
Nanostructured, Metal-Ion Modified Ceria and Zirconia Oxidation Catalysts

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properties of the oxide support, and with potentially higher stability for the practical application than the current generation of catalysts.

Abstract

The project, in its second year in 2007, involves a close collaboration between investigators at Tufts and Columbia Universities aimed at the design and evaluation of novel oxidation catalysts based on nanoscale ceria and doped cerium oxide carrying metal ions and clusters strongly bound on the surface and subsurface layers of the oxide matrices. A well-controlled synthesis of monodispersed ceria nanoparticles, also yielding a significant fraction of Ce^{3+} recently developed at Columbia University,¹ is one of the methods under investigation to produce nanoscale ceria and doped ceria. This is a solution preparation at room temperature resulting in single crystals of ceria octahedra with (111) surfaces, or truncated octahedra with extra (100) surfaces. The (100) surfaces are known to have more intrinsic oxygen vacancies due to charge balance. The vacancies can stabilize the added metal ions and readily participate as sinks and sources of oxygen in catalytic redox reactions. Particles with special surface planes will be exploited in this project to answer some of the fundamental questions. A number of key analytical techniques, such as *in situ* Raman and UV-VIS (DRS), HREM, and STM/STS, are used to characterize surface metal cluster-oxygen defect complexes, to follow catalyst structural changes, and correlate them to reactivity. The reactions under study at Tufts include the water-gas shift reaction, selective CO oxidation, and steam reforming of methanol, all important reactions in hydrogen generation. Time-resolved XAS, *in situ* XANES and EXAFS experiments will be performed at Brookhaven National Lab under the direction of senior researchers J. Rodriguez and J. Hanson.

Objectives

This project is based on a recent finding by the PI's group at Tufts University that the activity of ceria-supported gold or platinum catalysts for the water-gas shift reaction is not due to the presence of metal nanoparticles. Rather, $[Au_n-O-Ce]$ or $[Pt_n-O-Ce]$ sites are responsible for the reaction activity. The overall goal of this project is to elucidate the role of metal ions and metal clusters as catalytic sites on nanoscale oxide supports, and the role of oxide defects in stabilizing the metal species in an active state for reactions of interest to fuel reforming for hydrogen generation. Novel synthesis (with size and facet control) and characterization methods are investigated in the project to meet this goal and guide the design and development of practical catalysts for low-cost hydrogen production.

Technical Barriers

Traditional catalysts used for the water-gas shift and other fuel processing reactions in the production of clean hydrogen must be replaced in order to meet the more stringent requirements of practical fuel cell systems, including air and moisture stability, resistance to poisons, no methanation activity, and longevity required for efficient energy production. Platinum group metals are being brought into this area of catalysis to meet these requirements. Successful demonstration and development of our technology will overcome the cost associated with implementation of platinum metal catalysts on a large scale. This will be accomplished by designing catalysts with a minimum loading of gold, copper or platinum, in amounts dictated by the surface

Project Report and Future Directions

Since the project start in late 2005, progress has been made on several fronts. On the catalysis side at Tufts University, a new method was identified to stabilize the activity of Au- and Pt-ceria catalysts for the water-gas shift reaction in cyclic start-stop operation, and after shutdown to ambient conditions.² This is achieved with the addition of a very small amount of gaseous oxygen in the fuel gas mixture that keeps the cerium oxide from forming Ce (III)hydroxycarbonate and deactivate.

At Columbia, the investigation of Ce-Zr-O phase stability as a function of nanoparticle size has come to a satisfactory conclusion. In particular, it was found that the stability range of ceria solid solutions extends to 90%

ZrO₂ when annealed in a reducing atmosphere³. Further work will focus on correlating the 600cm⁻¹ Raman peak, identified with oxygen vacancies, with the Ce³⁺ concentrations measured by XANES for pure ceria of different particle size and for Ce-Zr-O with different Zr content. With proper processing, pure nano ZrO_{2-y} can be maintained in cubic form. The amorphous to cubic transition was captured in a time-resolved in-situ X-ray diffraction⁴.

In recent work⁵⁻⁷, we have shown the importance of the interaction between gold or platinum and the oxygen of ceria by identifying that only the oxidized gold or platinum species strongly bound to ceria, [Au_n-O-Ce] or [Pt_n-O-Ce], are the active sites for the WGS reaction. In this project, we have evaluated different catalyst preparation techniques to maximize the number of M-O-S sites. Firstly, among various synthesis methods (IMP, DP and UGC), the UGC method was found the best for the preparation of nano-ceria (3 nm particle size) with more oxidized Pt species strongly bound to it, as evidenced by XPS and H₂-TPR.⁸ A high stability of Pt/CeO_x in realistic reformat gases was found, unlike what has been reported in the literature⁹. In the same paper, oxygen gas addition (~1mol%) in the reformat gas mixture was shown to effectively prevent the deactivation of the PtCeO_x catalysts during RT shutdown/re-start cycles.

Secondly, we found that the dry CO oxidation reaction is much more facile on Au⁰ than on oxidized gold clusters in Au-CeO₂ catalysts. In collaboration with the group of Flora Boccuzzi, U. Torino, we found by FTIR that CO binds stronger on Au⁰ than on the Au_n⁺ clusters¹⁰. XANES, TPR and XPS of the fresh and used catalysts were performed to demonstrate the high stability of ionic gold in ceria up to 393 K in the reaction gas.

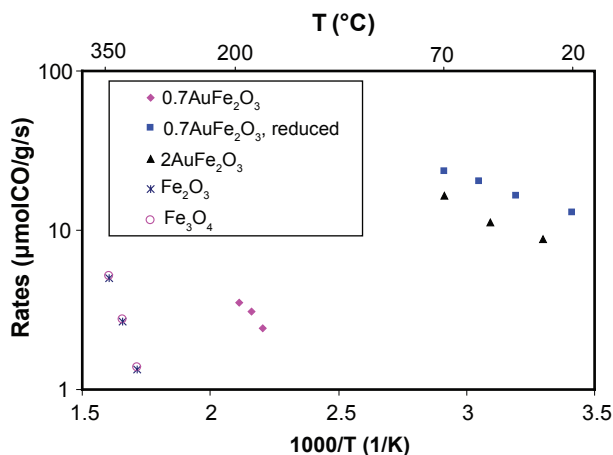


FIGURE 1. Steady-state CO oxidation reaction rates over gold-iron oxide catalysts measured in a gas composed of 2%CO-1%O₂-balance He¹¹.

In the literature, most catalysts incorporating Au⁰ also contain cationic gold and it is very difficult to separate the function of the one from the other. In work carried out at Tufts last year¹¹, we were able to prepare the low-content gold catalysts with only oxidized gold species strongly bound to both supports (iron oxide and ceria). As shown in Figure 1, the activity of the leached gold-iron oxide in CO oxidation is two orders of magnitude lower than that of the parent material. Once reduced, the catalyst activity increases more than 100 times. XANES, XPS, TPR and UV-Vis analyses show that reduction is needed to activate the catalyst. On the other hand, the WGS reaction rates are similar for samples containing both Au⁰/Au_n⁺ or Au_n⁺ clusters only. The activation energies are the same, 49±7 kJ/mol, for Au on ceria or iron oxide. Thus, activation of -OH from the oxide support by the strongly bound CO on Au^{δ+} sites is a plausible mechanism for this reaction.

In collaboration with researchers from Queens University, Belfast, we investigated the WGS reactivity of species formed on the surface of 0.6 at.%Au/Ce(La)_xO_x by DRIFTS during steady-state isotopic transient kinetic analyses (SSITKA). The formation of CO₂ and the disappearance of formate and carbonate surface species were followed by isotopic exchange of CO in a DRIFT cell reactor. The rate of CO₂ formation was more than 10x higher than the rate of formate decomposition, indicating that formates seen by DRIFTS are not the key reaction intermediates¹².

Recently, we improved our synthetic strategy for gold-doped by (1) one-step precipitation of different metal ions (Au³⁺, Ce⁴⁺, etc.) under optimized experimental parameters (base, pH value, etc.) to prepare a metal hydroxide solid-solution; and (2) calcination of the dried samples at 400 °C for 10 h in air to obtain gold-oxide composite with various nanostructures. Here, we show two of the Au doped CeO₂-ZrO₂-La₂O₃ samples prepared *via* this co-precipitation (CP) method.

Table 1 shows that the particle sizes and surface areas for both NaOH- and NH₃·H₂O-precipitated samples were very close. Thus, the synthesis conditions had little effect on the textural properties of the calcined CeO₂-ZrO₂-La₂O₃ support. However, the Au-doped materials had different reducibilities and activities in the CO oxidation reaction. H₂-TPR tests were carried out from RT to 200°C (5°C/min) in 20% H₂/N₂. Figure 2 and Table 1 show that the reduction peak temperatures for the NaOH-precipitated sample were much lower than that for the NH₃·H₂O-precipitated one. The latter contained an atomic distribution of gold strongly bound to ceria. A larger amount of surface oxygen was measured on this sample, but its activity for the CO oxidation reaction was inferior to the NaOH-precipitated sample, as can be seen in Table 1.

TABLE 1. Synthesis Conditions and Characterizations of $\text{Au}_{0.02}\text{Ce}_{0.68}\text{Zr}_{0.21}\text{La}_{0.09}\text{O}_x$ Samples

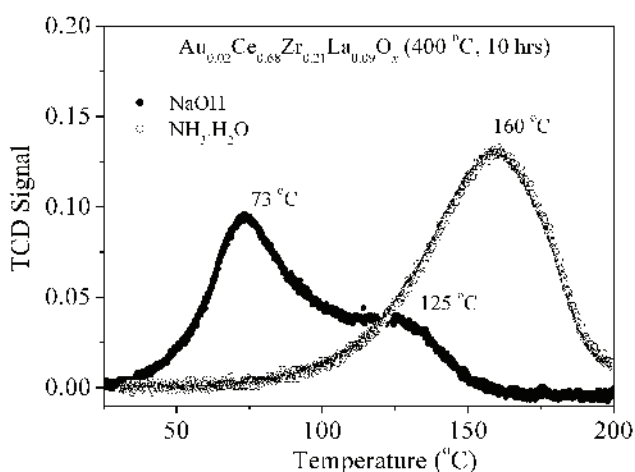
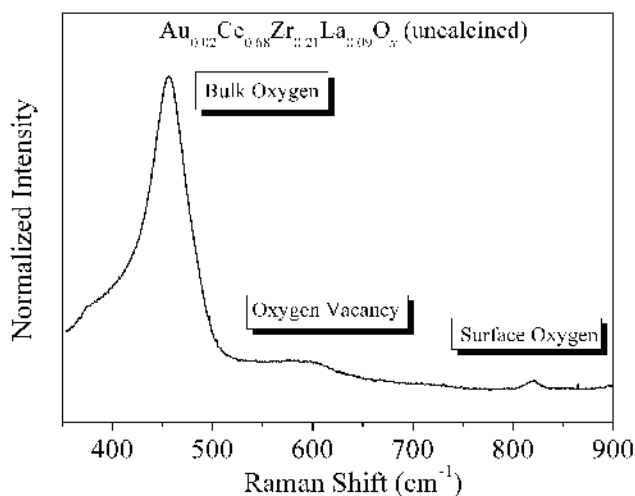
Base	pH value	Particle size ^b	Surface area	Reduction Peak ^c	H ₂ consumption ^c	T ₁₀₀ ^d
NaOH	12–13	4.7 ± 0.7 nm	158 m ² /g	73°C, 125°C	580 μmol/g	150°C
NH ₃ ·H ₂ O	8–9	5.0 ± 0.7 nm	131 m ² /g	160°C	750 μmol/g	250°C

a: Determined by ICP;

b: calculated from ~100 particles in TEM;

c: obtained from H₂-TPR;

d: temperature of 100% conversion of CO oxidation reaction

**FIGURE 2.** H₂-TPR of the Calcined Samples**FIGURE 3.** Raman Spectrum of the Uncalcined Sample

Raman spectra were obtained at RT in air by Ar ion excitation (488 nm). An example is shown in Figure 3. A strong peak at ~460 cm⁻¹, a weak one at ~820 cm⁻¹ and another weak band at ~600 cm⁻¹ are seen, assigned to bulk oxygen, surface-adsorbed peroxide and oxygen vacancies, respectively¹⁵. *In situ* Raman under WGS reaction conditions will identify the importance of

different oxygen species. STM/STS studies currently underway at Columbia, and *in situ* EXAFS experiments at BNL will be used to study the evolution of gold clusters under reaction conditions.

References

1. F. Zhang, S.-W. Chan, J.E. Spanier, E. Apak, Q. Jin, R.D. Robinson, and I.P. Herman, *Appl. Phys. Lett.*, **80**(1) (2002) 127-9.
2. W. Deng and M. Flytzani-Stephanopoulos, *Angew. Chem. Int. Ed.* **45** (2006) 2285-2289.
3. F. Zhang, J. M. Raitano, C.-H. Chen, J. C. Hanson, W. Caliebe, S. Khalid, and S.-W. Chan, *J. Appl. Phys.*, **99** (2006) 0843131-0843138.
4. F. Zhang, P.J. Chupra, S. Lun, A. Lui, J. C. Hanson, W. A. Calieb, P. L. Lee, and Siu-Wai Chan, submitted to *Chemistry of Materials*, 2006.
5. Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science* **301** (2003) 935.
6. Q. Fu, W. Deng, H. Saltsburg, M. Flytzani-Stephanopoulos, *Appl. Catal. B* **56** (2005) 57.
7. Q. Fu, S. Kudriavtseva, H. Saltsburg, M. Flytzani-Stephanopoulos, *Chem. Eng. J.* **93**(2003)41.
8. D. Pierre, W. Deng, M. Flytzani-Stephanopoulos, Invited paper, *Topics in Catalysis*, in press.
9. J.M. Zalac, V.Sokolovskii, D.G.Loffler, *J.Catalysis* **206** (2002) 169.
10. M. Manzoli, F. Boccuzzi, W. Deng, M. Flytzani-Stephanopoulos, *J. Catal.* **245** (2007)306.
11. W. Deng, C. Carpenter, N. Yi, and M. Flytzani-Stephanopoulos, *Topics in Catalysis*, in press.
12. F. C. Meunier, D. Reid, A. Goguet, S. Shekhtman, C. Hardacre, R. Burch, W. Deng, M. Flytzani-Stephanopoulos, *J. Catalysis*, in press.
13. J. Guzman, S. Carrettin, A. Corma, *J. Am. Chem. Soc.* **127** (2005) 3286.

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