Communications

Nanoparticle Catalyst

DOI: 10.1002/anie.200503808

Ultrastable Gold Nanocatalyst Supported by Nanosized Non-Oxide Substrate**

Wenfu Yan, Suree Brown, Zhengwei Pan, Shannon M. Mahurin, Steven H. Overbury, and Sheng Dai*

Since the discovery of the surprisingly high catalytic activity possessed by gold nanoparticles for the oxidation of CO at low temperature, investigations into the potential uses of gold for various industrially important catalytic processes have been actively pursued.^[1,2] Notably, gold nanoparticles on oxide supports were regarded as highly active catalysts for the selective oxidation of hydrocarbons, methanol synthesis by hydrogenation of carbon dioxide, water-gas shift reaction, reduction of nitric oxide by hydrogen, propylene epoxidation, and preferential oxidation of CO (PROX reaction).^[3-8] A number of oxides, such as TiO_2 ,^[9-21] Fe₂O₃,^[1,22-24] Co₃O₄,^[1,25,26] NiO,^[1,25,26] SiO₂,^[27-29] Al₂O₃,^[30,31] ZrO₂,^[32] MgO,^[33-35] $\begin{array}{l} \text{CuO}_{2}^{[25,26,36]} \text{ZnO}_{2}^{[25,26,36-38]} \text{MnO}_{3}^{[25,39,40]} \text{Cr}_{2}\text{O}_{3}^{[25,26]} \text{CaO}_{2}^{[25]} \\ \text{La}_{2}\text{O}_{3}^{[25,26,41]} \text{CeO}_{2}^{[41-43]} \text{Y}_{2}\text{O}_{3}^{[26,44]} \text{ and } \text{U}_{3}\text{O}_{8}^{[26]} \text{ have been} \end{array}$ investigated as supports for gold nanocatalysts. A strong dependence of Au catalytic activity on the type of oxide support was observed experimentally. Recent theoretical and experimental studies have also indicated that the interaction of Au nanoparticles with oxide surfaces could be essential in activating the catalytic properties through oxygen-vacancy Fcenter defects and charge transfer from the surface of metal oxides to gold nanoparticles.^[45,46] A model based on the strong metal-support interaction (SMSI) investigated for

[*]	Dr. W. F. Yan, ^[+] Dr. S. Brown, Dr. Z. W. Pan, Dr. S. M. Mahurin,
	Dr. S. H. Overbury, Dr. S. Dai
	Chemical Sciences Division
	Oak Ridge National Laboratory
	Oak Ridge, TN 37831-6201 (USA)
	Fax: (+1) 865-576-5235
	E-mail: dais@ornl.gov
[+]	Present address: State Key Laboratory of Inorganic Synthesis ar

 Present address: State Key Laboratory of Inorganic Synthesis and Preparative Chemistry College of Chemistry Jilin University Changchun 130012 P.R. China

[**] This work was conducted at the Oak Ridge National Laboratory and supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, US Department of Energy, under contract no. DE-AC05-000R22725 with UT-Battelle, LLC. We thank the SHARE Facility at ORNL for the transmission electron microscopy. This research was supported in part by an appointment for W.F.Y. to the ORNL Postdoctoral Research Associates Program, administered jointly by the Oak Ridge Institute for Science and Education and ORNL.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

Group VIII metals on oxide supports was proposed to rationalize such a dependence on the oxide support.^[47,48]

On the contrary, few investigations of the catalytic properties of gold nanoparticles on non-oxide supports have appeared, with the exception of gold nanoparticles supported on carbon materials.^[49,50] In the latter case, no appreciable catalytic activity for oxidation reactions was observed. Herein, we report the preparation of an ultrastable Au nanocatalyst supported on a non-oxide material based on LaPO₄ nanoparticles. The stability of this Au nanocatalyst under high-temperature treatment in O_2 is much better than that of the TiO2-supported Au reference nanocatalyst supplied by the World Gold Council as part of an initiative to promote the use of gold in this type of industrial procedure. The application of the phosphate-based supports opens up a new avenue in the search for highly active, stable, and selective gold catalysts for a number of catalytic reactions. The unique structural features of this non-oxide support (such as difficulty in undergoing oxygen exchange and reduction) could shed new light on the mechanism associated with goldbased catalysis.

The LaPO₄ nanoparticles were synthesized by a sonication method.^[51] transmission electron microscopy (TEM) analyses showed that the average particle size of the assynthesized LaPO₄ nanoparticles is about 6-8 nm (see Supporting Information); their Brunauer-Emmett-Teller (BET) surface area is $111 \text{ m}^2\text{g}^{-1}$. The X-ray diffraction (XRD) pattern of the as-synthesized LaPO₄ nanoparticle substrate (see the Supporting Information) does not show any resemblance to that of the monoclinic LaPO₄ phase (LaPO₄-M), but can be assigned to the pattern attributed to a hexagonal LaPO₄ phase (LaPO₄-H; see the XRD patterns and indexing (Figure 3a)). However, the two XRD peaks with $2\theta \approx 20.3$ and 26.1° are shifted slightly from the corresponding peaks in the simulated hexagonal LaPO₄ XRD pattern, which could be attributed to the potential lattice distortion induced by the nanoparticles. A search of the commercial XRD database JADE (Materials Data, Livermore,) excluded the possibility of the presence of any impurity phases that originate from lanthanum oxide, lanthanum chloride, or lanthanum hydroxide. Research is currently under way to investigate the indexing of these two peaks.

To further rule out the possibility of the presence of amorphous La₂O₃, the calcination of LaPO₄-H was conducted at high temperature (950°C) to induce the crystallization of potential amorphous La₂O₃. No detectable La₂O₃ phase or any other impurity was observed (see the Supporting Information). A clean and complete transformation of LaPO₄-H to LaPO₄-M was indicated, which further supported the basic elemental composition of LaPO₄-H with negligible impurities. Additional spectroscopic characterization and elemental analysis as well as phase-transition behaviors are given in the Supporting Information. The average particle size calculated on the basis of the line widths of the XRD peaks for the as-synthesized LaPO₄ nanoparticles is approximately 7 nm, which is consistent with the TEM estimation (see the Supporting Information). For comparison, a high-surfacearea LaPO₄ sample with a monoclinic structure (Sigma-Aldrich; see the XRD pattern in Figure 3b) was also used as a



support in the preparation of Au nanocatalysts. The average particle size estimated from the line widths of the XRD peaks is approximately 10 nm, which accounts well for the relatively small surface area ($55 \text{ m}^2 \text{g}^{-1}$) of this LaPO₄-M sample. The gold precursor species were introduced on the hexagonal LaPO₄ (termed Au/LaPO₄-H) and the monoclinic LaPO₄ (termed Au/LaPO₄-M) samples using a deposition–precipitation (DP) method originally developed by Haruta and coworkers.^[52] The Au loadings of Au/LaPO₄-H and Au/LaPO₄-M are 8.3 and 4.2 wt %, respectively. However, both catalysts have almost the same Au areal density for gold through normalization with respect to their corresponding surface areas. A TiO₂-supported Au reference nanocatalyst (termed Au/TiO₂-R) supplied by the World Gold Council was also used in catalyst testing for comparative purposes.

The light-off curves for CO oxidation were measured from low conversion to 100% conversion for the above three gold catalysts with and without treatment at 500°C in 8% O₂/He for 2 h. The high-temperature calcination treatment is a very stringent test for the stability of gold nanocatalysts against sintering.^[47,53] Conventional TiO₂-supported gold nanocatalysts are known to be readily deactivated under such conditions.^[47] The sample weights of the three Au catalysts used in our plug-flow reactor tests were adjusted to maintain a constant Au content of 0.75 mg.

Figure 1 a shows a comparison of the light-off curves for the three catalysts without the high-temperature calcination treatment. Based on these curves, the temperatures at which the specific rate reaches $0.66 \text{ mol}_{CO} g_{Au}^{-1} h^{-1}$ (50% conver-



Figure 1. Light-off curves of a) as-synthesized and b) calcined Au/ LaPO₄-H, Au/LaPO₄-M, and Au/TiO₂-R.

sion) were obtained for Au/LaPO₄-H, Au/LaPO₄-M, and Au/ TiO₂-R (Figure 2). All the catalysts are very active, with Au/ LaPO₄-M having the highest activity. However, after calcination at 500 °C in 8 % O₂/He for 2 h (heating rate: 10 °C min⁻¹),



Figure 2. Temperature at which the specific rate reached 0.66 mol_{co} $g_{Au}^{-1}h^{-1}$ (50% conversion) for Au/LaPO₄-H, Au/LaPO₄-M, and Au/TiO₂-R.

the activity sequence changed totally (see Figure 1b). Surprisingly, Au/LaPO₄-H was activated strongly, while both Au/LaPO₄-M and Au/TiO₂-R were deactivated. The latter observation is consistent with previous reports^[14,15,54] showing that Au catalysts on oxide supports can be readily deactivated through sintering induced by calcination at high temperature (e.g., 500°C). The calcined Au/LaPO₄-H unexpectedly reached the specific rate of 0.66 mol_{CO} g_{Au}⁻¹h⁻¹ (50 % conversion) at a temperature as low as -71°C, whereas 41 and 6°C were required for Au/LaPO₄-M and Au/TiO₂-R to reach this specific rate, respectively (Figure 2). However, a slow conversion-increasing step in the light-off curve of Au/LaPO₄-H from -50 to -40°C was observed, which might be indicative of carbonate formation at low temperature.^[55]

To rule out the possibility that the observed activation at 500 °C was induced by potential amorphous La₂O₃ impurities, a gold catalyst supported on La₂O₃ (Au/La₂O₃) was prepared.^[25] The catalysis test shows that Au/La₂O₃ can be readily deactivated by calcination at 500 °C in 8% O₂/He, which indicates that the structure of LaPO₄-H is the key to the observed activation process. Accordingly, the considerable activation of the Au/LaPO₄-H system by calcination at 500 °C in 8% O₂/He is very unusual.

Figure 3a shows the XRD pattern of the as-synthesized Au/LaPO₄-H; no metallic gold peaks are visible. The Au loading of Au/LaPO₄-H is as high as 8.3 wt % based on inductively couple plasma (ICP) analysis, and thus it is reasonably inferred that the absence of the Au peaks in the XRD pattern of the as-synthesized Au/LaPO₄-H sample can be related to the cationic nature of the Au precursors. Another interesting phenomenon which can be clearly seen from Figure 3a is that the XRD line widths of the LaPO₄-H sample remain broad after calcination at 500 °C. This observation further supports the fact that the LaPO₄-H nanoparticles are highly sinter-resistant. However, a very broad gold XRD peak at $2\theta \approx 38.2^{\circ}$ and a weak peak at $2\theta \approx 44.5^{\circ}$ appeared. This observation suggests that metallic Au nanoparticles with a very small particle size (≈ 2 nm,

Angew. Chem. Int. Ed. 2006, 45, 3614-3618

© 2006 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

Communications



Figure 3. a) Comparison of the simulated XRD patterns of Au and hexagonal LaPO₄ with the experimental XRD patterns of the assynthesized LaPO₄-H nanoparticles and both as-synthesized and calcined Au/LaPO₄-H. b) Comparison of the simulated XRD patterns of Au and monoclinic LaPO₄ with the experimental XRD patterns of asreceived LaPO₄-M, and as-synthesized and calcined Au/LaPO₄-M.

Figure 4b) were formed during calcination through autoreduction.

In contrast, the situation is very different with respect to the calcined Au/LaPO₄-M sample. Two sharp XRD peaks attributed to metallic gold particles appeared in its XRD pattern, which indicate the formation of much larger gold particles during calcination (Figure 3b). This observation is in agreement with the trend of the corresponding catalytic activities for CO oxidation and shows that the catalytic activity of Au/LaPO₄-H is much higher than that of Au/ LaPO₄-M. Clearly, this observed difference can be correlated to the size of the gold nanoparticles. As discussed above, the areal density of Au for Au/LaPO₄-H and LaPO₄-M is very similar. Accordingly, the dispersion of gold nanoparticles on both substrates should be basically identical and have a similar stability against sintering if the surface properties of both LaPO₄-H and LaPO₄-M are similar. This is clearly in contradiction to our experimental observations. Thus, a stronger surface interaction of metallic gold species with LaPO₄-H than LaPO₄-M is indicated.

Our microscopy investigations provide further support for the strong interaction of metallic gold species with $LaPO_4$ -H. As seen in Figure 4 a, imaging with a high-angle annular darkfield (HAA-DF, also known as Z-contrast) scanning trans-



Figure 4. Z-contrast TEM image of a) as-synthesized Au/LaPO₄-H, b) calcined Au/LaPO₄-H, c) as-synthesized Au/LaPO₄-M, and d) calcined Au/LaPO₄-M. Scale bar = 20 nm.

mission electron microscope (STEM) shows tiny, highly uniform Au nanoparticles (0.8–2.0 nm diameter) distributed on LaPO₄-H for the as-synthesized Au/LaPO₄-H. Figure 5 a shows a high-resolution TEM (HRTEM) image of the same material. The Au particles in the as-synthesized form are quite small and uniform with a mean size of about 1–2 nm, which is consistent with STEM analyses. The gold precursors exist in a



Figure 5. HRTEM images of a) as-synthesized and b) calcined Au/ $LaPO_4$ -H. For details, see text.

cationic form on LaPO₄-H, and thus the lattice structure of the Au nanoparticles is not very clear in the HRTEM image. After high-temperature calcination, the Z-contrast image recorded on Au/LaPO₄-H at an identical magnification shows slight growth of the gold nanoparticles (Figure 4b) as a result of high-temperature sintering. The average size of the Au nanoparticles reaches 2-4 nm. The sintering of the gold nanoparticles of Au/LaPO₄-M (Figure 4c and d) is much more severe, which agrees with the above XRD observation and further indicates that the interaction of LaPO₄-H with gold nanoparticles is stronger than that of LaPO₄-M. The HRTEM image shown in Figure 5b clearly reveals the crystalline nature of the resulting Au metallic nanoparticles of calcined Au/LaPO₄-H. The distance between two (111) lattice planes measured from the HRTEM image is approximately 2.35 Å, which is consistent with the value of 2.36 Å measured from an Au model structure with the MS modeling program supplied by Accelrys (see the middle inset of Figure 5b). The top-right inset of Figure 5b is the electrondiffraction pattern of this Au nanoparticle, which demonstrates nicely the crystalline structure of the metallic particles.

The high dispersion and well-developed crystalline structure revealed by HRTEM for the Au nanoparticles supported on LaPO₄-H provide structural evidence for the unusual activation of the Au/LaPO₄-H system by calcination at 500 °C in 8% O₂/He. Our selected-area electron diffraction study indicates that the gold nanoparticles are mainly attached epitaxially on LaPO₄-H through the most densely packed (111) plane (Figure 5).^[55] This activation process under the oxidative conditions is in sharp contrast to those required for the oxide-supported catalyst system.^[47,48] Based on the SMSI model, the latter system requires the reduction of support oxides to invoke SMSI. The negligible reducibility of LaPO₄ implies that Au/LaPO₄-H needs to rely on other means of activation to enhance SMSI. One possible activation mechanism during the calcination of Au/LaPO₄-H could involve the surface restructuring of the gold/support interfaces. Deactivation of Au/LaPO₄-M was observed under the same calcination conditions, and hence the surface restructuring might be unique to the specific surface configuration of LaPO₄-H. Clearly, the smaller particle size of the LaPO₄-H support may play a key role in this surface-restructuring process through the supply of a high surface-defect concentration relative to that of the LaPO₄-M support. This observation is very similar to that of Corma and co-workers, which showed that gold nanoparticles deposited on CeO₂ nanocrystals by co-precipitation yielded an activity for CO oxidation that was two orders of magnitude higher than that for particles deposited on bulk CeO2.^[43] The unique restructuring properties of nanoparticles with ionic lattices have been recently revealed and utilized in the generation of new nanoparticle phases.[8,56]

In conclusion, a new non-oxide support system based on $LaPO_4$ nanoparticles has been developed for gold catalysts used in CO oxidation. The key feature of this catalytic system is that activation can be achieved through calcination under an oxidative atmosphere. This observation is in sharp contrast to conventional SMSI catalytic systems, which can only be activated under a reductive atmosphere. The high stability

and activity of the gold nanoparticles deposited on the LaPO₄ nanoparticles suggest a unique interaction between the gold and the phosphate support, which highlights new opportunities in the development of ultrastable gold catalysts for reactions in oxidative and high-temperature environments.

Received: October 27, 2005 Revised: February 11, 2006 Published online: April 26, 2006

Keywords: gold \cdot lanthanum \cdot nanoparticles \cdot oxidation \cdot supported catalysts

- M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, J. Catal. 1989, 115, 301.
- [2] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M. J. Genet, B. Delmon, J. Catal. 1993, 144, 175.
- [3] G. C. Bond, D. T. Thompson, Catal. Rev. Sci. Eng. 1999, 41, 319.
- [4] G. J. Hutchings, Catal. Today 2002, 72, 11.
- [5] M. C. Daniel, D. Astruc, Chem. Rev. 2004, 104, 293.
- [6] C. W. Corti, R. J. Holliday, D. T. Thompson, *Appl. Catal. A* 2005, 291, 253.
- [7] G. J. Hutchings, Catal. Today 2005, 100, 55.
- [8] D. H. Son, S. M. Hughes, Y. D. Yin, A. P. Alivisatos, *Science* 2004, 306, 1009.
- [9] F. Moreau, G. C. Bond, A. O. Taylor, Chem. Commun. 2004, 1642.
- [10] M. Valden, X. Lai, D. W. Goodman, Science 1998, 281, 1647.
- [11] W. F. Yan, B. Chen, S. M. Mahurin, S. Dai, S. H. Overbury, *Chem. Commun.* 2004, 1918.
- [12] M. S. Chen, D. W. Goodman, Science 2004, 306, 252.
- [13] E. E. Stangland, K. B. Stavens, R. P. Andres, W. N. Delgass, J. Catal. 2000, 191, 332.
- [14] S. D. Lin, M. Bollinger, M. A. Vannice, Catal. Lett. 1993, 17, 245.
- [15] W. F. Yan, S. M. Mahurin, Z. W. Pan, S. H. Overbury, S. Dai, J. Am. Chem. Soc. 2005, 127, 10480.
- [16] J. D. Grunwaldt, C. Kiener, C. Wogerbauer, A. Baiker, J. Catal. 1999, 181, 223.
- [17] W. F. Yan, B. Chen, S. M. Mahurin, E. W. Hagaman, S. Dai, S. H. Overbury, J. Phys. Chem. B 2004, 108, 2793.
- [18] J. D. Grunwaldt, A. Baiker, J. Phys. Chem. B 1999, 103, 1002.
- [19] M. A. P. Dekkers, M. J. Lippits, B. E. Nieuwenhuys, *Catal. Lett.* 1998, 56, 195.
- [20] W. F. Yan, S. M. Mahurin, B. Chen, S. H. Overbury, S. Dai, J. Phys. Chem. B 2005, 109, 15489.
- [21] B. Schumacher, V. Plzak, J. Cai, R. J. Behm, Catal. Lett. 2005, 101, 215.
- [22] M. J. Kahlich, H. A. Gasteiger, R. J. Behm, J. Catal. 1999, 182, 430.
- [23] F. Boccuzzi, A. Chiorino, M. Manzoli, D. Andreeva, T. Tabakova, J. Catal. 1999, 188, 176.
- [24] M. M. Schubert, S. Hackenberg, A. C. van Veen, M. Muhler, V. Plzak, R. J. Behm, J. Catal. 2001, 197, 113.
- [25] G. Y. Wang, W. X. Zhang, Y. C. Cui, H. L. Lian, D. Z. Jiang, T. H. Wu, *Chin. J. Catal.* **2001**, *22*, 408.
- [26] N. S. Patil, B. S. Uphade, D. G. McCulloh, S. K. Bhargava, V. R. Choudhary, *Catal. Commun.* 2004, 5, 681.
- [27] M. Daté, M. Okumura, S. Tsubota, M. Haruta, Angew. Chem. 2004, 116, 2181; Angew. Chem. Int. Ed. 2004, 43, 2129.
- [28] S. H. Overbury, L. Ortiz-Soto, H. G. Zhu, B. Lee, M. D. Amiridis, S. Dai, *Catal. Lett.* **2004**, *95*, 99.
- [29] M. T. Bore, H. N. Pham, E. E. Switzer, T. L. Ward, A. Fukuoka, A. K. Datye, J. Phys. Chem. B 2005, 109, 2873.
- [30] G. K. Bethke, H. H. Kung, Appl. Catal. A 2000, 194, 43.

Communications

- [31] C. K. Costello, M. C. Kung, H. S. Oh, Y. Wang, H. H. Kung, *Appl. Catal. A* 2002, 232, 159.
- [32] A. Knell, P. Barnickel, A. Baiker, A. Wokaun, J. Catal. 1992, 137, 306.
- [33] B. Yoon, H. Hakkinen, U. Landman, A. S. Worz, J. M. Antonietti, S. Abbet, K. Judai, U. Heiz, *Science* 2005, 307, 403.
- [34] J. Guzman, B. C. Gates, J. Am. Chem. Soc. 2004, 126, 2672.
- [35] L. M. Molina, B. Hammer, *Phys. Rev. Lett.* **2003**, *90*, 206102.
- [36] G. J. Hutchings, M. R. H. Siddiqui, A. Burrows, C. J. Kiely, R. Whyman, J. Chem. Soc. Faraday Trans. 1997, 93, 187.
- [37] G. Y. Wang, W. X. Zhang, H. L. Lian, D. Z. Jiang, T. H. Wu, *Appl. Catal. A* 2003, 239, 1.
- [38] F. Boccuzzi, A. Chiorino, S. Tsubota, M. Haruta, J. Phys. Chem. 1996, 100, 3625.
- [39] S. J. Lee, A. Gavriilidis, Q. A. Pankhurst, A. Kyek, F. E. Wagner, P. C. L. Wong, K. L. Yeung, J. Catal. 2001, 200, 298.
- [40] G. B. Hoflund, S. D. Gardner, D. R. Schryer, B. T. Upchurch, E. J. Kielin, *Appl. Catal. B* **1995**, *6*, 117.
- [41] F. Marino, C. Descorme, D. Duprez, Appl. Catal. B 2004, 54, 59.
- [42] Q. Fu, A. Weber, M. Flytzani-Stephanopoulos, *Catal. Lett.* 2001, 77, 87.
- [43] S. Carrettin, P. Concepcion, A. Corma, J. M. L. Nieto, V. F. Puntes, Angew. Chem. 2004, 116, 2592; Angew. Chem. Int. Ed. 2004, 43, 2538.
- [44] J. Guzman, A. Corma, Chem. Commun. 2005, 743.
- [45] A. Sanchez, S. Abbet, U. Heiz, W. D. Schneider, H. Hakkinen, R. N. Barnett, U. Landman, J. Phys. Chem. A 1999, 103, 9573.
- [46] U. Heiz, W. D. Schneider, J. Phys. D 2000, 33, R85.
- [47] D. W. Goodman, Catal. Lett. 2005, 99, 1.
- [48] S. J. Tauster, S. C. Fung, R. L. Garten, J. Am. Chem. Soc. 1978, 100, 170.
- [49] L. Prati, G. Martra, Gold Bull. 1999, 32, 96.
- [50] M. M. Maye, N. N. Kariuki, J. Luo, L. Han, P. Njoki, L. Y. Wang, Y. Lin, H. R. Naslund, C. J. Zhong, *Gold Bull.* **2004**, *37*, 217.
- [51] S. S. Brown, H. J. Im, A. J. Rondinone, S. Dai, J. Colloid Interface Sci. 2005, 292, 127.
- [52] S. Tsubota, M. Haruta, T. Kobayashi, A. Ueda, Y. Nakahara, Stud. Surf. Sci. Catal. 1991, 63, 695.
- [53] B. K. Min, W. T. Wallace, D. W. Goodman, J. Phys. Chem. B 2004, 108, 14609.
- [54] W. F. Yan, B. Chen, S. M. Mahurin, V. Schwartz, D. R. Mullins, A. R. Lupini, J. Pennycook, S. Dai, S. H. Overbury, *J. Phys. Chem. B* 2005, *109*, 10676.
- [55] M. Haruta, CATTECH 2002, 6, 102.
- [56] H. Z. Zhang, B. Gilbert, F. Huang, J. F. Banfield, *Nature* 2003, 424, 1025.