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Research Note

On the importance of nanocrystalline gold for Au/CeO$_2$ water–gas shift catalysts

Chang Hwan Kim, Levi T. Thompson *

Department of Chemical Engineering, University of Michigan, 2300 Hayward Street, Ann Arbor, MI 48109, USA

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Abstract

The purpose of the research described in this paper was to assess the importance of nanocrystalline gold on the water–gas shift (WGS) activities of Au/CeO$_2$ catalysts. A series of Au/CeO$_2$ catalysts with gold loadings up to 8.3 wt% and average gold crystallite sizes ranging from 4 to 7 nm was prepared using the deposition-precipitation method. Gold was leached from one of these materials using a procedure that has been reported to remove nanocrystalline gold. We report two key observations: (1) Reaction rates for catalysts before leaching were significantly higher than those for the catalysts after leaching, and (2) estimated turnover frequencies for the unleached catalysts were higher than those for the leached catalysts. The results emphasize the importance of nanocrystalline gold, at least for the WGS reaction.

Keywords: Nanocrystalline gold; Water–gas shift; Dispersion; Turnover frequencies

1. Introduction

Since Haruta's discovery that catalysts containing nanosized gold particles have extraordinary activities for reactions including CO oxidation [1], there has been substantial interest in their use [2] and the origin of their exceptional catalytic properties [3–5]. Many reports suggest that the active centers are located on the surfaces of nanosized gold particles [6,7] or at the interface between these particles and the support [4,8]. It has also been argued that the active sites are associated with small ensembles of anionic gold [3]. Recently, Flytzani-Stephanopoulos and co-workers reported that the water–gas shift (WGS) activities of Au/CeO$_2$ catalysts were not significantly altered when most of the gold was leached from the surface [4,9,10]. By deduction they concluded that the WGS activities were associated with atomically dispersed, cationic gold species and not with nanocrystalline gold. The support also appears to play an important role, in that the most active WGS catalysts have typically employed reducible oxide supports like Fe$_2$O$_3$ and CeO$_2$ [11,12]. While these oxides alone do not possess significant catalytic activities, their redox and oxygen storage properties appear to be important in catalyzing a bifunctional mechanism for WGS catalysis over supported gold catalysts [12].

The goal of the work described in this paper was to assess the importance of nanocrystalline gold by comparing the WGS rates and turnover frequencies of Au/CeO$_2$ catalysts before and after most of the gold was leached from the surface. Catalysts containing nanocrystalline gold were prepared using the deposition-precipitation method. Gold was leached from one of these catalysts by the Flytzani-Stephanopoulos group using a method that has been reported to selectively leach nanocrystalline gold [4,10].

2. Experimental

The ceria was synthesized via decomposition of cerium carbonate [$Ce_2(CO_3)_3\cdot xH_2O$, Alfa Aesar]. The cerium carbonate was hydrolyzed in a mixture of 75% steam in N$_2$ at 150 °C, then calcined in dry air at 400 °C for 4 h. The resulting material had a surface area of 203 m^2/g. Details regarding the deposition-precipitation procedure used to prepare the Au/CeO$_2$ catalysts have been provided elsewhere [13]. Gold was leached from the 5 wt% Au/CeO$_2$ catalyst using a method described in detail

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* Corresponding author. Fax: +1 734 763 0459.
E-mail address: ltt@umich.edu (L.T. Thompson).

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elsewhere [4,10,14]. Briefly, this leaching process was carried out in an aqueous solution of 2% NaCN under O_2 gas sparging at room temperature. After most of the Au was leached from the surface, the resulting material was washed thoroughly to remove contaminants [10].

Before characterization, the Au/CeO_2 powder was pelletized, ground, and sieved to control the grain size between 12.5 and 25.0 µm (60 and 120 mesh). A commercial Cu–Zn–Al WGS catalyst (surface area, 60 m^2/g) was used to benchmark the performance of the Au/CeO_2 catalysts. This material was obtained from Süd Chemie Inc.

The BET surface areas and pore size distributions were evaluated from N_2 physisorption isotherms using a Micromeritics ASAP 2010. The metal content was determined using inductively coupled plasma spectroscopy (ICP) at the University of Michigan or Galbraith Laboratories, Inc. The high-resolution transmission electron microscopy (HRTEM) was performed using a JEOL 3011F operating at 300 kV. Average crystallite sizes were typically determined for more than 200 Au particles in a given sample.

Between 15 and 30 mg of catalyst was loaded into a quartz microreactor for the catalytic measurements. Inert SiO_2 (Alfa, surface area of $\sim$5 m^2/g) was used to dilute the catalyst to 50 wt%. The materials were pretreated in a mixture of 4% H_2 in N_2 at 200 °C for 4 h before the activity measurements. The catalytic properties were measured at atmospheric pressure and temperatures ranging from 200 to 240 °C using a reactant gas with composition designed to simulate reformate from gasoline partial oxidation. In particular, the CO, H_2O, CO_2, H_2, and N_2 concentrations were 10, 22, 6, 43, and 19 mol%, respectively. All of the rate measurements were carried out under differential conditions, and the initial rates were determined after 30 min on stream.

3. Results and discussion

Surface areas for the Au/CeO_2 catalysts were similar to those for the support and are listed in Table 1. WGS rates for the Au/CeO_2 catalysts decreased significantly during the first 12 h, subsequently reaching a pseudo-steady state. Fig. 1 compares rates obtained after 12 h on stream for Au/CeO_2 catalysts with loadings of 5 wt% (unleached) and 0.76 wt% (leached) gold, a 0.54 wt% $AuCe(Gd)O_x$ catalyst received from the Flytzani-Stephanopoulos group, and a commercial Cu–Zn–Al catalyst. Rates for the Cu–Zn–Al catalyst were consistent with those provided by the manufacturer. Rates for the two leached catalysts were within the limits of experimental error of each other; however, the unleached catalyst was significantly more active than the leached catalysts. This response is very different from that reported by Fu et al. [4], who indicated that WGS rates for the unleached and leached catalysts were similar. A possible explanation for the reduced rate is contamination by residue from the leaching process, the elemental analysis results do not support such a conclusion. For example, sodium contents for the unleached and leached catalysts were <10 ppm, the detection

Table 1
Properties for Au/CeO_2 catalysts and the water–gas shift rates measured at 240 °C

Catalyst	Au loading (wt%)	Surface area (m^2/g)	Mean particle size (nm)	Dispersion (%)	WGS rate (µmol/(g s))	Turnover frequency (s^{-1})
2% Au/CeO_2	2.05	196	4.5	30	70	2.2
5% Au/CeO_2	4.86	198	4.8	27	293	4.4
7.5% Au/CeO_2	7.84	195	6.6	20	325	4.1
8.5% Au/CeO_2	8.28	194	7.0	19	327	4.1
0.76% Au/CeO_2 (leached)	0.76	190	–	90	18	0.5

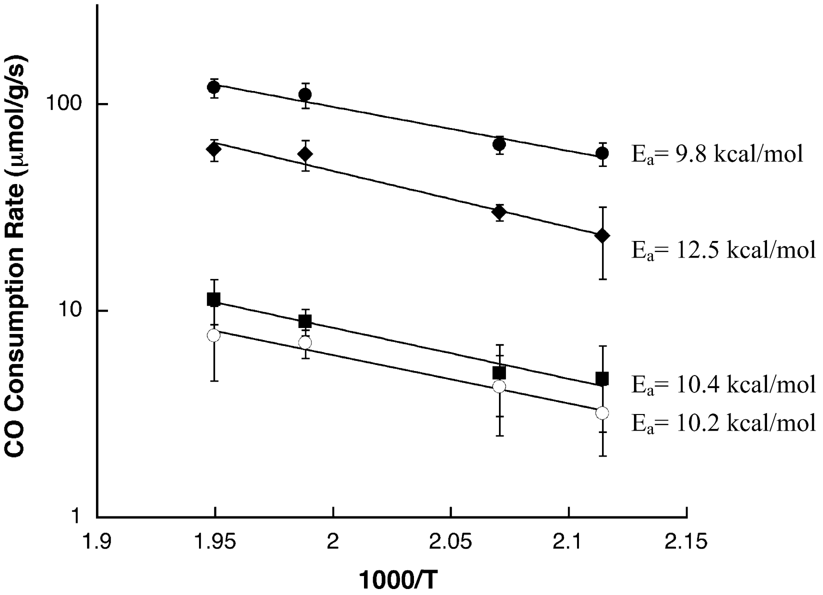

Fig. 1. Arrhenius plots of water–gas shift rates and apparent activation energies for the fresh 5 wt% Au/CeO_2 (●) and leached (○) 0.76 wt% Au/CeO_2 catalysts, (■) 0.54 wt% $AuCe(Gd)O_x$ catalyst, and a commercial Cu–Zn–Al (◆) catalyst.

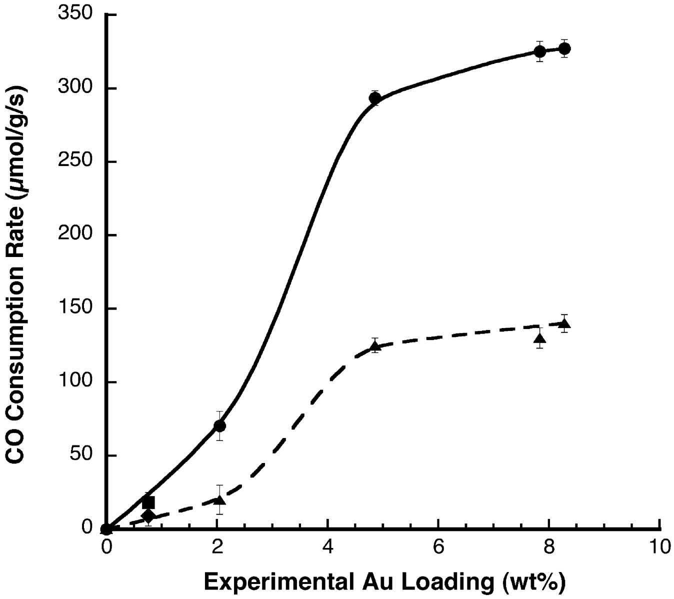

Fig. 2. Initial water–gas shift rates for the fresh (●) and leached (■) Au/CeO_2 catalysts, and final water–gas shift rates for the fresh (▲) and leached (◆) Au/CeO_2 catalysts as a function of Au loading.

limit for the ICP instrument. Consequently, differences between these catalysts were not likely due to contamination.

Another potential explanation for the lower rates is the lower Au loading. Initial and final CO consumption rates obtained after 12 h on stream for the catalysts, including those from which nanocrystalline gold was leached, increased with gold loading up to approximately 5 wt% (Fig. 2). This result suggested that the dispersion remained approximately constant up to a loading of 5 wt% or that turnover frequencies for the unleached catalysts were higher than those for the leached catalysts.

It is difficult to determine the gold dispersion for Au/CeO_2 catalysts using chemisorption methods due in part to the adsorption of probe molecules like CO on CeO_2 [13]. Therefore, we estimated the surface site densities based on the gold particle sizes determined using HRTEM. The unleached catalysts contained a significant density of gold nanocrystallites. Average crystallite sizes ranged from 4 to 7 nm. The particles appeared to be regularly shaped and could be modeled as cubo-octahedral. Van Hardeveld and Hartog provided relationships between the total number of atoms and the number of surface atoms for regular truncated cubo-octahedron particles [15]. The gold dispersions for the unleached catalysts were estimated to be 20–30%. Gold in the leached catalysts was not clearly visible by microscopy suggesting, as reported by Fu et al. [4], that the Au was very highly dispersed. For the purpose of estimating turnover frequencies, we assumed a dispersion of 90% for the leached catalyst. This corresponds to 0.5 nm particles, the practical limit of our ability to image particles.

Turnover frequencies based on the initial WGS rates and estimated densities of surface gold atoms are compared in Table 1. Estimated turnover frequencies for the unleached catalysts were as much as 9 times higher than those for the leached catalyst. This observation indicates the importance of nanocrystalline gold and is contrary to reports that atomically dispersed gold is more active than nanocrystalline gold for the WGS reaction [4]. Previously we observed that the Au/CeO_2 catalysts contained cationic gold [13], suggesting that the high WGS activity was associated with nanocrystalline, cationic gold domains. Recent results from extended X-ray absorption spectroscopy and DFT calculations also support the importance of nanocrystalline gold for the WGS reaction [7].

4. Conclusion

A series of ceria-supported gold catalysts with loadings up to 8.3 wt% were prepared, evaluated for the WGS reaction, and characterized. Rates for the unleached, nanocrystalline gold-containing catalysts were significantly higher than those for the leached catalyst, which contained very highly dispersed gold. The surface site densities and dispersions were estimated from average particle sizes measured using HRTEM. Turnover frequencies for the unleached catalysts were more than 5 times higher than those for the leached catalyst. This suggests that active sites associated with nanocrystalline gold domains are much more active than those associated with atomically dispersed gold.

Acknowledgments

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