



Preferential CO oxidation in a H₂-rich gas by Au/CeO₂ catalysts: Nanoscale CeO₂ shape effect and mechanism aspect

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ARTICLE INFO

Article history:

Available online 21 February 2010

Keywords:

Gold
CeO₂
CO preferential oxidation
Shape effect
Hydrogen isotope effect
Mechanism

ABSTRACT

The Au/CeO₂ catalysts with nanoscale CeO₂ shapes of rods, cubes and polyhedra were evaluated for the CO preferential oxidation (CO-PROX) in a hydrogen-rich gas, showing a strong effect of CeO₂ morphology followed by this order: rods > polyhedra > cubes. The results of pulse experiment and kinetic study indicated that the oxidation of CO could be enhanced by H₂ and H₂O moisture, behaving a hydrogen isotope effect by H₂/D₂. The catalyst Au/CeO₂-rods exhibited the lowest apparent activation energy for the CO oxidation either with or without hydrogen in comparison with the Au/CeO₂-polyhedra and Au/CeO₂-cubes. It was proposed that hydrogen reacted with adsorbed oxygen to yield highly oxidizing surface H-containing intermediates that could readily converted CO to CO₂ at lower temperatures. The generation of such key intermediates might be involved into the rate-determining step.

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1. Introduction

The preferential oxidation of CO in a hydrogen-rich gas (CO-PROX) has been attracted much attention due to its unique role in purifying the gas feeding for proton-exchange-membrane (PEM) fuel cells [1–3]. Hydrogen produced after the steam reforming process and water-gas shift reaction usually contains trace amount of CO (0.5–1%) which will poison the platinum-based electrode that converts hydrogen to electricity [4]. The acceptable CO concentration is below 10 ppm at Pt anode and below 100 ppm at CO-tolerant alloy anodes. Among the approaches investigated to remove the trace amount of CO in H₂-rich stream [5,6], the CO-PROX has been considered to be suitable for sufficient CO removal.

Various efforts have been made with the development of CO-PROX catalysts by employing precious and non-precious metals. In particular, the supported noble metals, such as Au, Pt, Rh, Ru, and Ir were very active for this reaction [6–10]. Specifically, some selected metal oxides supported Au nanoparticles, were found to be of potentially superiority, since they are able to remove CO from reformed fuels with an extraordinarily high reaction rate and good selectivity at much lower temperatures [11–13]. The influence of metal oxides on the catalytic activity of gold nanoparticles has obtained great scientific interest. The active (reducible) supports such as TiO₂ [14–16], CeO₂ [13,17–19] and FeO_x [12,20–22] can improve the stability of gold particles and furnish oxygen atoms for

higher activity. Interface, geometry, and quantum size effects determine the catalytic activity of gold nanoparticles supported on metal oxides.

CeO₂ is an attractive oxide with unique catalytic properties due to its distinct defect chemistry and the ability to exchange lattice oxygen with the gas phase [23]. These properties include the promotion of the precious metal dispersion, the enhancement of the catalytic activity at the interfacial metal-support sites and the promotion of CO removal through oxidation employing lattice oxygen. Nanosized gold supported on CeO₂ has been reported to be good catalyst in the CO-PROX in H₂ stream, owing to their high activity and selectivity to CO oxidation, and their resistance toward H₂O and CO₂ [13,17–19]. Quite recently, we have discovered that the catalytic activity of Au/CeO₂ on CO-PROX was significantly influenced by the morphology and crystalline planes of CeO₂ [24]. The nanoscaled Au supported on CeO₂ with the shape of rods exhibited extra higher activity than CeO₂ with the shapes of polyhedra and cubes.

On the other hand, even though numerous reports are available on the effect of metal oxide support on the activity of gold nanoparticles for the PROX reaction, there is less attention toward the CO-PROX reaction mechanism [19,22]. As for the total oxidation of CO, in general, the CO molecule is considered to be adsorbed on gold; the oxygen species activated on the surface of CeO₂ diffuse to the Au–CeO₂ interface and react with CO to produce CO₂ [25]. However, the CO-PROX reaction may not be described by such traditional mechanism. Concerning the hydrogen effect, Quinet et al. proposed that hydrogen reacted with oxygen to yield highly oxidizing intermediate HOO[•] that promoted CO oxidation

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over Au/Al₂O₃ catalyst [26]. Recently, Tanaka et al. reported a novel catalyst FeO_x/Pt/TiO₂ and demonstrated that the PROX reaction of CO occurred via a HCOO intermediate and its oxidation with OH instead of oxygen, which was different from the ordinary oxidation of CO with O₂ [27].

The aim of this work is to further discuss the key issues relevant to the CeO₂ shape effect and mechanism aspects of the Au/CeO₂ catalysts for the CO-PROX by means of kinetic study, pulse experiment, effects of H₂/D₂ and water moisture. The results support the aforementioned morphology effect of CeO₂ and allow us to propose a H₂-promoted CO-PROX reaction mechanism.

2. Experimental

2.1. Catalyst preparation

Ceria oxides with shapes of rods, cubes and polyhedra were prepared by an established method [24,28]. The Au/CeO₂ catalysts with different shapes were prepared using a routine deposition-precipitation (DP) method described previously [29]. In brief, the CeO₂ samples were dispersed in aqueous solution of HAuCl₄·3H₂O at a pH of 8–9 using (NH₄)₂CO₃ as buffer solution. The precipitates were aged at room temperature and further washed with hot deionized water. Finally, the catalysts were obtained by calcination in air at 673 K for 4 h.

The nominal gold loading was controlled to be 1 wt%. The actual Au content was determined by an inductively coupled plasma-optical emission spectrometry (ICP-OES) using a Thermo Electron IRIS Intrepid II XSP. The received values were 0.92 wt% for the Au/CeO₂-rods, 0.83 wt% for the Au/CeO₂-polyhedra and 0.92 wt% for the Au/CeO₂-cubes.

2.2. Catalytic testing

The catalytic performances were examined in a conventional fixed-bed flow reactor by using 100 mg of catalyst at 0.1 MPa as previously reported [24]. The reactant mixture of CO/O₂/H₂/N₂ was adjusted to 1/1/50/48 (mol%) by mass flow controllers. The mixed gas passed through a tube containing NaOH pellets for purification. The typical performances were conducted at a total flow rate of 50 mL min⁻¹, corresponding to a gas hourly space velocity (GHSV) = 30,000 mL g⁻¹ h⁻¹. The effect of CO₂ and H₂O co-existed in the feed gas was performed at the reactant mixture of 1% CO, 1% O₂, 50% H₂, 15% CO₂ and 10% H₂O balanced with N₂. The outlet stream line from the reactor to the gas chromatograph was heated at about 373 K to avoid condensation of reaction products. The composition of the influent and effluent gas was analyzed by an on-line gas chromatograph equipped with two packed columns (Molecular sieve 5A and Porapak Q) and thermal conductivity detector. The CO conversion and O₂ selectivity were calculated by the equations as previously reported [24].

The kinetic study was performed using different catalyst amounts (5 mg of Au/CeO₂-rods, 10 mg of Au/CeO₂-polyhedra and 50 mg of Au/CeO₂-cubes) in order to control the CO conversion below 20%. The flow rate of the reaction gas was maintained as 50 mL min⁻¹. The kinetic data were collected after the reaction for 30 min at each temperature when it attained a steady state.

2.3. Pulse experiment

Pulse experiments were performed on a lab-built microreactor equipped with a quadrupole mass spectrometer (Hiden Analytical) by using Ar as the carrier gas in a flow rate of 40 mL min⁻¹. The catalyst sample (20 mg) was pretreated at 523 K in 5%O₂/95%N₂ flow for 30 min and then cooled down to 323 K. The sample was then purged with Ar 30 min at 323 K. After that, the amount of ca.

0.5 mL of CO/H₂/Ar = 5/45/50 (mol%) or O₂/Ar = 20/80 (mol%) was pulsed into the catalyst bed at an interval of about 5 min. All the mixed gases were purified by the NaOH pellets before being pulsed into the catalyst bed. The effluent gas from the reactor was detected by the mass spectrometer by monitoring *m/e* = 28 for CO and *m/e* = 44 for CO₂.

2.4. Effects of hydrogen isotope and H₂O moisture

Hydrogen isotope effect and influence of water vapor were evaluated using the same reactor system as in the activity test by using 100 mg of catalyst at 0.1 MPa. Before D₂/H₂ or H₂O was introduced into the catalyst bed, the CO oxidation was executed from room temperature to 333 K with a reactant mixture of CO/O₂/N₂ (1/1/98, mol%) and then the temperature was held at 333 K. For the hydrogen isotope effect, D₂ (25 mL min⁻¹) or H₂ (25 mL min⁻¹) was added to a flow of 1%CO + 1%O₂ balanced with N₂. The total flow rate was kept as 50 mL min⁻¹, where the N₂ flow rate was lowered from 49 to 24 mL min⁻¹ when H₂ or D₂ (25 mL min⁻¹) was added. At each stage, the activity data was collected every 30 min after the reaction attained the steady state.

Effect of H₂O moisture on the CO oxidation was conducted by adding water vapor to the reactant mixture of CO/O₂/N₂ (1/1/98, mol%). The content of H₂O vapor was controlled by mixing dry N₂ with the N₂ bubbled through a water tank at room temperature, keeping the total flow rate at 50 mL min⁻¹.

2.5. High-resolution transmission electron microscopy

Transmission electron microscopy (TEM) images were performed on a Tecnai F30 electron microscope operated at an acceleration voltage of 300 kV. Samples for TEM measurements were ultrasonically dispersed in ethanol. Drops of suspensions were deposited on a copper grid coated with carbon.

3. Results and discussion

We have demonstrated the CO-PROX performance on the Au/CeO₂ catalysts with different CeO₂ shapes were dependent of CeO₂ morphology [24]. The CO-PROX performance over the same Au/CeO₂ ones with different shapes in the presence of CO₂ and H₂O vapor is displayed in Fig. 1. It can be seen that the Au/CeO₂-rods showed much higher activity than the Au/CeO₂-polyhedra and the Au/CeO₂-cubes in the temperatures ranging from 310 K to 393 K.

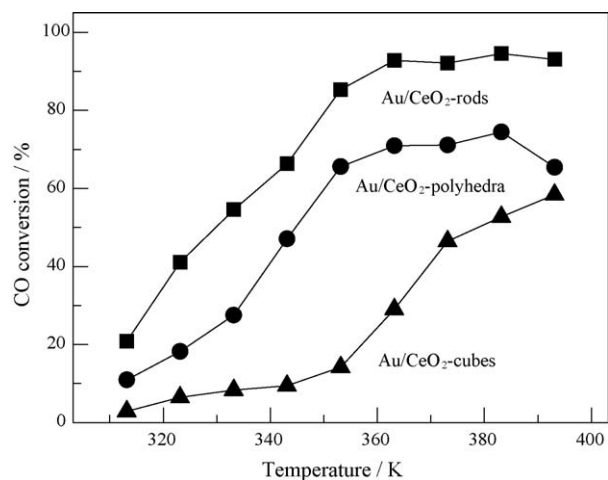


Fig. 1. Reaction temperature dependence of CO conversion over Au/CeO₂ with different CeO₂ shapes in the PROX reaction with a reactant mixture of 1% CO, 1% O₂, 50% H₂, 15% CO₂ and 10% H₂O balanced with N₂ under GHSV = 30,000 mL g⁻¹ h⁻¹.

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