Angewandte
International Edition Chemie

Catalytic Oxidation

DOI: 10.1002/anie.201000762

Selective Oxidation of Glycerol under Acidic Conditions Using Gold Catalysts**

Alberto Villa, Gabriel M. Veith, and Laura Prati*

Herein, we report progress towards eliminating the need for a base while maintaining high activity and selectivity for the aqueous-phase oxidation of glycerol. We have discovered that by using the right alloy nanoparticle and support material, we are able to prepare an active and durable catalyst that is highly selective towards the formation of oxidized C_3 molecules from glycerol under acidic conditions. This discovery is significant because previous investigations of Pd and Pt catalysts at pH 2–4 reported that the main products derived from these catalysts under acidic conditions are C_1 and C_2 molecules produced from C–C bond scission.[1–3] Furthermore, the groups of Claus and Hutchings showed that by using Pt catalysts it is possible to obtain quite a high selectivity to hydroxyacetone (C_3 molecule) or hydroxypyruvic acid, but that selectivity rapidly declines with increasing conversion.[1,4–6]

Glycerol is a highly functionalized bioderived molecule that is recognized as one of the most promising chemical building blocks for the synthesis of fine chemicals from renewable sources.[7,9] The selective oxidation of glycerol has been shown to produce valuable products, such as glyceric acid, hydroxyacetone, tartronic acid, and ketomalonic acid. The activity and product distribution for the catalytic oxidation of glycerol depend on the catalyst, reaction conditions, and oxidant source.[7–9] In general, carbon-supported metal catalysts combined with dioxygen under basic conditions and moderate temperature are the most investigated catalysts for the oxidation of glycerol.[1,4–6,10,11] Pd and Pt nanoparticles supported on activated carbon (AC) were the first investigated for the oxidation of glycerol, but gold was recently shown to be highly active and very selective in this reaction.[1–10] A key advantage in using gold, compared to Pt and Pd, is the improved resistance of Au to overoxidation under liquid-phase oxidation conditions with O_2 as the oxidant.[1,10–13]

However, in alcohol oxidation with gold catalysts, a severe limitation arises because of the required addition of a base to improve the oxidation kinetics and reduce deactivation. As a consequence of using basic conditions, salts of acids are obtained instead of free carboxylic acids. From an industrial point of view, working under an acidic regime allows the direct formation of acid products. It should also be noted that basic conditions could modify the intrinsic selectivity of the catalyst as a result of base-catalyzed interconversions.

Given the industrial importance of operating under acidic conditions, we began investigating the synergistic effect of support material and nanoparticle composition on the oxidation of glycerol without base. For comparison purposes, a series of monometallic clusters were deposited on AC, TiO_2, $MgAl_2O_4$, and acidic H-mordenite by a sol immobilization technique and tested under similar conditions. TiO_2 was investigated because it is the prototypical gold support with an intermediate isoelectric point (IEP), and basic $MgAl_2O_4$ (IEP = 11.8) was recently reported by Christensen et al. for the oxidation of ethanol using monometallic Au on $MgAl_2O_4$ at 100 °C without any addition of base.[14,15] Upon comparing just the gold clusters, the average diameter on H-mordenite was (3.76 ± 1.90) nm (Figure 1), as determined by scanning transmission electron microscopy (STEM). This value is slightly larger, but within experimental error, than the corresponding mean diameter of Au particles on AC [(2.98 ± 1.31) nm].

Initial catalytic testing performed at 50 °C (0.3 M aqueous glycerol solution, glycerol/metal ratio 500 (mol/mol), $pO_2 =$ 3 atm) showed all these catalysts to be inactive at this temperature. At elevated temperatures (100 °C) the mono-

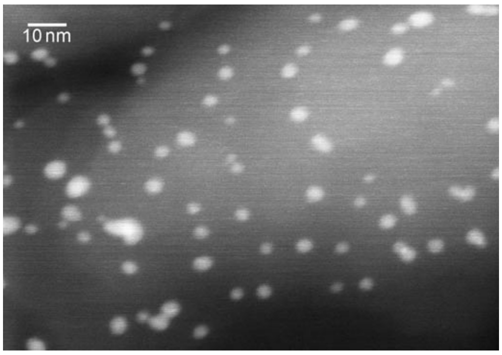

Figure 1. STEM image of Au on H-mordenite.

---

[*] Dr. A. Villa, Prof. L. Prati
Department of Inorganic Chemistry L. Malatesta
Università degli Studi di Milano
via Venezian 21, 20133 Milano (Italy)
Fax: (+39) 02-503-14405
E-mail: laura.prati@unimi.it

Dr. G. M. Veith
Materials Science and Technology Division
Oak Ridge National Laboratory
Oak Ridge, TN 37831 (USA)

[**] A.V. and L.P. gratefully acknowledge Fondazione Cariplo for financial support. A portion of this research, at Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (STEM), was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy and by the Division of Materials Sciences and Engineering, U.S. Department of Energy under contract with UT-Battelle, LLC (G.M.V.).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201000762.

metallic gold and palladium catalysts exhibited a very low activity (<8%), compared to platinum (78%), for the conversion of glycerol (Table 1). However, there was significant formation of C_1 products, such as formic acid and CO_2, for all monometallic catalysts through the oxidative degradation of glycerol. Surprisingly, gold and platinum catalysts deposited on the acidic oxide H-mordenite exhibited a significant reduction in C_1 product formation compared to catalysts deposited on neutral to basic supports (5–10 versus 41–51% C_1 product formation, respectively; Table 1). Furthermore, there was also an enhancement in the overall selectivity to C_3 products, up to 79–81% (glyceric + tartronic acids) for the H-mordenite-supported monometallic catalysts. These results further confirm that the support material plays a key role in the selectivity of this reaction.[10] The role of particle size in activity has been studied on the same support (AC), and revealed higher activity (and less selectivity) for smaller particles.[10,11,13,16,17] The behavior of similarly sized particles for glycerol oxidation on substantially different supports has not yet been reported.

Table 1: Base-free glycerol oxidation on monometallic supported metals.[a]

Catalyst	Conv.[b]	Selectivity [%]		
		Glyceric acid	Tartronic acid	C_1 products[c]
1% Au/AC	3	39	–	51
1% Pd/AC	5	43	5	47
1% Pt/AC	78	45	7	46
1% Au/$MgAl_2O_4$	6	35	6	41
1% Au/TiO_2	8	38	7	32
1% Au/H-mordenite	5	70	9	5
1% Pt/H-mordenite	20	79	2	10

[a] Reaction conditions: 0.3 M, $pO_2 = 3$ atm, 1250 rpm, 100°C, glycerol/metal = 500 (mol/mol). [b] Conversion after 2 h. [c] C_1 products include CO_2 and HCOOH.

Clearly the use of H-mordenite as a support reduces the oxidative degradation of the glycerol. H_2O_2 formed during the reaction can be responsible for the C–C bond scission.[11,18,19] The first step of the reaction mechanism of Au-catalyzed alcohol oxidation involves hydride abstraction with AuH formation.[20] The reduction of this species by O_2 forms H_2O_2. Therefore, we performed experiments to determine the amount of H_2O_2 present during the reactions. When the H-mordenite was employed as a support material for Au, very little H_2O_2 was detected (0.025 mmol L^{-1}). In contrast, in the case of Au/AC almost 30 times more H_2O_2 was detected (0.70 mmol L^{-1}).

Moreover, under acidic conditions (pH 2) at 100°C, H_2O_2 rapidly degrades in the presence of Au/AC, whereas in the presence of Au/H-mordenite the degradation proceeds slower, as evidenced by the blank experiment starting from a 1 mM solution of H_2O_2 (Figure 2). Thus, it could be concluded that Au/H-mordenite produced H_2O_2 to a lesser extent than Au/AC. Since we are comparing similar conversion rates, it is likely that Au/H-mordenite follows a different reaction mechanism from Au/AC, possibly acting as a bifunctional catalyst in which the acidic sites (Broensted and Lewis type) can possibly play an active role. In fact the peculiar nature of acidic sites in H-mordenite has been reported.[21,22]

It is well known that the introduction of a second metal component to a nanoparticle changes the activity. In fact, by alloying Au with Pd or Pt a strong synergistic effect was reported in the oxidation of alcohol, even under neutral/acidic conditions.[23–25] The magnitude of the effect (positive or negative) depends on the nature of the reactant and its match with the geometrical/electronic requisites of AuPd and AuPt catalysts.[26] For example, previous reports show that AuPt catalyst on AC exhibits an increase or decrease in reactivity simply by changing the molecule reacted.[26] Following a procedure recently developed by our group that ensures the formation of homogeneously alloyed AuPd nanoparticles, we prepared a series of Au-based alloy catalysts.[27] The bimetallic nanoparticles were prepared by the sequential deposition of gold clusters followed by the second metal component. Gold was first deposited on the support as poly(vinyl alcohol) (PVA)-protected nanoclusters. Pt was then slowly reduced by H_2 in the presence of the Au/support material. The importance of using PVA-protected nanoclusters and a slow reduction process for obtaining alloyed nanoparticles has been recently reported.[28,29]

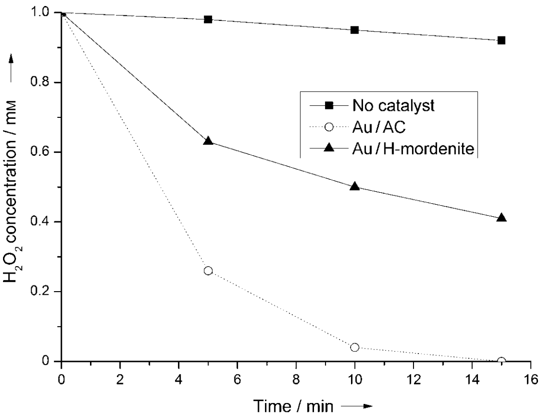

Figure 2. H_2O_2 decomposition at pH 2 and 100°C.

In comparison to the monometallic clusters, a significant enhancement in catalytic activity is observed for alloy nanoparticles. AuPt (58% conversion) and AuPd (12% conversion) catalysts on AC, the typical support for these reactions, showed not only significant increases in the conversion of glycerol but also selectivity towards the formation of glyceric acid along with a concomitant decrease in the C_1 products formed (Table 2).

Based on the above results where gold catalysts on mordenite showed a significant decrease in C_1 product formation and AuPt catalysts showed significant increases in catalytic activity, AuPt nanoparticles were prepared on the H-

Table 2: Base-free glycerol oxidation on bimetallic Au-based catalysts.[a]

Catalyst	Conv.[b]	Selectivity [%]		
		Glyceric acid	Tartronic acid	C_1 products[c]
1% AuPd(6:4)/AC	12	65	–	24
1% AuPt(6:4)/AC	58	79	1	12
1% AuPt(6:4)/H-mordenite	70	83	2	10

[a] Reaction conditions: 0.3 M, $pO_2 = 3$ atm, 1250 rpm, 100°C, glycerol/metal = 500 (mol/mol). [b] Conversion after 2 h. [c] C_1 products include CO_2 and HCOOH.

mordenite by following the same procedure as that used for AC-supported nanoparticles. By adding Pt to the Au catalyst supported on H-mordenite, a strong enhancement of activity was observed (58 to 70%) accompanied by an enhancement of selectivity to C_3 up to 85% from 80% along with a 2% decrease in C_1 product formation. Furthermore, upon comparing AuPt nanoparticles supported on AC and on H-mordenite we observed that the same initial activity of the two catalysts (after 2 h) did not correspond to the same reaction profile with time (Figure 3). Only in the case of AuPt on H-mordenite can full conversion be achieved.

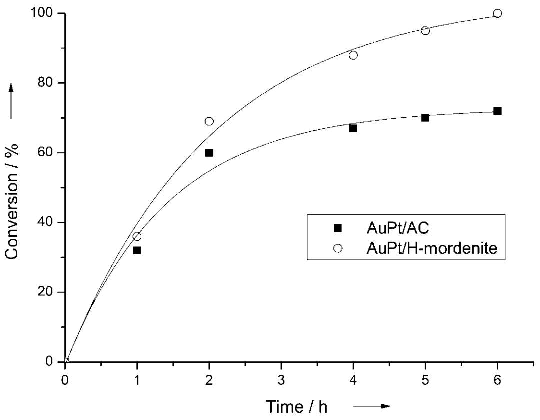

Figure 3. Reaction profile of AuPt nanoparticles supported on AC and H-mordenite.

A full characterization of AuPt on H-mordenite was performed. STEM data indicated a slight increase in the average particle size with the addition of Pt to the gold clusters (from (3.76 ± 1.90) to (4.0 ± 1.80) nm; Figure 4). X-ray photoelectron spectroscopy (XPS) data are presented in the Supporting Information. Energy-dispersive spectroscopy (EDS) analysis of 20 randomly selected clusters indicated that all of the clusters contained a mixture of Pt and Au. However, the Au/Pt ratio was inhomogeneous from cluster to cluster. Regardless, the increase in particle size, the EDS data, and the activity data confirm the presence of AuPt alloys that modify the properties of the resulting catalyst.

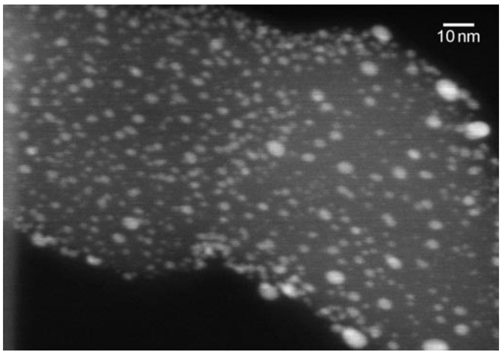

Figure 4. Representative STEM image of AuPt on H-mordenite.

As no leaching of Pt or Au was observed, differences in catalytic behavior can be ascribed to a deactivation of the “on-carbon” catalyst, possibly because of an irreversible adsorption of by-products. In this case the effect of reactant concentration could be important. Thus, we carried out tests by increasing the concentration of glycerol from 0.3 to 1 M (see the Supporting Information) and observed in the case of AuPt/H-mordenite a slight decrease of activity (and selectivity) upon increasing the concentration. As the pH of the final reaction mixtures was similar, the decrease in activity results from the high chelating properties of products that, when increasing their concentration, could be irreversibly adsorbed.

In summary, AuPt nanoparticles supported on the zeolite H-mordenite are able to selectively oxidize glycerol directly to glyceric acid without the use of basic conditions. AuPt on AC showed similar initial activity, but the major effect of using mordenite as the support lies in the enhanced selectivity that allows the production of glyceric acid with a selectivity of 81% at full conversion. Moreover, it has been shown that by alloying Au to Pt, the leaching of metals was avoided and the catalyst life improved. AuPt on H-mordenite opens the way to a new-generation gold catalyst where the support plays an active role during alcohol oxidation and prevents H_2O_2 formation that leads to C–C bond scission, thus improving selectivity and materials utilization. To assess the general use of AuPt/H-mordenite as a catalyst we plan to test other substrates. A preliminary study using ethylene glycol and 1,3-propanediol (see the Supporting Information) showed that the use of AuPt/H-mordenite is not limited to glycerol oxidation.

Received: February 8, 2010

Keywords: glycerol · gold · oxidation · platinum · supported catalysts

---

[1] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely, G. J. Hutchings, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1329–1336.
[2] R. Luque, V. Budarin, J. H. Clark, D. J. Macquarrie, *Appl. Catal. B* **2008**, *82*, 157–162.
[3] D. Liang, J. Gao, J. Wang, P. Chen, Z. Hou, *Catal. Commun.* **2009**, *10*, 1586–1590.
[4] H. Kimura, K. Tsuto, T. Wakisaka, Y. Kazumi, Y. Inaya, *Appl. Catal. A* **1993**, *96*, 217–228.

[5] A. Brandner, K. Lehnert, A. Bienholz, M. Lucas, P. Claus, *Top. Catal.* **2009**, *52*, 278 – 287.
[6] R. Garcia, M. Besson, P. Gallezot, *Appl. Catal. A* **1995**, *127*, 165 – 176.
[7] C.-H. Zhou, J. N. Beltramini, Y.-X. Fan, G. Q. Lu, *Chem. Soc. Rev.* **2008**, *37*, 527 – 549.
[8] F. Jérôme, Y. Pouilloux, J. Barrau, *ChemSusChem* **2008**, *1*, 586 – 613.
[9] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411 – 2502.
[10] F. Porta, L. Prati, *J. Catal.* **2004**, *224*, 397 – 403.
[11] W. C. Ketchie, Y. Fang, M. S. Wong, M. Murayama, R. J. Davis, *J. Catal.* **2007**, *250*, 94 – 101.
[12] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, G. J. Hutchings, *Chem. Commun.* **2002**, 696 – 697.
[13] S. Demirel-Gulen, M. Lucas, P. Claus, *Catal. Today* **2005**, *166*, 102 – 103.
[14] H. Zhang, X. Jia, Z. Liu, Z. Li, *Mater. Lett.* **2004**, *58*, 1625 – 1628.
[15] C. H. Christensen, B. Jørgensen, J. Rass-Hansen, K. Egeblad, R. Madse, S. K. Klitgaard, S. M. Hansen, M. R. Hansen, H. C. Andersen, A. Riisager, *Angew. Chem.* **2006**, *118*, 4764 – 4767; *Angew. Chem. Int. Ed.* **2006**, *45*, 4648 – 4651.
[16] N. Dimitratos, J. A. Lopez-Sanchez, D. Lennon, F. Porta, L. Prati, A. Villa, *Catal. Lett.* **2006**, *108*, 147 – 153.
[17] G. M. Veith, A. R. Lupini, S. J. Pennycook, A. Villa, L. Prati, N. J. Dudne, *Catal. Today* **2007**, *122*, 248 – 253.
[18] L. Prati, P. Spontoni, A. Gaiassi, *Top. Catal.* **2009**, 52, 288 – 296.
[19] M. Sankar, N. Dimitratos, D. W. Knight, A. F. Carley, R. Tiruvalam, C. J. Kiely, D. Thomas, G. J. Hutchings, *ChemSusChem* **2009**, *2*, 12, 1145 – 1151.
[20] M. Conte, H. Miyamura, S. Kobayashi, V. Chechik, *J. Am. Chem. Soc.* **2009**, *131*, 7189 – 7196.
[21] J. H. Lunsford, *J. Phys. Chem.* **1968**, *72*, 4163 – 4168.
[22] H. A. Benesi, B. H. C. Winquist in *Advances in Catalysis*, *Vol. 27*, Academic Press, New York, **1978**, p. 97.
[23] N. Dimitratos, A. Villa, D. Wang, F. Porta, D. Su, L. Prati, *J. Catal.* **2006**, *244*, 113 – 121.
[24] 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* **2006**, *311*, 362 – 365.
[25] W. Hou, N. A. Dehm, R. W. J. Scott, *J. Catal.* **2008**, *253*, 22 – 27.
[26] L. Prati, A. Villa, C. Campione, P. Spontoni, *Top. Catal.* **2007**, *44*, 319 – 324.
[27] D. Wang, A. Villa, F. Porta, D. Su, L. Prati, *Chem. Commun.* **2006**, 1956 – 1958.
[28] A. Villa, D. Wang, D. Su, G. M. Veith, L. Prati, *Phys. Chem. Chem. Phys.* **2010**, 2183 – 2189.
[29] D. Wang, A. Villa, F. Porta, L. Prati, D. Su, *J. Phys. Chem. C* **2008**, *112*, 8617 – 8622.