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Article

Selective reduction of carbon dioxide to carbon monoxide over Au/CeO₂ catalyst and identification of reaction intermediate

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ABSTRACT

CO₂ selective reduction to CO with H₂ over a CeO₂-supported nano-Au catalyst at atmospheric pressure was investigated. A high CO₂ conversion, approaching the thermodynamic equilibrium value, and nearly 100% CO selectivity were obtained. The surface formate intermediates generated during the reverse water-gas shift reaction at 400 °C were identified using in situ diffuse-reflectance infrared Fourier-transform spectroscopy. The formate consumption to give CO and H₂O, determined using mass spectrometry, indicated that the reaction proceeded via an associative formate mechanism; this contributes to the high Au/CeO₂ catalytic activity at low temperatures.

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1. Introduction

The increase in greenhouse gas concentrations in the atmosphere, especially as a result of anthropogenically produced CO₂, is causing climate change [1]. The capture and conversion of CO₂ to produce chemicals or carbonaceous fuels via photochemical [2–4], electrochemical [5–8], and catalytic methods [9–12] is a challenge. CO₂ reduction by photo- and/or electro-catalytic approaches is currently the subject of much research, but efficient electrocatalysts for CO₂ reduction to desirable fuels are still not available. An alternative of particular interest is the reduction of CO₂ to CO with H₂, which can be generated by water electrolysis, using renewable electricity, via the reverse water-gas shift (RWGS) reaction.

The RWGS, which is a key reaction in the heterogeneous catalytic hydrogenation of CO₂, is mildly endothermic with an enthalpy change of $\Delta H_{298K}^{\circ} = 41.2 \text{ kJ/mol}$ [13,14]:

CO produced by the RWGS reaction can be further hydrogenated to fuels, e.g., methanol, providing a sustainable source of liquid fuel [15,16].

Catalysts that are active in the WGS reaction are generally also active in the RWGS reaction. Various catalysts for the WGS reaction have been investigated [17–20], e.g., Cu-based Cu/ZnO/Al₂O₃, Fe-based Fe-Cr, and Ce-based Pt/CeO₂. Supported Au nanocatalysts have been developed for CO oxidation at low temperatures [21,22] and the WGS reaction [21,23–26]. Because of its high oxygen-storage capacity, the CeO₂ support in Ce-based catalysts promotes strong interactions with Au, particularly in the WGS reaction [27–30]. However, only a few studies [10,11] have focused on Au/CeO₂ catalysts for the RWGS reaction. Localized surface plasmon resonance can enhance the catalytic activities of TiO₂-supported Au catalysts under visible-light illumination in the RWGS reaction [10].

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Quantitative temporal analysis of products has been used to investigate the mechanism of the RWGS on a supported Au/CeO₂ catalyst to determine the ability of CO₂ to reoxidize a prereduced Au/CeO₂ catalyst surface and its activity [11].

Here, we show that a Au/CeO₂ catalyst is highly active in the low-temperature RWGS reaction and highly selective for CO production at atmospheric pressure. The effects of the operating conditions, namely temperature, gas hourly space velocity (GHSV), and the molar ratio of the reactants (i.e., H₂/CO₂) on CO₂ conversion were investigated. In situ diffuse-reflectance infrared Fourier-transform spectroscopy (DRIFTS) and mass spectrometry were used to identify the reaction intermediates to clarify how the reaction proceeds over a Au/CeO₂ catalyst. High-resolution transmission electron microscopy (HRTEM) and N₂ adsorption desorption measurements were conducted on the Au/CeO₂ catalyst before and after a 6 h catalytic reaction to investigate the catalyst durability.

2. Experimental

2.1. Catalyst preparation

A Au/CeO₂ catalyst was prepared using a modified incipient wetness impregnation method [22,31]. A commercial CeO₂ powder support (Rare-Chem Hi-Tech Co., China) was impregnated with HAuCl₄ solution under stirring, followed by aging overnight at room temperature, rinsing twice with aqueous ammonia solution and deionized water, and drying at 80 °C for 8 h to give the Au/CeO₂ catalyst.

2.2. Catalyst characterization

The Au loading on the Au/CeO₂ catalyst was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Optima 2000DV, USA). The specific surface area of the catalyst was determined using the Brunauer Emmett Teller (BET) method, based on N₂ adsorption desorption at −196 °C (NOVA2200e, Quantachrome Corporation, USA). The catalyst surface morphology and microstructure were examined using HRTEM (Tecnai F30 microscope, operated at 200 kV).

2.3. Catalytic activity evaluation

The reaction was performed in a quartz-tube reactor of inner diameter 7.5 mm at atmospheric pressure and temperatures ranging from 300 to 500 °C. The reactor was loaded with 1 g of the Au/CeO₂ catalyst or CeO₂. Prior to the reaction, the catalyst or support was activated in N₂ (60 mL/min) by heating from room temperature to 500 °C at a rate of 10 °C/min and then maintaining the temperature for 2 h. After activation, mixtures of CO₂ and H₂ with H₂/CO₂ molar ratios of 1, 2, or 3 were fed into the reactor to start the reaction. The gas flow rates were controlled using mass flow controllers. The inlet and outlet gases were analyzed online using two gas chromatography (GC) systems, by the internal standard method [32]. N₂ was used as the internal standard gas for determining CO₂ and CO, and He was used for determining H₂.

The conversions of CO₂ (X_{CO_2}) and H₂ (X_{H_2}), and the CO selectivity (S_{CO}) were calculated as follows:

$$X_{\text{CO}_2}/\% = \left(1 - \frac{F_{\text{N}_2}}{F_{\text{CO}_2}^{\text{in}}} \cdot \frac{C_{\text{CO}_2}^{\text{out}}}{C_{\text{N}_2}^{\text{out}}}\right) \times 100 \quad (2)$$

$$X_{\text{H}_2}/\% = \left(1 - \frac{F_{\text{He}}}{F_{\text{H}_2}^{\text{in}}} \cdot \frac{C_{\text{H}_2}^{\text{out}}}{C_{\text{He}}^{\text{out}}}\right) \times 100 \quad (3)$$

$$S_{\text{CO}}/\% = \frac{F_{\text{N}_2}}{F_{\text{CO}_2}^{\text{in}} \cdot X_{\text{CO}_2}} \cdot \frac{C_{\text{CO}}^{\text{out}}}{C_{\text{N}_2}^{\text{out}}} \times 100 \quad (4)$$

where $C_{\text{CO}_2}^{\text{out}}$, $C_{\text{H}_2}^{\text{out}}$, $C_{\text{CO}}^{\text{out}}$, $C_{\text{N}_2}^{\text{out}}$, and $C_{\text{He}}^{\text{out}}$ denote the concentrations of CO₂, H₂, CO, N₂, and He in the outlet gas, $F_{\text{CO}_2}^{\text{in}}$ and $F_{\text{H}_2}^{\text{in}}$ denote the inlet flow rates of CO₂ and H₂, and F_{N_2} and F_{He} denote the flow rates of the internal standard gases N₂ and He. The time-on-stream for each performance data point analyzed online using GC in Figs. 2–5 was 1 h. GC data were recorded every 20 min. The mean CO₂ conversion was obtained as the average of three measurements.

Thermodynamic equilibrium (TE) conversion values were calculated by the Gibbs free-energy minimization method using HSC Chemistry software (v7.0).

The durability of the Au/CeO₂ catalyst was tested by performing the reaction for 6 h under the conditions 400 °C, H₂/CO₂ molar ratio = 1, and GHSV = 12000 mL/(h·g).

2.4. In situ DRIFTS and mass spectrometry

In situ DRIFT spectra were recorded from 4000 to 1000 cm^{−1} at a resolution of 4 cm^{−1} using an FT-IR spectrometer (Nicolet 6700, USA) with a mercury cadmium telluride detector. The intensities were evaluated in Kubelka Munk units. A sample of around 0.2 g was loaded in a DRIFTS cell. DRIFTS was performed as follows. (1) The sample was pretreated in Ar (50 mL/min) at 500 °C for 2 h. (2) The temperature was decreased to 400 °C. (3) The Ar was switched to CO₂ and H₂ (25 mL/min), and the reaction was performed at 400 °C for 1 h. (4) The system was purged with Ar (50 mL/min) at 400 °C for 0.5 h. (5) The temperature was increased to 500 °C at a rate of 10 °C/min. (6) The temperature was kept at 500 °C. The DRIFTS data were recorded for in situ observation of formate formation during step 4 (Fig. 6), and for investigating the decomposition of formate to CO and H₂O as a function of time after step 5 (Fig. 7). The outlet gas from the DRIFTS cell was monitored simultaneously using a mass spectrometer (HPR-20QIC, Hiden, UK).

3. Results and discussion

3.1. Catalyst characterization

The Au loading on the Au/CeO₂ catalyst, determined using ICP-AES, was 3.0 wt%. The BET surface areas of the Au/CeO₂ catalyst before and after reaction for 6 h were 68 and 64 m²/g, respectively.

Fig. 1 shows high resolution TEM images of the Au/CeO₂ catalyst before and after catalytic reaction for 6 h. The lattice fringe spacing values of 0.20, 0.31, and 0.27 nm represent Au (200), CeO₂ (111), and CeO₂ (200), respectively, enabling them

Fig. 1. HRTEM images of Au/CeO₂ catalyst (a) before and (b) after catalytic reaction for 6 h.

to be distinguished although the contrasts in the TEM images are very similar. The size of the Au particles on the Au/CeO₂ catalyst was 4–5 nm, and did not change much after reaction for 6 h. X-ray diffraction (XRD) did not detect Au in a Au/CeO₂ catalyst for the WGS reaction [33] because of the low Au loading (1.85 wt%). Similarly, for our Au/CeO₂ catalyst for the RWGS reaction, the Au loading was low (3 wt%), therefore the intensity of the Au peak was low and could not be observed in the XRD patterns; no clear difference was observed between the CeO₂ patterns before and after reaction for 6 h (data not shown).

Our previous X-ray photoelectron spectroscopy [22] study suggested that Au is present in a mixture of oxidation states, i.e., Au⁰, Au¹⁺, and Au³⁺, in the fresh Au/CeO₂ catalyst. In situ reduction of cationic Au occurs during CO oxidation at room temperature [22], which implies that Au⁰ primarily catalyzes the reaction. The significant decrease in the reduction temperature observed in H₂ temperature-programmed reduction implies that the presence of Au facilitates the reduction of surface oxygen species [22].

3.2. Catalytic activity evaluation

Fig. 2 shows the effect of temperature on CO₂ conversion over the Au/CeO₂ catalyst. GC analysis showed that CO is the only carbonaceous product. The GC results suggest that CO selectivity was nearly 100% under all the conditions used in this study. The CO₂ conversion over the Au/CeO₂ catalyst in-

Fig. 2. CO₂ conversion as a function of temperature over (1) Au/CeO₂ catalyst and (2) CeO₂ support, under conditions H₂/CO₂ molar ratio = 1 and GHSV = 12000 mL/(h·g). Dashed line (3) represents TE values for reaction under same conditions.

Fig. 3. Effect of H₂/CO₂ molar ratio on conversions of CO₂ and H₂, and molar ratios of consumed H₂ to consumed CO₂ over Au/CeO₂ catalyst. Conditions: 400 °C, GHSV = 12000 mL/(h·g).

creased rapidly from 2.9% at 300 °C to 30.3% at 500 °C. It is worth noting that the CO₂ conversion approached the TE value above 450 °C. In the absence of Au, the CeO₂ support was almost inactive in the reaction below 500 °C. Fig. 2 therefore shows that Au contributed significantly to the catalytic activity of Au/CeO₂ in CO₂ conversion.

Fig. 3 shows that the CO₂ conversion increased from 15.4% to 25% to 27.6%, and the H₂ conversion decreased from 16.1% to 13.2% to 9.2%, with increasing H₂/CO₂ ratio from 1 to 2 to 3. The enhanced CO₂ conversion was attributed to the reaction equilibrium shifting forward as the concentration of the other reactant, i.e., H₂, increased. The molar ratio of consumed H₂ to consumed CO₂ remained at approximately 1 for all three H₂/CO₂ ratios; this is consistent with the stoichiometric ratio in CO₂ reduction via equation 1. The results show that selectivity for CO was nearly 100% in CO₂ reduction with H₂ over the Au/CeO₂ catalyst.

Fig. 4 shows the effect of the GHSV on CO₂ and H₂ conversions over the Au/CeO₂ catalyst at a H₂/CO₂ molar ratio of 1. The CO₂ or H₂ conversion decreased linearly with increasing GHSV, with identical slopes; this is consistent with the H₂/CO₂ stoichiometric ratio of 1 in Equation (1). At a low GHSV, the long residence time would enable TE to be achieved. At a GHSV

Fig. 4. Effect of GHSV on CO₂ and H₂ conversions over Au/CeO₂ catalyst at 400 °C and H₂/CO₂ molar ratio of 1.

Fig. 5. Durability test of Au/CeO₂ catalyst at 400 °C for 6 h. Reaction conditions: H₂/CO₂ molar ratio = 1, and GHSV = 12000 mL/(h·g).

of 6000 mL/(h·g), which is much lower than the typical GHSV of 12000 mL/(h·g), CO₂ conversion reached 20.7%, approaching the TE value of 22.4%.

The effects of temperature, H₂/CO₂ molar ratio, and GHSV on the conversions of CO₂ and H₂ over the Au/CeO₂ catalyst were investigated. The CO₂ conversion approached the TE value under various conditions, i.e., above 450 °C at a GHSV of 12000 mL/(h·g) (Fig. 2), or at 400 °C and a GHSV of 6000 mL/(h·g) (Fig. 4). The molar ratios of consumed H₂ to consumed CO₂ for various H₂/CO₂ molar ratios were approximately the same and consistent with the stoichiometric ratio of the reaction; this is evidence of nearly 100% CO selectivity. GC showed that the only carbonaceous product was CO, providing further evidence that the CO selectivity was nearly 100%. Figs. 3 and 4 show the approximate ratios of consumed H₂ to consumed CO₂; the changes in H₂ and CO₂ conversions with changes in GHSV had the same slope, confirming that the reaction follows Equation (1).

3.3. Catalyst durability test

Fig. 5 shows the durability of the Au/CeO₂ catalyst during reaction for 6 h. The CO₂ and H₂ conversions decreased slightly

and the conversion values were consistent with those in Fig. 3; the CO selectivity remained at around 100%. HRTEM images of the Au/CeO₂ catalyst before and after reaction for 6 h (Fig. 1) showed that the Au particle size was unchanged. The catalytic activity of a Au-based catalyst is generally highly sensitive to the Au particle size at the nanometer level. The HRTEM images in Fig. 1, which show no obvious changes in the Au particle during the durability test, therefore indicate only slight variations in the catalytic activities, i.e., CO₂ and H₂ conversions.

3.4. Identification of formate intermediate using in situ DRIFTS and mass spectrometry

Supported metal catalysts for CO₂ reduction with H₂ to CO (the RWGS reaction), e.g., Pd-In/SiO₂ [34] and Ni/CeO₂ [27], that give nearly 100% CO selectivity [34] or low CO selectivity because of the formation of methane as a byproduct [27] have been developed. Figs. 2–5 show that our Au/CeO₂ catalyst gave nearly 100% CO selectivity, and a high catalytic activity for CO₂ conversion approaching the TE value. Because such high catalytic activities and nearly 100% CO selectivity were achieved, we examined the mechanism of the reaction over the Au/CeO₂ catalyst.

Two main reaction mechanisms for the RWGS reaction, i.e., the redox mechanism and the associative formate mechanism, have been proposed and are still the subject of debate [11,12]. We investigated the mechanism by examining in situ DRIFT spectra of the Au/CeO₂ catalyst and CeO₂ support to identify the surface species formed during the reaction; the spectra are shown in Fig. 6. The bands at 1540, 1374, and 2865 cm⁻¹ in the spectrum of the Au/CeO₂ catalyst, and at 1525, 1366, and 2842 cm⁻¹ in the CeO₂ support spectrum, are ascribed to $\nu_{as}(\text{COO})$, $\nu_s(\text{COO})$, and $\nu(\text{CH})$, respectively, of surface formate species [35–37]. The amount of surface formate species on the Au/CeO₂ catalyst was much larger than that on the CeO₂ support, which suggests that the Au/CeO₂ catalyst greatly accelerates the formation of formate species. The results confirm that surface formate species are formed during CO₂ reduction with H₂. We used in situ DRIFTS and mass spectrometry to study the decomposition of surface formate species to determine whether the formate species are intermediates in formation of the

Fig. 6. In situ DRIFT spectra of (1) Au/CeO₂ catalyst and (2) CeO₂ support at (a) 2000–1000 cm⁻¹ and (b) 3200–2700 cm⁻¹, after purging for 13 min with Ar (50 mL/min) after reaction at 400 °C.

target products.

Fig. 7 shows the profiles of the normalized peak areas of $\nu(\text{COO})$ and $\nu(\text{CH})$, and the integrated mass spectral signals of CO and H₂O formed by decomposition of surface formate species as a function of time on the Au/CeO₂ catalyst. The DRIFT and mass spectra basically show the same change profiles. The normalized peak areas of $\nu(\text{COO})$ and $\nu(\text{CH})$ were acquired by integration from 1800 to 1100 cm⁻¹ and 3100 to 2700 cm⁻¹, respectively. The amounts of CO and H₂O formed were determined by integration of the mass spectral signals at $m/z = 28$ and 18, respectively. The profiles of the normalized peak areas of $\nu(\text{COO})$ and $\nu(\text{CH})$ obtained using DRIFTS and the amounts of CO and H₂O formed, determined from the mass spectra, represent the decomposition of surface formate species with time on the Au/CeO₂ catalyst. The DRIFTS peak area gradually decreased and then stabilized on approximately the same time scale as the corresponding decrease in the mass spectral signal before stabilization. The data for the CeO₂ support are not presented here because of the low intensity of the signal. It can be concluded that CO₂ selective reduction with H₂ to CO and H₂O over the Au/CeO₂ catalyst involves a surface formate intermediate.

4. Conclusions

In summary, we synthesized a Au/CeO₂ catalyst that was highly active in CO₂ reduction with H₂ to CO (the RWGS reaction) at low temperatures (<500 °C) and atmospheric pressure. The Au in the Au/CeO₂ considerably increased the catalytic activity for CO₂ conversion compared with that of the CeO₂ support. The catalyst showed high activity, approaching the TE value under the conditions H₂/CO₂ molar ratio = 1, at temperatures above 450 °C and GHSV = 12000 mL/(h·g), or 400 °C and GHSV = 6000 mL/(h·g); nearly 100% CO selectivity was achieved. The CO₂ conversion increased with increasing H₂/CO₂ ratio, and the ratio of consumed H₂ to consumed CO₂ was approximately consistent with the stoichiometric ratio of the reaction. In terms of the mechanism, DRIFTS and mass spec-

Fig. 7. Changes in integrated mass spectral signals of gaseous products and normalized peak areas of $\nu(\text{COO})$ and $\nu(\text{CH})$ during decomposition of surface formate species as function of time on Au/CeO₂ catalyst in Ar at 500 °C.

troscopy showed that the reaction over the Au/CeO₂ catalyst proceeds via a surface formate intermediate; this accounts for the high activity of the Au/CeO₂ catalyst at low temperature in the RWGS reaction.

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Graphical Abstract

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Selective reduction of carbon dioxide to carbon monoxide over Au/CeO₂ catalyst and identification of reaction intermediate

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We showed that Au contributes significantly to the high activity of an Au/CeO₂ catalyst in CO₂ conversion. Conversions approaching the thermodynamic equilibrium values were achieved at temperatures above 400 °C.

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Au/CeO₂ 催化剂上 CO₂ 选择加氢为 CO 反应及其中间物种研究

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摘要: CO₂ 的化学转化具有环境及科学双重研究意义. CO₂ 具有很高的化学稳定性, 加氢还原是一种有效的转化途径. 其中将 CO₂ 选择性还原为 CO, 即逆水汽变换 (RWGS) 反应 (CO₂ + H₂ → CO + H₂O), 具有重要的理论意义和应用价值: (1) CO 作为合成气的重要原料, 可以通过 F-T 合成生产更有价值的液体燃料; (2) H₂ 可通过可再生能源电解水制取, 实现了全过程的零排放碳循环利用.

从热力学角度分析, RWGS 反应是一个吸热反应, 高温有利于平衡转化率的提高. 从动力学角度, 一个对正反应有活性的催化剂可同时催化逆反应进行. 可还原性载体负载贵金属催化剂, 如 Pt/CeO₂, Au/FeO_x, Au/CeO₂ 等, 具有很好的低温 WGS 催化活性, 但它们在 RWGS 反应上的研究较少. 我们制备了 CeO₂ 负载纳米 Au 催化剂 (HRTEM 表征结果表明金高度分散于 CeO₂ 载体表面, 粒径为 4–5 nm), 其在常压 CO₂ 加氢还原为 CO 反应中表现出优异的低温活性, 分别在 450 °C, CO₂/H₂ = 1, WHSV = 12000 mL/(h·g), 及 400 °C, H₂/CO₂ = 1, WHSV = 6000 mL/(h·g) 条件下, CO₂ 转化率接近平衡转化率, 且 CO 的选择性为 100%. 随着 H₂/CO₂ 比例增加, CO₂ 转化率明显提高, 且维持 H₂/CO₂ 为 1 的化学计量比反应. 通过原位漫反射红外光谱与质谱相结合的技术, 研究了 Au/CeO₂ 催化剂上的 RWGS 反应路径: Au/CeO₂ 催化剂表面形成了甲酸盐中间物种, 它的消耗伴随着 CO 和 H₂O 产物的生成. 说明 Au/CeO₂ 催化剂遵循中间体机理, 这应该是其具有优异低温 RWGS 反应性能的微观机制.

关键词: 二氧化碳还原; Au/CeO₂ 催化剂; 一氧化碳; 甲酸盐中间物种; 原位红外漫反射光谱

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