

Highly active CeO₂-supported Au clusters for butadiene hydrogenation

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Introduction

Despite the availability of methods to synthesize supported gold particles in the nanometer size domain in a controlled manner, the preparation of catalysts containing very small, subnanometer gold clusters with a high thermal stability remains a challenge. Recently, a leaching process employing cyanide ions has been reported to effectively remove nanometer-sized gold particles from ceria-supported gold [1]. Since Haruta's discovery that gold nanoparticles display unique catalytic properties not exhibited by bulk gold, it has been established that finely dispersed gold is an excellent catalyst for a variety of reactions such as CO oxidation, epoxidation and alcohol oxidation. Although metallic gold is generally considered to be inert towards hydrogen [2], metallic gold displays high activity in the hydrogenation of unsaturated compounds [3]. Others have claimed that Au³⁺ ions are the active sites [4]. Theoretical findings predict that low coordinated gold atoms are required for H₂ dissociation, in line with indications for hydrogen dissociation on corner and edge sites [5]. Another hypothesis relates to the non-metallic character of Au below a critical diameter.

Materials and Methods

A ceria-supported gold catalyst was prepared by deposition-precipitation [21] of HAuCl₄ on ceria (80 m²/g). After filtering and washing, the catalyst was calcined at 673 K for 4 h (Au/CeO₂; 1.8 wt.% Au). A large fraction of gold in Au/CeO₂ was dissolved by treatment with a 2 wt.% NaCN solution according to the method given by Fu et al. [1]. Au/CeO₂-CN (0.08 wt.% Au) was obtained by calcining the cyanide-treated catalyst at 673 K for 4 h. X-ray absorption spectroscopic measurements were carried out at the Au L_{III} edge (11.919 keV) in fluorescence mode. An in situ XAS cell was used as a single-pass flow reactor to record XANES and EXAFS spectra after reduction or oxidation. Six (three) scans were recorded and averaged for catalysts with low (high) gold loading.

For 1,3-butadiene hydrogenation catalytic activity experiments, the feed consisted of 2.5 vol.% 1,3-butadiene in hydrogen. An amount of 5 mg catalyst was diluted with 250 mg SiC in a quartz microflow reactor. The gas hourly space velocity was kept at 240 l/gcat.h. The reaction rate was determined from the 1,3-butadiene conversion after 15 min time on stream.

Results and Discussion

By in situ X-ray absorption spectroscopy, we have found that such a leached Au/CeO₂ material is an ideal precursor to a highly active hydrogenation catalyst containing subnanometer gold clusters upon reduction. EXAFS analysis indicates that these clusters contain about 6 gold atoms. They are thermally stable against sintering up to quite high temperature, owing to their interaction with the ceria support. Their activity in 1,3-butadiene hydrogenation is extremely high, at least one order of magnitude higher than the nanometer sized gold particles in the unleached precursor catalyst. The parallel between the catalytic

activity and the decrease of the fraction of cationic gold as probed by analysis of Au L_{III} near-edge spectra provides solid evidence for the catalytic relevance of reduced gold particles.

These results point to a very strong particle size dependence of the hydrogenation activity for gold. The high proportion of coordinatively unsaturated gold atoms in clusters of a few gold atoms can explain the much higher intrinsic activity compared to nanometer-sized gold particles. The proposal that the structure dependence pertains to hydrogen dissociation tallies with computational results of hydrogen dissociation over low coordinated gold atoms [5]. An additional factor could be the importance of positive charge in the small gold clusters due to their interaction with ceria. Empty *d* orbitals in positively charged gold clusters can facilitate the surface reaction between the carbon-carbon double bond and a hydrogen adatom. As its barrier is mainly due to formation of antibonding occupied orbitals between the hydrogen and the reacting carbon atom, backdonation of electrons from the C-H bond into empty 5*d* orbitals of the metal lowers the barrier energy [6].

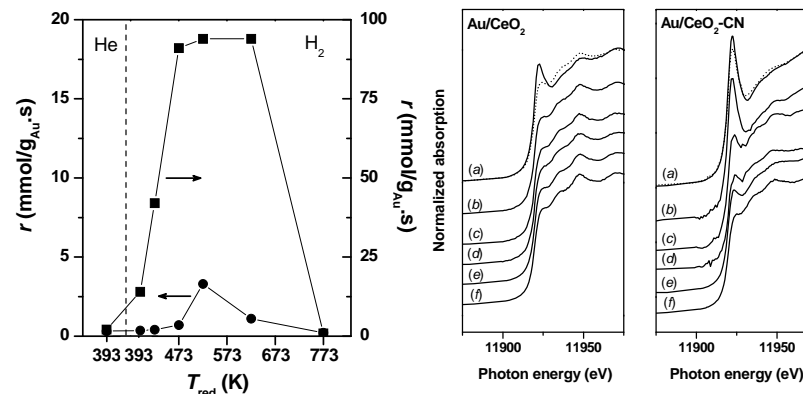


Figure 1. (left) Reaction rate of butadiene hydrogenation of (●) Au/CeO₂ and (■) Au/CeO₂-CN at 393 K as a function of the reduction temperature; (right) near-edge spectra dried at 393 K (b) reduced at 393 K (c) reduced at 423 K (d) reduced at 473 K (e) reduced at 523 K (f) reduced 773 K.

Significance

Not gold cations retained by ceria after cyanide leaching but very small Au clusters consisting of about 6 atoms outperform nanometer-sized gold in 1,3-butadiene hydrogenation.

References

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