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## Active Nonmetallic Au and Pt Species on Ceria-Based Water-Gas Shift Catalysts

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**Traditional analysis of reactions catalyzed by supported metals involves the structure of the metallic particles. However, we report here that for the class of nanostructured Au- or Pt-cerium oxide catalysts, which are active for the water-gas shift reaction, metal nanoparticles do not participate in the reaction. Non-metallic Au or Pt species strongly associated with surface Ce-O groups are responsible for the activity.**

The heterogeneously catalyzed water-gas-shift (WGS) reaction ( $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ ) is a key step in fuel processing to generate  $\text{H}_2$ . Such catalysts should combine both high activity and structural stability in air and in cyclic operation; these are stringent requirements not met by the commercially available low-temperature WGS catalysts. A new class of WGS catalysts based on cerium oxide (ceria) has been investigated extensively in recent years (1–6). To provide low-temperature WGS activity, Pt-group metals (PM), Au or Cu are suitably added in amounts varying from ~1 to 10 wt%. A critical problem with a Pt/ceria catalyst is its prohibitive economics (3), due to the cost of Pt, even if its issues of deactivation with time-on-stream are resolved. However, ceria containing only trace amounts of Pt would be economical. Similarly attractive would be ceria containing base metals or oxides. We have reported recently that an excellent shift catalyst results by supporting gold or copper on nanocrystalline ceria (4–6). This type of catalyst, if properly developed, would of course be much more economical, i.e. practical for large-scale fuel cell application. We show here that low loadings of metal can be as effective as much higher loadings.

The PM/ceria catalysts have received considerable attention because of their use in the automobile catalytic converter (7, 8). It is widely accepted that the oxygen of ceria plays an important role in the reaction pathway (1, 4, 9). However, identification of the active sites for low-temperature CO oxidation, WGS, and other oxidation reactions on PM/ceria catalysts remains an issue of contention. In most reports, the active sites are placed at the metal-ceria interface (1, 9), while in others Pt ions dispersed on the surface of ceria are assumed active (10). Encapsulation of Pt by reduced ceria nanoparticles has also been proposed (11).

In the work reported here all catalyst components are nanocrystalline. Nanocrystalline ceria can be prepared by various techniques (2, 4). Ceria particles with diameter less than 10 nm have extremely increased electronic conductivity (12), and doping with a rare earth oxide, such as  $\text{La}_2\text{O}_3$ , can be used to create oxygen vacancies, and stabilize ceria particles against sintering (13). We have prepared such nanosize La-doped ceria in this work and deposited Au or Pt

on it. After thermal annealing, these materials have excellent and as yet unexplained properties for low-temperature WGS. Au or Pt exists as nanosize particles and in ionic state in these catalysts. We report that the catalytic activity is not affected by the removal of metallic gold or platinum particles by cyanide leaching. Thus, metallic nanoparticles are not necessary for the activity; they are mere spectators in WGS. Non-metallic gold or platinum species embedded in ceria are shown to catalyze the reaction of CO with  $\text{H}_2\text{O}$ .

Most of the gold-ceria catalysts presented in this report were prepared by the same technique; ceria (doped with 10 at% La) was synthesized by urea gelation/coprecipitation (UGC) (4) and then calcined in air at 400°C for 10 hours. This treatment produced ceria with a mean particle size ~5 nm (5) with a surface area of ~150 m<sup>2</sup>/g. Gold was then applied onto ceria by deposition-precipitation (DP) (5) at room temperature via dropwise addition of  $\text{HAuCl}_4$  into a suspension of the ceria particles in an aqueous solution of  $(\text{NH}_4)_2\text{CO}_3$  at constant pH (~8). After several washes and drying, the Au-ceria particles were calcined in air at 400°C for 10 hours. Most of the Au thus prepared is in the form of metal nanoparticles, ~5 nm avg. size (5, 6). The deposition step has a negligible effect on the total surface area of ceria. For comparison, we also report on a Au-ceria sample prepared by a single co-precipitation step (CP). This involved mixing an aqueous solution of  $\text{HAuCl}_4$ ,  $\text{Ce}(\text{NO}_3)_3$  and  $\text{La}(\text{NO}_3)_3$  with  $(\text{NH}_4)_2\text{CO}_3$  at 60 to 70°C, keeping a constant pH (~8) and aging the precipitate at the same temperature for 1h. Leaching of gold took place in an aqueous solution of 2% NaCN at room temperature. Sodium hydroxide was added to keep the pH at ~12. [This same process is used to extract gold during gold mining (14).] No Ce or La was found in the leachate. The leached samples were washed, dried (120°C, 10 hours) and heated in air (400°C, 2 hours). More than 90% of the gold loading was removed from the ceria by this leaching procedure. Scanning transmission electron microscopy/EDX showed no gold particles remaining, only what appeared to be very fine clusters or atomically dispersed gold. X-ray photoelectron spectroscopy (XPS) identified ionic gold as the major or only gold species present in the leached materials (see below).

A similar procedure was used to remove 'excess' Pt from the ceria surface. First, Pt-ceria was prepared by incipient wetness impregnation (IMP). La-doped ceria powders were prepared by UGC as described above. They were then impregnated with an aqueous solution of  $\text{H}_2\text{PtCl}_6$  of appropriate concentration, whose volume equaled the total pore volume of ceria. After impregnation, the samples were degassed and dried at room temperature under vacuum. After drying in a vacuum oven at 110°C for 10 hours, the samples were crushed and calcined in air at 400°C for 10 hours. Calcined Pt-ceria samples were leached by the same

procedure as the gold catalysts; the leached sample is denoted as Pt-CL(IMP, NaCN1). To further reduce the amount of Pt, Pt-CL(IMP, NaCN1) was leached in 2% NaCN solution at 80°C for 12 hours. The corresponding sample is denoted as Pt-CL(IMP, NaCN2). The properties of Au- and Pt-ceria samples prepared and tested in this work are presented in Table 1.

Arrhenius-type plots of the WGS reaction rate measured over the as prepared Au-ceria catalysts and the Au-free ceria (CL) are shown in Fig. 1. The reacting gas mixture simulates a reformat gas composition: 11% CO, 7% CO<sub>2</sub>, 26% H<sub>2</sub>, 26% H<sub>2</sub>O, in an inert gas carrier. Activation of catalysts was not necessary (15). Similar rates of CO<sub>2</sub> production (per m<sup>2</sup> catalyst surface area) were measured over the parent [4.4 (CP), 4.7 (DP) or 2.8 (DP) at% Au] and the corresponding leached (0.7, 0.44 or 0.23 at% Au) ceria catalysts. The apparent activation energy E<sub>a</sub> for the reaction is the same for parent and leached catalysts, 47.8 ± 1.5 kJ/mol for the DP and 36.8 ± 0.9 kJ/mol for the CP samples. The rate over the Au-free nanosize CL sample was much lower over the temperature range of interest, with an E<sub>a</sub> of 83 kJ/mol. Also shown in Fig. 1 is the rate measured over a commercial Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> (UCI, G-66A) low-temperature WGS catalyst, which contains 42 wt% Cu. Although the rate is greater over this catalyst, the use of the latter in fuel cell applications is highly unlikely due to its air sensitivity and narrow operating temperature window. Moreover, a careful activation in H<sub>2</sub> is required for Cu/ZnO catalysts. However, ceria-based WGS catalysts require no activation and are not air sensitive.

The data in Fig. 1 show that the reaction pathway on the Au-ceria catalysts is different than that on Au-free ceria. Also, only the Au species present on the leached catalyst are associated with the active sites, because the extra Au present in the parent material does not increase the rate; nor does it change the E<sub>a</sub> for the reaction. If we assume complete dispersion of Au in the leached catalysts, we can calculate the turnover frequency from the data of Fig. 1. For example, at 300°C, the TOF is 0.65 molecules of CO<sub>2</sub>/Au atom per second.

In kinetic studies with the Pt-ceria catalysts (16) (fig. S1), the E<sub>a</sub> over the parent (3.7 at% Pt) and the leached Pt-ceria (2.7 or 1.5 at% Pt) was the same, 74.8 ± 0.6 kJ/mol. The WGS rate over these samples was similar. The isokinetic temperature for the Pt- and Au-ceria (DP) samples is 250°C. Transient light-off curves for WGS over the Pt-ceria catalysts are shown in Fig. 2, collected in temperature-programmed reaction mode. These profiles were reproduced after cooling down from the high end-point temperature. The light-off temperature was lower for the catalyst containing the lowest amount of Pt (by leaching). Thus, the removed Pt was not important for the reaction, and leaching must have increased the number of active sites.

The oxidation states of Au and Pt in both the parent and leached ceria samples were checked by XPS (Fig. 3). The common features in both systems were: (i) the existence of ionic states (Au<sup>+1, +3</sup> and Pt<sup>+2, +4</sup>) both before and after leaching; and (ii) the complete removal of metallic Au or Pt nanoparticles after the leaching step. No cerium or lanthanum loss took place during the leaching step as verified by ICP analysis of the leachate solutions. The absence of Au or Pt particles on the leached ceria samples was also confirmed by HRTEM. We note that the intensities shown in Figure 3A cannot be used to compare the amounts of gold between parent and leached samples. In fact, as shown in Table 1, the surface metal content of the parent DP and CP samples is

grossly underestimated because average metal particle sizes greatly exceed the electron escape depth. The agreement is better for the leached Au-ceria samples. Finally, all Pt-ceria samples show much less Pt on the surface than what is expected on the basis of the ICP analysis and the surface area of each sample. In both Au- and Pt-ceria, diffusion of Au or Pt ions into subsurface layers of ceria is plausible.

The 4.4 at% Au-CL catalyst prepared by CP shows Au<sup>0</sup> binding energies at 83.8 and 87.4 eV; this sample contains metallic Au particles with a mean size of 12.2 nm (Table 1). Leaching removed all metallic gold (Fig. 3A) for sample 0.7% Au-CL. Both Au<sup>+1</sup> and Au<sup>+3</sup> were present in the leached sample. The 4.7 at% Au-CL catalyst prepared by DP shows Au<sup>0</sup> lines as well as ionic gold. The corresponding leached material shows ionic gold binding energies, as well as a positively shifted (by ~ 0.1 eV) binding energy of Au<sup>0</sup>. This shift is within the experimental error of the analysis. Deconvolution of the spectra shows that the zerovalent species amount to only 14 % of the total gold present in the leached 0.44 at% Au-CL sample of Fig. 3A (17–19).

It may be argued that the oxidic gold observed in our samples is due to the preparation conditions (air calcination at 400°C), and that during reaction under net reducing conditions, zerovalent gold dominates. This possibility would require further studies. An important observation that we have made here, however, is that the used catalyst, after more than 20 h at reaction conditions cannot be further leached; i.e., even if gold changes oxidation state during reaction, it does not migrate to form metallic particles. XPS analysis of Au-ceria catalysts after 15 hours use in the reaction gas mixture of Fig. 1 shows predominance of ionic gold (16) (fig. S2). The Au-O-Ce structures are stable under the conditions used in this work. Similar arguments can be made for the Pt-ceria catalysts. For this type of material, surface Pt-O phases strongly associated with ceria have been reported (10).

The use of dry CO in temperature-programmed reduction (TPR) identified oxygen species of importance to low-temperature WGS on the parent and leached catalysts. Various types of oxygen have been identified on cerium oxide (20, 21), ranging from weakly bound adsorbed oxygen to surface capping oxygen to lattice oxygen, depending on the operating temperature. A synergistic redox model for Metal/CeO<sub>2</sub> has been proposed in which the metal particle participates by providing adsorption sites for CO (1, 4, 22), while ceria supplies the required oxygen. This simple model does not provide atomic-level understanding and mechanistic resolution of several key questions; most importantly it assigns the CO adsorption sites on metal particles; however, as Fig. 1 and 2 show, the WGS activity of metal-free (leached) ceria is similar to that of the metal-containing samples.

CO-TPR (23) of fully oxidized parent and leached Au-ceria (DP) samples and the CL material are shown in Fig. 4. The first CO<sub>2</sub> peak produced on the parent Au-ceria sample is absent in the leached sample and the Au-free, CL material. This peak is thus assigned to oxygen adsorbed on metallic Au nanoparticles, present only on the parent 4.7% Au-CL sample. The high-temperature oxygen species, O<sub>b</sub>, is of similar reducibility in all three samples. Thus, the presence of Au does not affect the bulk (lattice) oxygen of ceria. However, the reducibility of the surface oxygen species of ceria, O<sub>s1</sub> and O<sub>s2</sub>, was greatly increased, as is clearly shown in Fig. 4 for both Au-containing samples. This result correlates well with the dramatically higher WGS activity of the latter compared to that of the CL material shown in Fig. 1.

The appearance of H<sub>2</sub> along with CO<sub>2</sub> elution during CO-TPR is attributed to surface hydroxyls remaining in ceria even after the oxidation pre-treatment step in dry O<sub>2</sub>/He mixture at 350°C (23). Indeed, when we repeated the CO-TPR after reoxidation at 400°C, very little H<sub>2</sub> was produced, and by the fourth cycle, only trace amounts of H<sub>2</sub> evolved. The amount of CO<sub>2</sub> eluted in all cycles was the same, and its production began and peaked at the same temperatures, as those shown for the first cycle in Fig. 4. A higher amount of CO<sub>2</sub> was eluted from the leached catalyst (see area under O<sub>s1</sub> peak, Fig. 4). This difference may be due to unmasking of sites after leaching away the metallic particles covering them.

How do gold ions or adatoms interact with ceria to weaken both its O<sub>s1</sub> and O<sub>s2</sub> surface oxygens? A distribution of electronic charges between atomic gold or a small cluster of gold atoms and ceria could weaken the Ce-O bond. Evidence from H<sub>2</sub>-TPR and separate pulse reactor experiments with CO in our lab (6), strongly suggests that gold increases the amount of surface oxygen of ceria. This increase can occur via partial lattice filling of vacant cerium sites with Au<sup>δ+</sup>, which would create additional oxygen vacancies on the surface of the Ce<sup>4+</sup>-O<sub>2</sub> fluorite type oxide.

The identification of Au ions, (Fig. 3A), along with the increased amount of surface oxygen in the leached sample (Fig. 4), argues in favor of lattice substitution. Diffusion of gold ions into ceria takes place during the heating step in the preparation process, as attempts to leach the gold immediately after deposition and before heating failed to produce an active catalyst. The minimum metal loading required for a desired WGS activity may be determined from the ceria surface properties. Assuming uniform monolayer dimensioned metal surface coverage on the CL material [Ce(10%La)O<sub>x</sub>, 160 m<sup>2</sup>/g], the coverage was calculated to be 13.5 at.% Au or 15.5 at.% Pt with Au and Pt radius equal to 0.174 nm and 0.139 nm, respectively. As can be seen in Table 1 and Figs. 1 and 2, only a small fraction of a monolayer of Au or Pt is present on the leached catalysts, but it correlates with the concentration of surface oxygen defect sites of ceria (24–26).

The importance of the surface defects of ceria as the ‘anchoring’ sites of Au, and in turn as the active sites for WGS, can be seen in ceria samples annealed at high temperatures, which effectively reduces the number density of these sites. The reaction rate measured over 3.4% Au-CeO<sub>2</sub> (calcined at 800°C for 4h, Table 1) was very low, but the activation energy was the same as for the other Au-ceria (DP) materials shown in Fig. 1. Removal of gold from this sample by leaching was essentially complete (see Table 1) and the leached sample was inactive for WGS up to 400°C.

Gold nanoparticles are essential for some oxidation reactions in view of their totally different oxygen adsorption properties compared with those of bulk gold (27, 28). However, they appear to be unimportant in the WGS reaction over Au-ceria.

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15. After heating in helium to the desired temperature, the reaction gas mixture was introduced in the flow microreactor containing a packed-bed of catalyst particles (<50 μm size). Rates were measured for 2 h at each temperature, and only steady-state data are reported. Measurements were conducted with the same catalyst charge in descending temperature mode; upon completion of the series of runs, the rate was measured again at 300°C. The new value was within 5% of the initial rate at this temperature.
16. Data available at *Science Online*.
17. Initial and final state effects on the binding energy of Au clusters on ceria are not available in the literature. Generally, final state effects cause a positive shift of the binding energy of metallic nanoparticles as their size is decreased (18), but below a certain cluster size (~2 nm), initial state effects prevail (19), causing negative binding energy shifts. Therefore, extensive compensation effects are possible. The observed minor positive energy shift may be due to partially oxidized gold clusters.
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23. CO-TPR was carried out in a Micromeritics Pulse ChemiSorb 2705 instrument. The samples were first oxidized in a 10% O<sub>2</sub>/He gas mixture (50 cm<sup>3</sup>/min (NTP)) at 350°C for 90 min, cooled down to room temperature and purged with pure helium (Grade 5) for 30 min. A 10% CO/He gas mixture (50 cm<sup>3</sup>/min (NTP)) was passed over the sample which was heated at 5°C/min to 900°C. The effluent gas was analyzed by mass spectrometry (MKS-model RS-1). The cyclic CO-TPR experiments were conducted only up to 400°C to avoid structural changes of the catalyst at higher temperatures.

24. Defects in ceria can be two types, intrinsic and extrinsic (25). Intrinsic defects are due to the oxygen anion vacancies created upon thermal disorder or the reduction of ceria (25). The extrinsic defects are due to oxygen anion vacancies created by the charge compensation effect of low valence foreign cations (25). The concentration of defects can be calculated from the lattice expansion measured by XRD (26). If we assume that gold only associates with the oxygen defects in ceria, the required Au (or Pt) is 0.13 at% for CeO<sub>2</sub>, and 0.57 at% for Ce(10%La)O<sub>x</sub> (both calcined at 400°C), and only 0.03 at% for the undoped CeO<sub>2</sub> calcined at 800°C (see Table 1). These values will increase if gold or platinum ions substitute in the ceria lattice.
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#### Supporting Online Material

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Figs. S1 and S2

**Table 1.** Physical properties of ceria-based catalysts. All samples were calcined at 400°C; CL is Ce(10%La)O<sub>x</sub>, calcined at 400°C, 10 hours; NM: not measured; ND: non detectable.

Sample	Surface area (m <sup>2</sup> /g)	Surface metal content <sup>†</sup> (at%) Au or Pt	Bulk composition (at%) <sup>‡</sup>			Particle size <sup>§</sup> (nm)		
			metal (Au or Pt)	Ce	La	metal (Au or Pt)	CeO <sub>2</sub>	
							<111>	<220>
4.7Au-CL (DP)	156.1	1.60	4.71	87.88	7.41	5.0	5.2	4.9
0.4Au-CL (DP) (NaCN)	157.9	0.61	0.44	91.24	8.32	ND	5.2	4.9
2.8Au-CL (DP)	159.2	1.58	2.81	89.16	8.03	4.7	5.0	4.9
0.2Au-CL (DP) (NaCN)	162.2	0.43	0.23	93.10	6.67	ND	5.0	4.9
3.4Au-CeO <sub>2</sub>    (DP)	25.9	NM	3.36	96.64	0	4.0	21.1	20.3
0.001Au-CeO <sub>2</sub> (DP)    (NaCN)	28.0	NM	~0.001	~99.99 9	0	ND	21.0	20.4
CL (UGC)	156.9	--	0	92.62	7.38	--	5.1	4.8
4.4Au-CL (CP)	47.8	3.29	4.35	88.00	7.65	12.9	7.2	6.3
0.7Au-CL (CP) (NaCN)	47.5	0.24	0.67	91.52	7.82	ND	7.0	6.0
3.7Pt-CL (IMP)	129.8	1.63	3.67	88.83	7.50	2.5 <sup>¶</sup>	6.2	6.1
2.7Pt-CL (IMP, NaCN1)	147.5	1.79	2.70	89.78	7.52	ND	6.2	6.1
1.5Pt-CL (IMP, NaCN2)	103.2	0.82	1.50	90.86	7.64	ND	6.2	6.1

<sup>†</sup> The surface metal content was determined by XPS; <sup>‡</sup> The bulk composition was determined by Inductively Coupled Plasma (ICP); <sup>§</sup> The particle size was determined by XRD with the Scherrer equation; || CeO<sub>2</sub> was calcined at 800°C; <sup>¶</sup> The particle size was determined by HRTEM

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**Fig. 1.** Water-gas-shift rates measured in 11% CO-7% CO<sub>2</sub>-26% H<sub>2</sub>-26% H<sub>2</sub>O-He reformat-type gas [see Table 1 for sample properties; (15) for details]. Solid squares, 4.4AuCe(La)O<sub>x</sub> (CP); open squares, 0.7AuCe(La)O<sub>x</sub> (CP, leached); solid triangles, 4.7AuCe(La)O<sub>x</sub> (DP); open triangles, 0.44AuCe(La)O<sub>x</sub> (DP, leached); solid circles, 2.8AuCe(La)O<sub>x</sub> (DP); open circles, 0.23AuCe(La)O<sub>x</sub> (DP, leached); asterisks, Ce(La)O<sub>x</sub>; diamonds, G-66A (United Catalysts Inc., 42wt% CuO-47wt% ZnO-10wt% Al<sub>2</sub>O<sub>3</sub>, 49 m<sup>2</sup>/g).

**Fig. 2.** Temperature programmed reaction of as prepared and leached Pt-ceria catalysts in 2% CO-3% H<sub>2</sub>O-He gas (see Table 1 for sample properties).

**Fig. 3.** XP spectra of as prepared and leached samples: (A) Au-ceria; and (B) Pt-ceria [see Table 1 for sample properties; (17) for comments].

**Fig. 4.** CO-TPR profiles of as prepared and leached Au-CL(DP) and CL samples; 10% CO/He, 50 cm<sup>3</sup>/min (NTP), 5(C/min [see Table 1 for sample properties; (23) for details].







