68	236	81	3	5	30
1% Au/NiO PVA Au/PVA (1:1)	3.6	50	4	1000	4	99	1418	55	11	9	30

[a]GLYA = glycerate; TA = tartronate; GLYCA = glycolate. [b]Not determined

dihydroxyacetone (DHA), and tartronic acid (TA)), C$_2$ products (glycolic acid (GLYCA) and oxalic acid (OXA)), and even C$_1$ products (formic acid (FA)) (Figure 2). Most of these products are useful intermediates in organic synthesis, but they presently have a limited market.

The majority of these products are manufactured using costly and non-environmentally friendly stoichiometric oxidants, such as potassium permanganate and chromic acid, or alternatively by low productivity fermentation processes. It has been demonstrated that supported metal nanoparticles, such as Pd or Pt, in the presence of relative inexpensive oxidizing agents (oxygen, air, hydrogen peroxide) represent an environmentally friendly and low cost alternative to these conventional methodologies.[4,5] Unfortunately, a major drawback of using Pd or Pt catalysts during liquid phase glycerol oxidation is the sensitivity to deactivation due to overoxidation and poisoning from (by)-products.[4,5] We initially demonstrated the superior performance of the gold catalyst[6] with respect to Pd- and Pt-based catalysts in particular in term of selectivity to glycerate (80%, 60%, and 50% for Au/graphite, Pt/graphite, and Pd/graphite, respectively; Table 1).[7,8] We synthesized graphite supported gold nanoparticles of around 25 nm mean particle size, and varying parameters, such as pressure, sodium hydroxide, and catalyst amount, we optimized the conversion of glycerol and the yield of glycerate.[7,8] We proposed that gold required the presence of NaOH to perform the H-abstraction, the first step of the dehydrogenation pathway.[8,9] In subsequent studies, Davis and co-workers, using labeling experiments with $^{18}O_2$ and $H_2^{18}O$ for glycerol oxidation over supported Au catalysts, demonstrated that oxygen atoms originating from hydroxide ions are incorporated into the alcohol during the oxidation reaction, instead of those from molecular oxygen.[10]

We investigated the effect of different preparation methods (sol immobilization, incipient wetness, deposition precipitation, and impregnation), where a variation of particle size (5−30 nm) could be achieved using activated carbon (AC) or TiO$_2$ as supports.[11,12] We concluded that gold particle size is crucially important in determining the activity and selectivity of the gold catalyst.[9−14] Small particles (3−5 nm) are more active than larger particles (10−30 nm), whereas larger particles give higher selectivity toward glyceric acid (Table 1).

Successive studies subsequently highlighted the role of the support in determining catalytic activity as well as gold catalyst stability.[15]

The basic and acidic properties of the support surface were studied for Au catalyzed glycerol oxidation.[13] Oxidative treatment of carbon nanofibers (CNFs) with HNO$_3$ introduced acid

functionalities, while chemical treatment with ammonia at different temperatures was performed to introduce N-containing groups in order to enhance their basic properties. Au nanoparticles were prepared via sol immobilization and impregnated on the modified supports. It was demonstrated that together with the increase of the basic functionalities, an increase in the activity of the catalyst occurred, in agreement with the dehydrogenation mechanism where a basic reaction environment promotes the alkoxide formation and the subsequent C−H bond cleavage. Moreover, the important role of controlling the hydrophobicity/hydrophilicity of the support was demonstrated, since selectivity to glycerate and tartronate as the main C$_3$ products increased from 65% to 82% at 90% conversion with the increase of the hydrophobic surface. This result was explained by the decrease in H$_2$O$_2$ production that is responsible for C−C bond cleavage.[16,17]

In subsequent studies, we investigated the role of a nanostructured support (NiO) for depositing Au nanoparticles and explored the catalytic performance of Au/NiO compared with Au/TiO$_2$ and a series of Au/NiO$_x$−TiO$_{2y}$ catalysts in the case of glycerol.[17] It was established that the dispersion of NiO nanoparticles on TiO$_2$ could significantly influence the Au nanoparticle activity and selectivity, depending on the relative ratio of NiO to TiO$_2$. Au/NiO catalysts showed high activity but lower selectivity to glycerate (55% selectivity at 90% conversion; Table 1). By varying the NiO/TiO$_2$ ratio and optimizing the desired ratio ((NiO)$_{10}$−(TiO$_2$)$_{90}$), the selectivity toward glycerate increased to 75%. To explain the improvement in activity by using NiO as support, it was observed that the most important parameter was the interaction of the support with the nanoparticles as evidenced using CO as a probe molecule. Moreover, HRTEM analysis showed that Au nanoparticles were preferentially associated with NiO either in the pure Au/NiO or Au/NiO/TiO$_2$ materials, with this interaction improving the stability of the Au nanoparticles. From these studies, we concluded that the interaction between NiO and Au nanoparticles is the essential factor for affecting activity and selectivity for Au/NiO-TiO$_2$ catalysts.

We also demonstrated that the structure of the support can also modify the structure of the Au nanoparticles. Indeed, it was shown that using two carbon nanofibers with different degrees of graphitization as supports can result in a restructuring of the Au nanoparticles.[18] The first carbon nanofiber was treated by pyrolytic stripping (labeled ad CNF-PS) to remove the polyaromatic carbon layer covering the outer surface, whereas the second one was heat-treated at high temperatures, about 1500 °C (labeled ad CNF-HT), resulting in a more graphitized

surface. HRTEM analyses revealed that despite similar Au mean size (3.8 and 3.5 nm for CNF-PS and CNF-HT respectively), the final shape of the Au particles was related to the surface structure of the support. In particular, Au was attached to the CNFs without a distinguishable orientation relation between the Au low-index crystallographic planes and the CNF surface. Among the examined Au particles, 21.6% were found to have one set of {111} planes parallel to the CNF surface and the rest were randomly oriented (Figure 3).
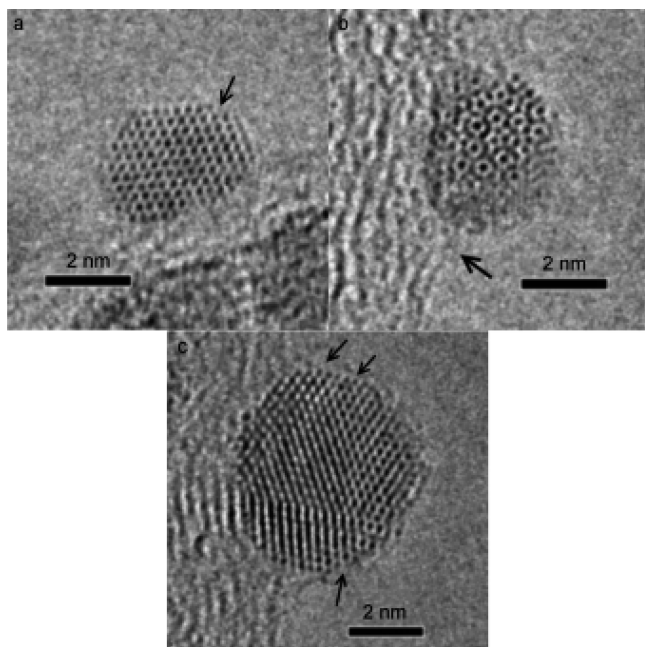
Figure 3. Aberration-corrected HRTEM images of Au particles supported on CNF-PS with (a) modified cuboctahedral configuration, (b) icosahedral configuration showing interaction between the particle and the CNF surface, and (c) surface carbon decoration with uncovered windows (each indicated by arrows). Reproduced with permission from ref 18. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

The {111} planes of Au particles on CNF-HT were observed to be more frequently parallel to the CNF (46.8%) surface than in the case of CNF-PS (Figure 4). The particle has a relatively large {111} base plane contacting with the supporting CNF. The catalytic activity for glycerol oxidation was observed to depend only on the metal particle size. Indeed, the two catalysts showed a similar activity (TOF of 948 and 982 h^{-1} for Au/CNF-PS and Au/CNF-HT, respectively), in good agreement with the similar particle size (3.8 and 3.5 nm for Au/CNF-PS and Au/CNF-HT, respectively; Table 1).

However, the different product distribution obtained revealed that the particle size is not the only parameter determining the selectivity. Using Au/CNF-PS, 56% C_3 products and 45% C_2 + C_1 products were obtained, whereas with Au/CNF-HT 22% C_3 products and 77% C_2 + C_1 were obtained. The direct contact between CNF-HT and the {111} surface of PVA Au nanoparticles led to the exposure of low index Au surfaces, suggesting that the active sites on these surfaces could promote the C_1 and C_2 products, deriving from the C−C bond cleavage. We correlated the high selectivity toward the C−C cleavage shown by low-indexed surface to H_2O_2 production, responsible, according to literature, for C−C cleavage. Moreover, it has
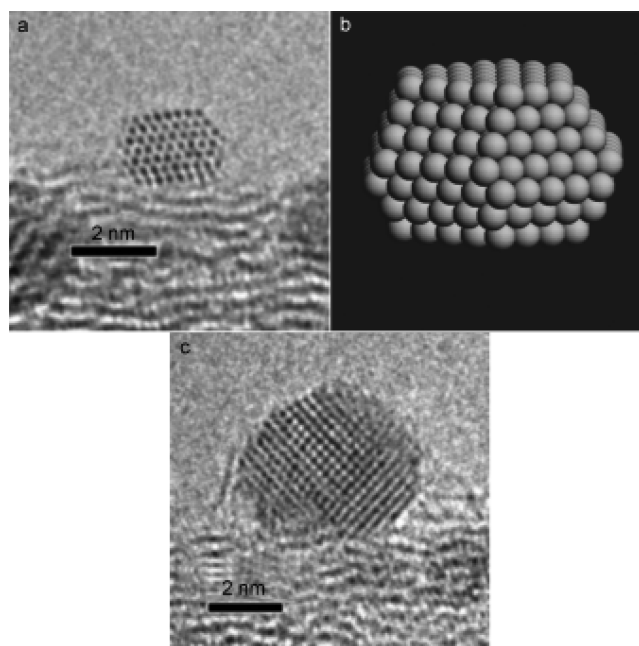
Figure 4. Aberration-corrected HRTEM images of Au particles supported on CNF-HT. (a) A representative 2−4 nm particle with {111} surface epitaxially parallel to the graphitic layer of the CNF. (b) Structure model derived from the image in part a. (c) A larger particle with spherical shape showing carbon binding to the CNF surface. Reproduced with permission from ref 18. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

recently been shown that Au(111) surfaces are the most suitable for H_2O_2 direct synthesis, which may be formed through O_2 reduction by metal hydride (Figure 5).
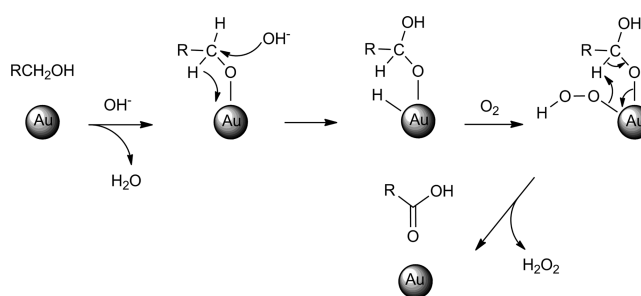
Figure 5. Proposed Mechanism of H_2O_2 formation on Au through O_2 reduction. Reproduced with permission from ref 18. Copyright 2013 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

H_2O_2 was used instead of oxygen for the oxidation of glycerol to produce glycolic acid (C_2 product), an important chemical used as a cleaning agent. In particular, it was shown that Au catalysts are more active and selective compared with Pd catalysts, with a maximum yield of 60% glycolate achieved.[19] The proposed glycolate formation pathway passes from the oxidation of glycerol to glycerate and subsequently to tartronate, with a final decarboxylation to glycolate, or a retro-aldol reaction, which leads directly to glycolate from glycerate (Figure 6).

The role and the influence of capping agent (poly(vinyl alcohol)) in terms of activity and selectivity in glycerol oxidation were also investigated.[20] Au/TiO₂ catalysts with different amounts of PVA were prepared by varying the poly(vinyl alcohol)/metal weight ratio or by selectively removing the
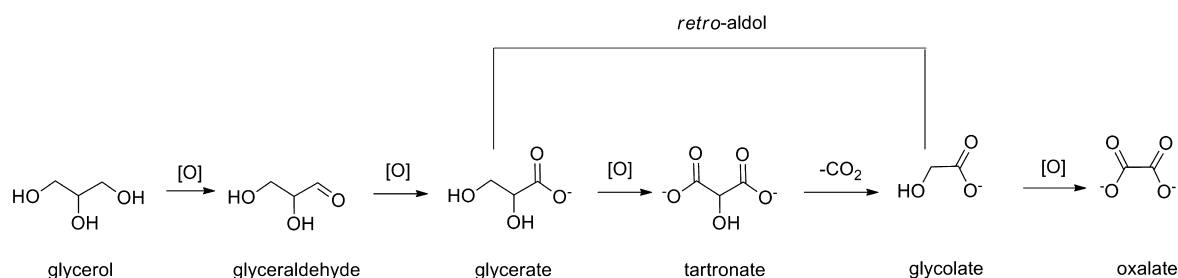
Figure 6. Proposed pathways for glycolate formation.

Table 2. Oxidation of Glycerol Using Supported Au−Pd Nanoparticles

catalyst	reaction conditions			conv. (%)	selectivity,[a] %			refs
	T (°C)	NaOH (eq)	Gly/Au mol/mol		GLYA	GLYCA	TA	
Au−Pd/AC	50	4	500	90	57	8	34	24
Au−Pt/AC	50	4	500	90	51	40	6	24
Pd@Au/AC	50	4	3000	90	77	b	b	26
Au$_{90}$-Pd$_{10}$/AC	50	4	1000	90	75	19	b	28, 29
Au−Pd/AC	60	4	2000	90	72			30, 31
0.1%Bi@1%Au−Pd/AC	60	4	1000	90	54	13	34	32

[a]GLYA = glycerate; TA = tartronate; GLYCA = glycolate. [b]Not determined.

protective agent from the metal surface. It was observed that the presence of high amounts of PVA lowered the catalytic activity of Au/TiO$_2$ catalyst, whereas a small amount of capping agent is beneficial for increasing the activity (Table 1). Moreover, the presence of PVA directed selectivity toward glycerate, whereas PVA-free Au nanoparticles promote C−C cleavage and therefore the production of C$_2$ and C$_1$ products. FTIR adsorption studies reveal a direct interaction between capping agent and the glycerol molecule, thus affecting the adsorption of glycerol on the active sites of the catalyst. It was concluded that the different adsorption modes of glycerol on the active sites in the presence or absence of capping agent could vary the selectivity. Finally, it should be mentioned that the presence of a protective agent is beneficial for the stability of the catalyst. Indeed, recycling tests revealed a better resistance of the catalyst obtained by protected particle deposition with respect to the catalyst obtained by the deposition−precipitation technique, where no protective agent is used. Therefore, a new way of designing metal supported catalysts by the careful choice of capping agent and amount has been demonstrated.

■ OXIDATION OF GLYCEROL USING SUPPORTED BIMETALLIC NANOPARTICLES

Supported bimetallic nanoparticles have shown tremendous potential in the fields of biomass and energy conversion, chemical production, and biomedical applications.[21] In the area of catalysis, a significant improvement in terms of catalytic reactivity and stability for a range of catalytic processes, such as hydrogenation, oxidation, hydrogenolysis, and reforming has been reported.[22,23] In the case of glycerol oxidation, we were one of the first who demonstrated the successful utilization of supported Au-based bimetallic nanoparticles (Table 2) for the transformation of glycerol under aerobic and mild conditions.[24,25]

By a colloidal approach, preformed Au−Pd and Au−Pt nanoparticles were supported on activated carbon, and the catalytic performance was compared with the analogous supported monometallic preformed Au, Pd, and Pt nanoparticles. Alloying Au with Pt or Pd could lead to an

enhancement in the activity for glycerol oxidation with respect to the monometallic catalysts, and the choice of the bimetallic catalyst (Au−Pd or Au−Pt) was shown to determine the product selectivity. The utilization of supported Au−Pd nanoparticles improved the selectivity toward the products of the oxidation of the terminal hydroxyl groups (glycerate and tartronate) with selectivities over 90% at high conversion levels (90%). In the case of supported Au−Pt catalysts, similar TOF values were obtained with respect to the supported Au−Pd catalysts, and an enhancement in the formation of glycolic acid was observed. The monometallic Pt and Pd catalysts were shown to deactivate on reuse, and it was reported that alloying gold with platinum not only led to an enhancement in the activity of the catalysts but also to significantly diminished deactivation of the catalysts on reuse. By a two-step experimental approach for the synthesis of bimetallic nanoparticles, which relies on the formation of preformed particles of the first metal as nucleation centers for the second metal, the synthesis of bimetallic nanoparticles with single phase and random alloy structure was achieved.[26] Detailed characterization of the synthesized bimetallic nanoparticles by means of HRTEM/EDX analysis showed the presence of similar Au/Pd ratio among the single particles regardless particle size, without Au or Pd segregation and with uniform structure within each particle, confirming that particles consist of random Au−Pd alloy with the Au−Pd ratio close to 6:4 (Figure 7). The catalytic performance of the supported single-phase Au−Pd nanoparticles showed a significant increase in catalytic activity with respect to monometallic Au and Pd supported nanoparticles and Au−Pd bimetallic nanoparticles prepared in the one step approach. In following studies, thorough recycling tests were carried out to show the high resistance of the catalyst to poisoning and the high stability of the catalysts, which retain similar catalytic activity after 11 cycles.[27] The used catalyst was characterized by means of SEM and TEM and showed a minimum degree of segregated particles and a low degree of metal leaching without significant reconstruction of metal particle on the support surface.

In subsequent studies, we investigated the effect of molar ratio of Au/Pd in supported carbon bimetallic Au−Pd catalysts in terms of activity and product distribution.[28,29] Besides the studies

(a)

(b)
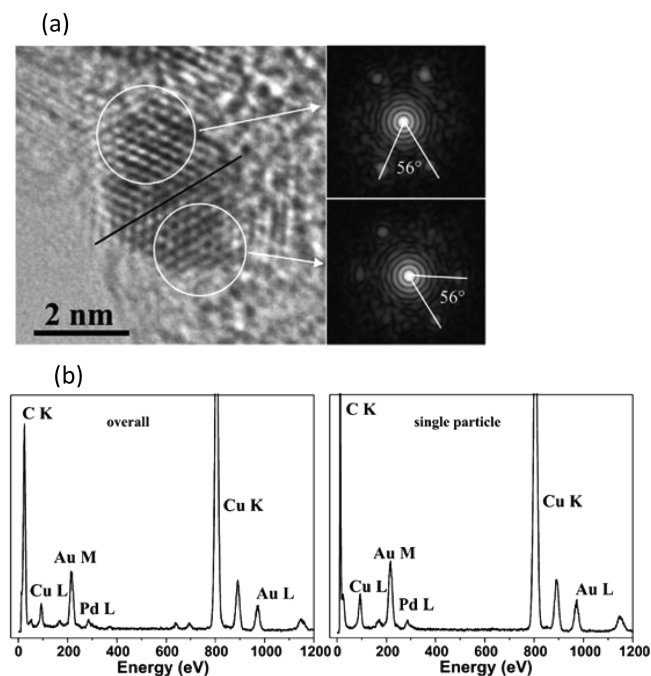
Figure 7. (a) Representative HRTEM image of single particles of Au−Pd/AC and (b) overall EDX spectrum and representative one for individual single particles for Au−Pd/AC. Reproduced from ref 26 (http://dx.doi.org/10.1039/B518069D) with permission of The Royal Society of Chemistry.

of the catalytic performance, detailed characterization studies were carried out to correlate the structure−activity relationship of the studied catalysts. The variation of the Au/Pd atomic ratio from 9:1 to 1:4 was carried out by using a two-step colloidal seed growth procedure, which facilitates the formation of uniformly single-phase homogeneous alloy particles. The particle size distribution of the supported bimetallic nanoparticles was in the range of 2.9−3.7 nm, and supported bimetallic nanoparticles were observed to be uniform alloy when the Au/Pd ratio was 9:1, 8:2, and 6:4. The variation of Au/Pd atomic ratio led to a significant difference in the catalytic performance with the gold-rich catalysts showing higher catalytic activity and stability. The highest levels of activity were found with Au/Pd ratio of 9:1, and the selectivity toward glycerate at 90% isoconversion was similar (70−80%) across the Au/Pd composition variation and slightly decreased with increasing Au content. From our studies, it was concluded that the improvement in terms of activity and lifetime of the catalyst is due to the presence of surface Pd monomers in contact with Au particles.

We synthesized supported bimetallic Au−Pd nanoparticles using two preparation methods (impregnation and sol-immobilization) and studied the catalytic performance of the synthesized materials in the liquid phase oxidation of glycerol under aerobic and alkaline conditions.[30,31] Higher activity with moderate selectivity for the desired product (glycerate, 60−70%) was observed with the bimetallic catalysts synthesized by the colloidal method because high activity can be achieved by gold-rich surface bimetallic nanoparticles with mean particle size of 3−5 nm and metallic oxidation state. In contrast, larger particles (over 6 nm) with surfaces enriched in Pd and prepared by the impregnation method led to significantly lower catalytic activity. Later, we investigated the role of Bi as a promoter for Au−Pd catalysts.[32] By using two different experimental approaches, we prepared Au−Pd−Bi catalysts, where Bi was either deposited

prior to or after the immobilization of Au−Pd preformed colloidal nanoparticles onto the support. Characterization studies (Figure 8) showed that the prior deposition of Bi and the Bi loading onto the support did not affect the particle size of the Au−Pd nanoparticles but did not allow us to obtain a homogeneous composition of the alloyed Au−Pd phase. Conversely, the deposition of Bi on preformed Au−Pd supported nanoparticles did not affect the alloy composition. In terms of catalysis, in the case of glycerol oxidation, a promotion of the consecutive reaction leading to tartronate was found with a yield of 34%. The enhanced catalytic performance was considered to be due to the selective inhibition of active Au−Pd sites by Bi.
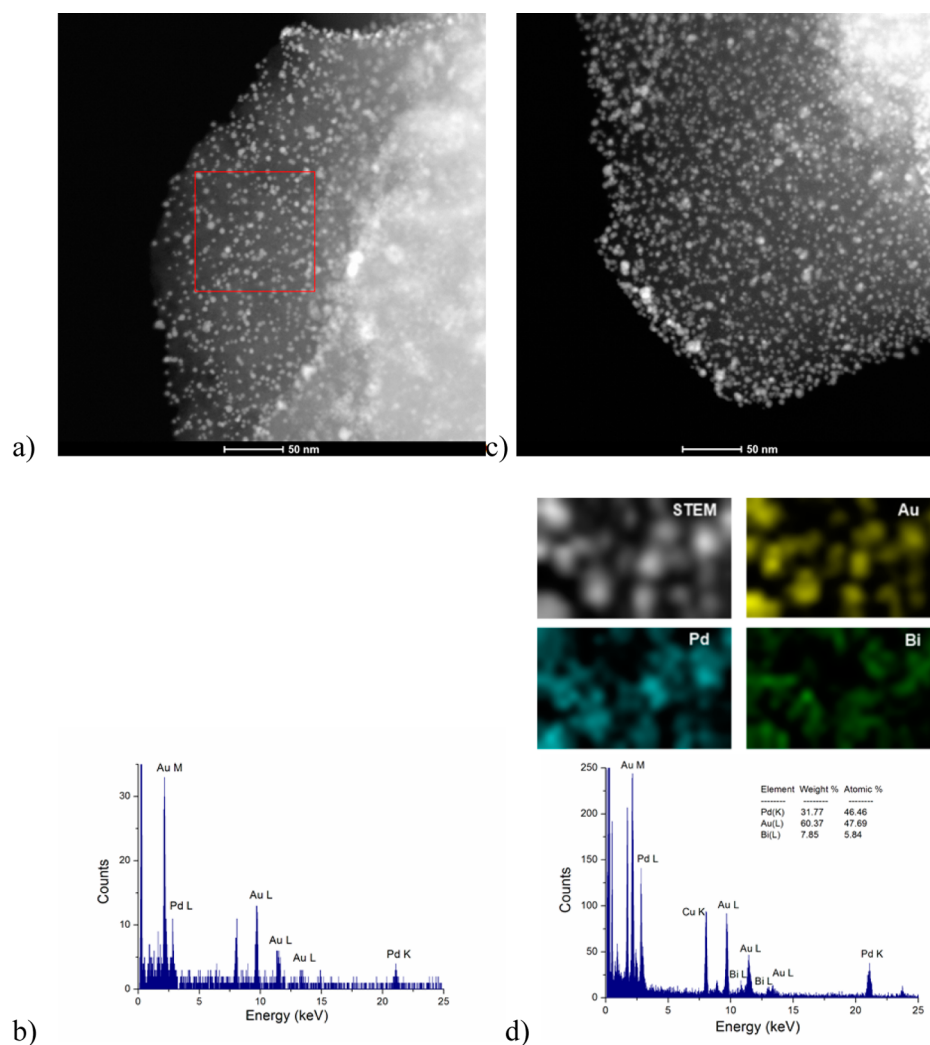
■ BASE-FREE OXIDATION OF GLYCEROL

In the previous sections, it has been demonstrated that by finely tuning the reaction conditions as well as the structure of the gold catalysts, it is possible to enhance both activity and selectivity to glyceric acid in the presence of a base. However, the use of basic conditions results in the formation of salts of the acids instead of free carboxylic acids. From an industrial point of view, direct formation of the acid is far more desirable. To satisfy this prerequisite, efforts were also focused on performing the oxidation of glycerol under base-free conditions. For that purpose, the role of the support, as well as the nanoparticle composition, was investigated.

The first attempt showed that Pt catalysts are effective in the base-free glycerol oxidation.[33] However, these catalysts promote the C−C cleavage, resulting in the formation of carbon dioxide and formic acid. Moreover, Pt catalysts showed a high tendency to deactivate due to leaching of Pt in the reaction media. We were the first to report that by alloying Au with Pt, it is possible to enhance the catalyst lifetime and avoid the leaching of Pt into the reaction solution. In particular, the utilization of zeolite H-mordenite instead of activated carbon as the support leads to an enhancement of the activity (99% and 62% after 6 h for AuPt/mordenite and AuPt/AC, respectively) (Table 3).[34] Moreover, AuPt/H-mordenite demonstrated a high selectivity (83%) to glyceric acid by lowering C−C cleavage and consequently the formation of C_1 products. Indeed, little H_2O_2, responsible for the C−C cleavage, was detected in reactions catalyzed using H-mordenite as support instead of activated carbon.

We also showed by using basic supports, such as MgO, that it is possible to obtain a high selectivity for C_3 products (85%) by careful tuning of the reaction conditions, specifically by controlling the reaction temperature (Table 3).[35] AuPt particles exhibited a simple cuboctahedral structure and are alloyed (Figure 9).

Reusability of the catalyst was tested both at ambient temperature and at 60 °C, and its activity remained unchanged. Using a basic support, AuPd alloys were also active in the target reaction. However, lower activity and selectivity to glyceric acid were obtained compared with the one obtained with the AuPt-based catalysts (Table 3). We then showed that with TiO$_2$ as support, a trimetallic Au−Pd−Pt had high activity whereas AuPt was almost inactive. However, Au−Pd−Pt/TiO$_2$ was found to be unstable, probably due to metal leaching, significant particle agglomeration, and irreversible adsorption of the products as revealed by DRIFTS studies.[36]

More recently, we highlighted the importance of the support in tuning the selectivity of the AuPt catalyst in the base-free glycerol oxidation.[37] At 80 °C, basic supports (MgO, NiO) promote the activity but also increase C−C bond cleavage

Figure 8. STEM image of (a) 1% Pd@Au/0.1% Bi on AC and (c) 1% Pd@Au/3% Bi on AC and EDX spectra corresponding to element mapping on (b) 1% Pd@Au/0.1% Bi on AC and (d) 1% Pd@Au/3% Bi on AC. Reprinted from ref 32 (http://www.sciencedirect.com/science/journal/00219517) with permission from Elsevier.

Table 3. Base-Free Glycerol Oxidation Using Au Catalysts

catalyst	reaction conditions				selectivity,[a] %					ref
	T (°C)	Gly/Au mol/mol	time (h)	conv %	GLYA	GLYCA	TA	GLYALD	C_2/C_1	
1% AuPt/AC	100	500	6	62	79	b	1			34
1% AuPt/H-mordenite	100	500	6	99	83	b	2			34
1% Au₁Pt₃/MgO	60	1000	4	43	72	3	15			35
1% Au₁Pt₃/MgO	25	1000	24	43	85	5	4			35
1% Au−Pt−Pd/TiO₂	100	2728	4	37	55	7	2			36
1% AuPt/MgO	80	500	12	99	21	8	1	7	59	37
1% AuPt/NiO	80	500	16	58	51	7	8	10	17	37
1% AuPt/MCM-41	80	500	16	66	35	1	1	46	2	37
1% AuPt/SiO₂	80	500	16	38	61	2	1	16	3	37
1% AuPt/H-Mordenite	80	500	16	36	53	1	0	19	4	37
1% AuPt/S-ZrO₂	80	500	16	35	57	1	3	19	3	37

[a] GLYA = glyceric acid; GLYALD = glyceraldehyde; TA = tartronic acid; GLYCA = glycolic acid. [b] Not determined.

reactions, whereas acidic supports (MCM41, SiO₂, H-mordenite and sulfated-ZrO₂) showed a higher selectivity to C₃ oxidation products (Table 3). Moreover, spectroscopic and micro-calorimetric measurements evidenced that the selectivity to glyceric acid or glyceraldehyde is strongly influenced by the amount of acid sites. In particular, the selectivity to

glyceraldehyde decreases upon increase of the number of acid sites (Brønsted sites or silanols). Indeed, the successive transformation of glyceraldehyde to glyceric acid proceeds via an acid catalyzed geminal diol formation and its dehydrogenation carboxylic acid (Figure 10). The use of basic metal oxides as supports for Au-based catalysts seems to be a promising area;
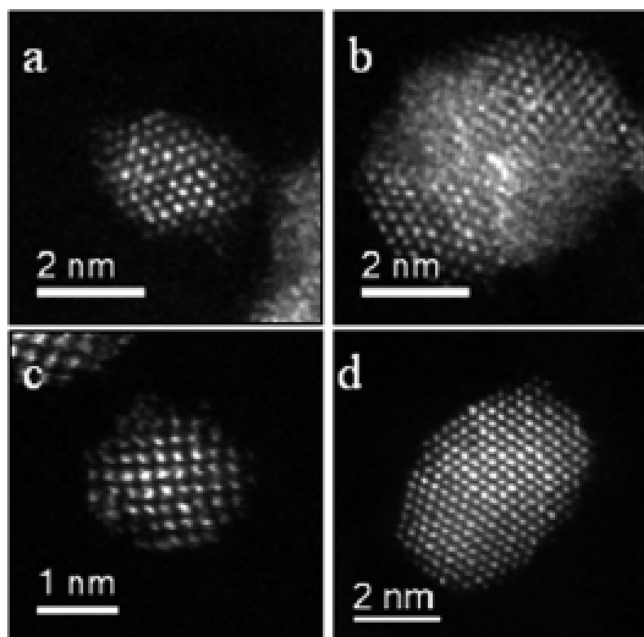
Figure 9. High-magnification STEM–HAADF image and corresponding particle-size distribution of (a, b) AuPd (1:3)/MgO and (c, d) AuPt (1:3)/MgO. Reproduced with permission from ref 35. Copyright 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

however more detailed studies are needed for studying the effect of dissolution of basic metal oxides as recently has been shown by Zope et al.[38]

CONCLUDING REMARKS

Glycerol is an important biochemical that can be utilized as a platform chemical, and high-added-value products can be produced via oxidative processes. We have shown that selective oxidation using heterogeneous catalysts represents an environmentally friendly and low cost replacement to the existing stoichiometric or enzymatic processes. First attempts using Pd and Pt catalysts resulted in active catalyst but with low selectivity and stability. Therefore, many efforts have been devoted to the design of a catalyst able to control the selectivity to the desired product and to limit deactivation phenomena. In this respect, gold catalysts, in particular when alloyed to Pd and Pt, fulfill these requisites. Indeed, AuPd and AuPt were confirmed to limit side reactions, in particular C–C cleavage, therefore enhancing the

selectivity to C_3 products and improving the lifetime of the catalyst, which is a key factor for potential industrial exploitation of supported metal nanoparticles. Finally, recent results obtained under base-free conditions allow the free carboxylic acid to be obtained, instead of the corresponding salts, a major technical advantage from an industrial point of view. The present research is mainly focused on the oxidation of glycerol to glyceric acid. The most challenging feature in glycerol oxidation catalyzed by the utilization of metal nanoparticles is represented by the production of other high value chemicals, such as dihydroxyacetone and lactic acid. One of the most promising routes to glycerol valorization in the near future is the production of acrolein and acrylic acid, which are important industrial intermediates for the chemical and polymer industries. Finally, understanding better the way in which the metal active sites interact with the substrates and products will lead to the development of better catalysts and better control of activity/selectivity parameters. These can be carried out by using in situ and in operando extended X-ray absorption fine structure and X-ray absorption near edge structure (XANES) and FTIR measurements coupled with theoretical calculations.

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Notes

The authors declare no competing financial interest.

Biographies

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Dr. Nikolaos Dimitratos studied chemistry at the University of Bath and received a Ph.D. at the University of Liverpool in 2003. He was a postdoctoral researcher at the University of Milan and Cardiff University. His current research field is catalysis, covering areas of synthesis, characterization, and reactivity in oxidation and hydrogenation reactions. He is currently University Research Fellow in the area of catalysis and nanoparticle synthesis at Cardiff University.
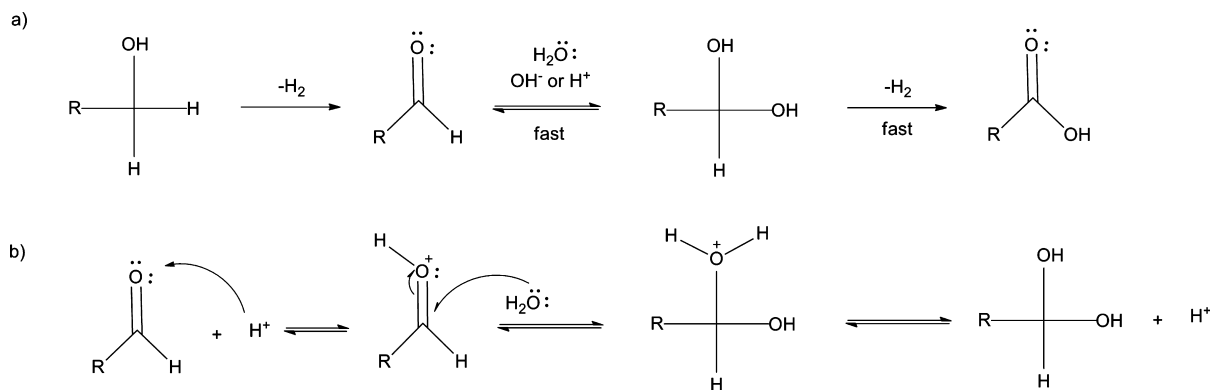
Figure 10. (a) Alcohol dehydrogenation mechanism in the presence of water and (b) acid catalyzed geminal diol formation. Reproduced from ref 37. Published by The Royal Society of Chemistry.

Dr. Carine E. Chan-Thaw is an assistant Researcher at the Università degli Studi di Milano. Her Ph.D. research was mainly carried out at the Fritz Haber Institute of the Max Planck Gesellschaft under the supervision of Prof. Robert Schlögl. She is a Postdoctoral fellow at the Technische Universität Berlin where she worked on testing a nitrogen rich highly porous framework for liquid phase oxidation. She is currently investigating the valorization of biomass.

Dr. Ceri Hammond received his Ph.D. from Cardiff University in 2012. After a Postdoctoral stay at ETH Zürich (2011−2014), he accepted a position at the Cardiff Catalysis Institute as a University Research Fellow. Since October 2014, he also holds dual affiliation as a RSC Research Fellow at Stanford University. His research team specializes in several aspects of applied catalysis, inorganic materials, and *in situ* spectroscopy.

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Professor Graham J. Hutchings, FRS, has specialized in the field of heterogeneous catalysis for over 35 years. During his initial industrial career with ICI Petrochemicals (1975−1981) and AECI Ltd (1981−1984), he made initial discoveries on gold catalysis. He was elected as a Fellow of the Royal Society in 2009. He is currently Professor of Physical Chemistry and Director of the Cardiff Catalysis Institute at Cardiff University and was also Head of Cardiff School of Chemistry from 1997 to 2006.

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