Comparative studies of low-temperature water–gas shift reaction over Pt/CeO$_2$, Au/CeO$_2$, and Au/Fe$_2$O$_3$ catalysts

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Abstract

We studied catalytic low-temperature water–gas shift (WGS) reaction over the Pt/CeO$_2$, Au/CeO$_2$ and Au/Fe$_2$O$_3$ catalysts. The activity of these catalysts was tested in the composition of 4% CO, 2.6–20% H$_2$O and helium in the range of 120–360 °C. It was found that CO and H$_2$O concentrations have significant effects on the catalytic activity. The 1% Pt/CeO$_2$ was substantially more active than other catalysts in the presence of 20% H$_2$O. The catalytic activity of these catalysts was compared in the presence of H$_2$ and deactivation test was also performed. BET, XRD, SEM and TEM analyses give additional information on the morphological structure of investigated samples.
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1. Introduction

Polymer electrolyte fuel cells (PEFC) are attractive for use in transportation applications. H$_2$ produced from on board steam reforming of gasoline and diesel fuel is the most logical means powering the PEFCs. However, the H$_2$ produced from reformed gas contains ∼10% CO. In general, water–gas shift (WGS) reaction is the preferred reaction for CO removal. Conversion of CO by the water gas shift (Eq. (1)) increases the hydrogen yield as well as getting reducing the CO concentration from ∼10% to ∼0.5–1% [1].

$$CO + H_2O \rightarrow CO_2 + H_2; \quad \Delta H = -41.1 \text{ kJ mol}^{-1}$$
(1)
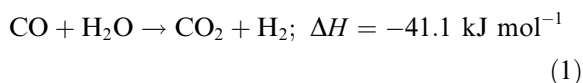
There are two types of WGS catalysts which are commercially used. One is a high temperature shift catalyst, which consists of oxides of iron and chromium and is used at 400–500 °C to reduce the carbon monoxide to around 2–5%. The second one is a low temperature shift catalyst composed of copper, zinc oxide and alumina normally used between 200 and 400 °C to reduce the CO concentration to ∼1%. The thermodynamics of the

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WGS reaction are well known in that at high temperatures the conversion is equilibrium limited and at low temperatures it is kinetically limited. Commercially a combination of the two catalysts is used with in between cooling. If more active low temperature shift catalysts can be found the conversion can then approach the equilibrium limit more closely.

Extensive research, in particular during the past 10 years, has shown that ceria affects in a number of catalytic reactions. Cerium oxide or Ceria (CeO_2) may exist in several oxidation states, due to the ease with which the oxidation state changes between +3 and +4. A number of functions have been ascribed to ceria, including promoting WGS activity [2], maintaining the dispersion of the catalytic metals [3] and stabilizing the surface area of the support [4]. In addition, it also promotes precious metal catalysts for WGS reaction [5–7]. Because of these beneficial effects of ceria, we chose it as the support for Pt and Au WGS catalysts. We wanted to compare the activities of Pt and Au under similar conditions with similar supports. Gold based catalysts have gotten attention recently because of their catalytic activity in low temperature CO oxidation, catalytic combustion of hydrocarbons and potentially high activity for WGS reaction when supported on Fe_2O_3 [8–11]. The Au/Fe_2O_3 catalyst has been promoted as a good catalyst for low temperature WGS reaction due to a specific interaction between gold and ferric oxide support. According to literature data, many studies indicate that the commercial catalysts are sensitive to sulfur and chloride poisoning which has led to the development of high activity long lifetime and poisoning resistance.

In our previous studies on selective CO oxidation in the presence of hydrogen, we found that the Pt/CeO_2 sol–gel and Au/CeO_2 co-precipitation catalysts exhibited high activity and selectivity. It is generally known that precious metals like Pt, Rh and Pd are not good shift catalysts because they are not easily oxidized by water. On the other hand, the oxidation of Ce_2O_3 by water to give hydrogen is thermodynamically favorable [12].

The aim of this study was to compare our catalysts which exhibit high activity on selective CO oxidation and WGS activities with the reference catalyst. We wish to summarize the features that we obtained on selective CO oxidation and low temperature WGS activities at 200–250 °C. In this paper we report the results of our characterization and activity studies of the low temperature WGS reaction on Pt/CeO_2 and Au/CeO_2 catalysts and their comparison to Au/Fe_2O_3 catalyst.

2. Experimental

2.1. Catalyst preparation

1% Pt/CeO_2 catalyst was synthesized using the sol–gel method. The single step sol–gel catalysts were prepared by hydrolyzing a solution of Ce acetate and $H_2PtCl_6 \cdot 6H_2O$ with NH_4OH. The reaction mixture was aged at 80 °C and pH of 9.0–9.5 for an hour. Then, HNO_3 was added until gelation. The catalysts were dried overnight at 110 °C and calcined at 500 °C for 5 h.

The 1% Au/CeO_2 was prepared using the co-precipitation from a mixture of $HAuCl_4 \cdot 3H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$ and Na_2CO_3 solution at room temperature and constant pH of 8.0. The precipitate was aged for an hour at room temperature. The precipitate was then filtered and washed with deionized water until there were no anions detectable in the wash. After washing, the catalysts were dried overnight at 110 °C and calcined in air at 500 °C for 5 h.

In the case of 3% Au/Fe_2O_3 catalysts, they were prepared using co-precipitation and deposition–precipitation methods [9]. For the co-precipitation method, $Fe(NO_3)_3 \cdot 6H_2O$ was used as a precursor.

The deposition–precipitation catalyst was prepared by deposition of gold hydroxide by adding a solution of Na_2CO_3 at 60 °C and pH of 8. The precipitate was aged for 1 h, filtered and washed carefully until absence of excess anions. Then, samples were dried at 110 °C and calcined at 400 °C for 2 h.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns were collected in air on a Rigaku Powder Diffractome-

ter using CuKα radiation with a nickel filter. The BET surface area of the samples was analyzed by nitrogen adsorption with an Auto-sorb automated gas sorption analyzer. Scanning electron microscope (SEM) measurements were performed by using JEOL JSM-5410LV scanning microscope operated at 15 kV. The transmission electron microscopy (TEM) was carried out using a JEM 2010 operating at 200 kV in bright and dark field modes. Crystallinity and crystal structure of the sample were evaluated from selected area electron diffraction pattern.

2.3. Catalytic activity

The catalytic activity tests of the catalysts in the WGS reaction were carried out at atmospheric pressure and in the temperature range of 120–360 °C in a U-tube pyrex reactor having an internal diameter of 6 mm. The catalysts were tested for their activities in a gas mixture typically containing 4% CO in He, saturated with water vapor. The temperature of the gas bubbler was controlled in order to obtain variable H_2O/CO ratio. The space velocity was 30,000 ml g h^{-1}. The 1% Pt/CeO_2 and 1% Au/CeO_2 catalysts were pretreated at 110 °C for 2 h in the O_2 atmosphere. In the case of 3% Au/Fe_2O_3 catalyst, the reduction of the sample was conducted at 250 °C for 12 h in a hydrogen/helium mixture (1% H_2). The reactant and product composition was analyzed by a gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a 10 ft × 1/8 in. stainless steel packed column filled with carbosphere.

3. Results and discussion

3.1. Sample characterization

The measured data of the BET surface areas of samples are listed in Table 1. The BET surface areas of the 1% Pt/CeO_2 sol–gel, 1% Au/CeO_2 co-precipitation and 3% Au/Fe_2O_3 co-precipitation and deposition–precipitation catalysts are 55.0, 124.1, 345.0 and 79.5m^2 g^{-1}, respectively. In addition, it was observed that the surface area of

Table 1
Surface area of the catalysts

Catalyst	Preparation method	BET surface area (m^2 g^{-1})
1% Pt/CeO_2	Sol–gel	55.0
1% Au/CeO_2	Co-precipitation	124.1
3% Au/Fe_2O_3	Co-precipitation	345.0
3% Au/Fe_2O_3	Deposition–precipitation	79.5

3% Au/Fe_2O_3 deposition-precipitation catalyst was slightly higher than that reported in the literature, which is 66.5 m^2 g^{-1} [10].

Fig. 1 shows the comparison of XRD patterns of Pt/CeO_2 and Au/CeO_2 catalysts. No evidence of metallic peaks was observed and it can be concluded that the average crystallite sizes of metals for both catalysts were smaller than 5 nm. The CeO_2 crystallite sizes of the catalysts were determined from X-ray line-broadening using the Debye Scherrer equation. This figure also shows that the ceria support is highly crystalline with an approximate crystallite size of 34.8 and 14.5 nm for Pt/CeO_2 and Au/CeO_2 catalysts, respectively.
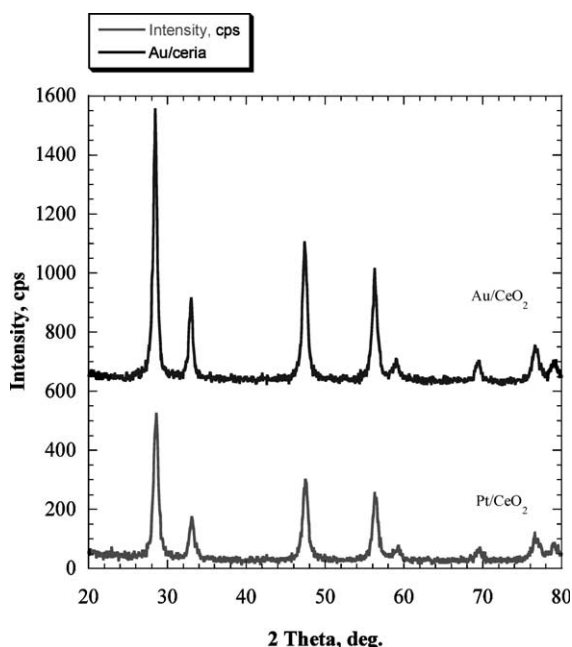

Fig. 1. XRD pattern obtained from the Pt/CeO_2 sol–gel, Au/CeO_2 co-precipitation catalysts.

In contrast, the sample of Au/Fe_2O_3 shows diffraction patterns which mainly correspond to amorphous ferrihydrite or comprise the poorly crystalline phases of ferrihydrite and α-Fe_2O_3 (hematite).

The morphological differences between the catalysts observed by SEM which is not shown here that the Pt/CeO_2 sol–gel catalyst shows a porous morphology. Au/CeO_2 co-precipitation catalyst is in the form of highly crystalline flakes and Au/Fe_2O_3 deposition–precipitation catalyst is amorphous and appears to consist of nonporous aggregates of primary spherical particles of $\sim$1000 Å diameter. The SEM result of Au/CeO_2 catalyst is confirmed by the XRD result, which shows that the crystallinity of CeO_2 in this catalyst is higher than that of Pt/CeO_2 catalyst and amorphous patterns of Au/Fe_2O_3 catalyst.

Basinka et al. [13] found that the most important parameter whose influence on the catalyst activity in WGS reaction is the mean size of particle of metallic ruthenium. In this work, XRD and SEM could not identify the metallic particles of our catalysts. Because of the sensitivity of XRD analysis only to crystallites larger than 5 nm. However, no obvious correlation in the literature was observed between the particle size of metal crystallites and catalyst activity in WGS reaction. It was concluded by Tabakova et al. [14] that the catalytic activity of gold/metal oxide catalysts depends strongly not only on the dispersion of gold particles but also on the nature and textural structure of the supports. The Pt and Au crystallite size of Pt/CeO_2 and Au/CeO_2 catalysts could be clearly observed in TEM images as shown in Fig. 2. The crystallite size distribution of the Pt/CeO_2 appears to have two very close peaks with 30% of the crystallites counted having a size of 6 nm and 15% having a size of 10 nm. The average crystallite size of Pt/CeO_2 was about 7.5 nm. For Au/CeO_2, it was about 4 nm and quite homogenous in size. XRD measurements did not show any detectable Pt and Au crystallites. However, the existence of Pt and Au particles on CeO_2 support was verified by using EDS focusing on the regions containing highly contrast spots under transmission electron microscope.
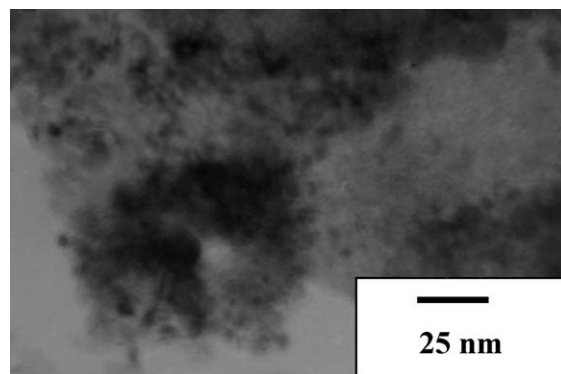
(a) Pt/CeO_2
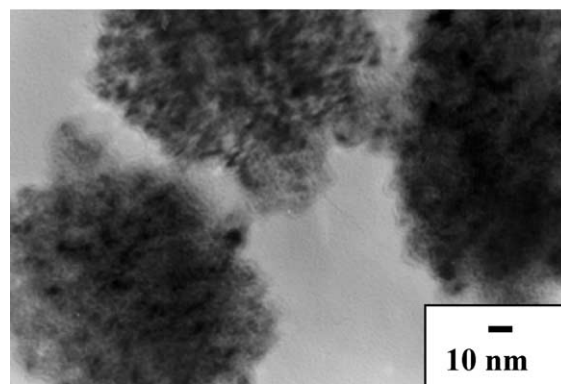
(b) Au/CeO_2

Fig. 2. TEM of metal particles (dark spots) on the CeO_2 surface; (a) Pt/CeO_2; (b) Au/CeO_2.

3.2. Catalytic activity

The catalytic activity of Pt/CeO_2, Au/CeO_2, and Au/Fe_2O_3 catalysts was examined in this work. The catalytic activity expressed as the percentage of the CO conversion in the WGS reaction versus reaction temperature was carried out with a feed stream typically consisting of 4% CO, 2.6% H_2O and helium and the results are shown in Fig. 3. The Au/Fe_2O_3 deposition–precipitation catalyst is very active in comparison to all other catalysts examined and reached a maximum CO conversion of 34% at 320 °C. The lowest activity is shown by highly crystalline ceria containing Au/CeO_2 catalyst. This catalyst gave a maximum conversion of 9% at 320 °C. It is clearly seen that the activity of the catalysts is related to the kind of
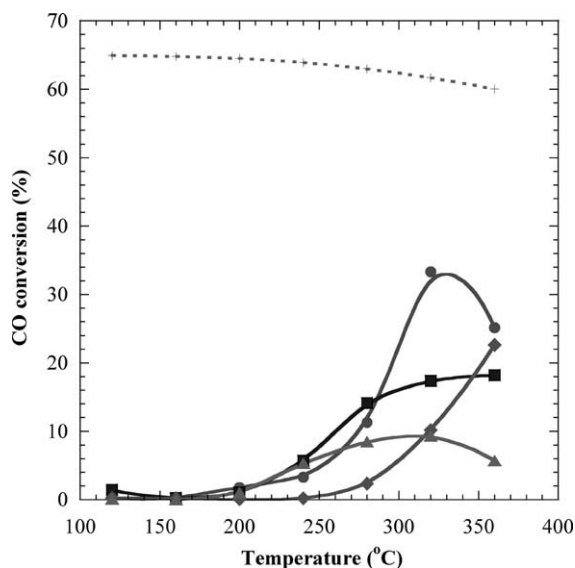
Fig. 3. Temperature dependence of the catalytic activity of the sample studied; (■) Pt/CeO$_2$ sol–gel; (σ) Au/CeO$_2$ co-precipitation; (●) Au/Fe$_2$O$_3$ deposition–precipitation; (υ) Au/Fe$_2$O$_3$ co-precipitation; (–) thermodynamic equilibrium.

Fig. 4. Effect of water on the catalytic activity of the Pt/CeO$_2$ sol–gel catalyst; (●) 2.6% water; (■) 20%water.

support used and there is no relation between activity and surface area [13].

Interestingly, when comparing the effect of preparation method on Au/Fe$_2$O$_3$ catalyst, it was found that deposition–precipitation gave higher CO conversion than co-precipitation. This has been explained by Andreeva et al. [10] as deposition–precipitation method giving a weaker interaction between gold particles and the support making it more favorable for catalysis. In contrast, co-precipitation method gave gold cluster formation which became inaccessible to catalysis. The lowest activity is shown by highly crystalline ceria containing Au/CeO$_2$ catalyst. This result disagrees with Tabakova et al. [14] who observed that the lowest activity is shown by the amorphous catalyst.

3.3. Effect of water vapor concentration

WGS reaction is thermodynamically unfavorable at elevated temperatures. In order to achieve high conversion, additionally excess steam is used to drive the reaction thermodynamically. We tested the dependence of activity on water vapor
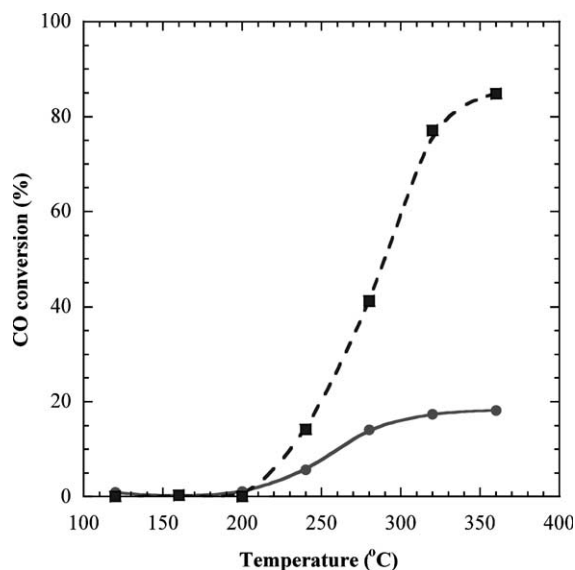
concentration by increasing the water vapor in the feed stream to 20%. It is clearly seen from Fig. 4 that the water vapor content significantly enhanced the catalytic performance of Pt/CeO$_2$ catalyst in the temperature range of 200–360 °C. The maximum CO conversion increased from 18% to 85% at 360 °C. The results are consistent with a PGM/CeO$_2$ interaction resulting in enhanced WGS activity [2]. When water is present, CO conversion is higher. On the other hand, the water content has slightly less of an effect on the activity of Au/CeO$_2$ and moderately influenced Au/Fe$_2$O$_3$ catalysts in the reaction temperature range of 300–360 °C. With 20% water content the maximum conversion increased from 8% to 15% and 33% to 53% for Au/CeO$_2$ and Au/Fe$_2$O$_3$ catalysts, respectively, which are not shown here.

In the literature, the water content is crucial for the activity of commercial CuO–ZnO catalysts [15]. The promoting effect of water vapor on CeO$_2$ can be explained as oxidation of the CeO$_2$ support by water [16]. The water in hydroxide form may play an important role as a good oxidant in WGS reaction. Holmgren et al. [16] speculated that CO reacts with OH to produce CO$_2$ and H$_2$ in the WGS reaction on Pt/CeO$_2$ catalyst by using FTIR.
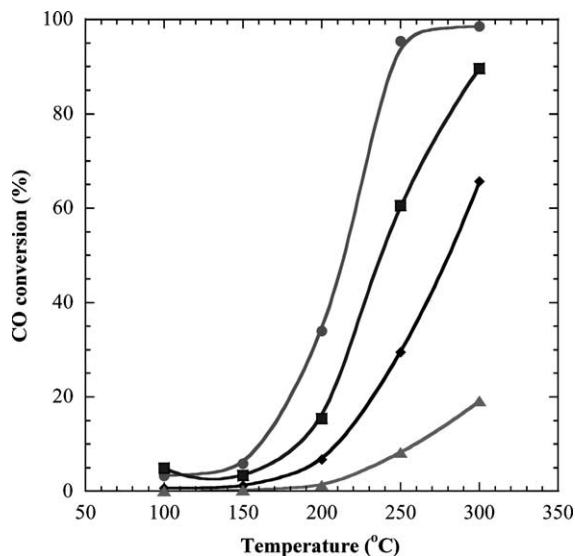
Fig. 5. Effect of CO upon the catalytic activity of the Pt/CeO_2 sol–gel catalyst; (●) 0.5% CO; (■) 1.0% CO; (υ) 2.0% CO; (σ) 4.0% CO.

From FTIR measurements, it was seen that Pt facilitates the formation of carbonates.

3.4. Effect of CO concentration

The effect of the CO concentration on the catalytic activity of Pt/CeO_2 sol–gel catalyst in the WGS reaction was studied and is illustrated in Fig. 5. In this experiment, the concentration of CO was varied from 0.5% to 2%, water concentration was 2.6% the rest being helium. As shown in Fig. 5, there is a significant effect of CO concentration in the temperature range of 160–250 °C. CO conversion increases with an increase in the reaction temperature over Pt/CeO_2 sol–gel catalyst. However, CO conversion decreases with increasing CO concentration in the feed. At 0.5% CO in the feed, CO conversion reaches a maximum of 95% at temperature of 250 °C. The decrease with increasing CO concentration is most likely due to the well-known poisoning effect of CO on Pt sites. Similar effect was also observed on Au/CeO_2 and Au/Fe_2O_3 catalysts.

3.5. Deactivation test

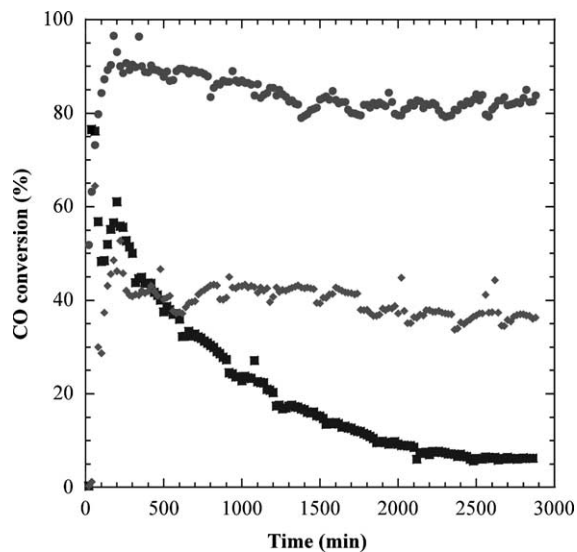The catalytic stability of Pt/CeO_2, Au/CeO_2 and Au/Fe_2O_3 catalysts which showed the maxi-

Fig. 6. Deactivation test of the Pt/CeO_2 sol–gel, Au/CeO_2 co-precipitation, and Au/Fe_2O_3 deposition–precipitation catalysts; (●) Pt/CeO_2; (■) Au/CeO_2; (υ) Au/Fe_2O_3.

mum activity was tested for 48 h at the temperature of 360, 360 and 320 °C, respectively. The catalytic stability was carried out with a feed stream typically consisting of 2% CO, 20% H_2O and helium. The result of the catalytic stability is shown in Fig. 6. It is seen that Pt/CeO_2 catalyst showed good stability compared to the other two catalysts. The stability of Au/CeO_2 catalyst was dramatically decreased from conversion of 60% to about 10% within 48 h. In the spent catalyst, the XRD and TEM results indicated an average size of Au catalyst was increased from 4 to 5.5 nm and this is considered to be the reason for the deactivation for the Au catalyst after long time of operation. The higher average size of the Au particles after reaction was expected because Au particles agglomerate into bigger sizes.

4. Conclusions

The catalytic activity of Pt/CeO_2, Au/CeO_2 and Au/Fe_2O_3 catalysts has been investigated for low temperature WGS reaction. We find that the crystallinity of the reducible oxide support negatively effects the activity of the catalyst. The

activity of metal/cerium oxide catalysts strongly depends on type of metal with Pt being a much more active catalyst than Au. These findings indicate that Pt as well as CeO_2 plays an important role in this reaction. We also observed that water had a positive effect on the Pt/CeO_2 catalysts and a moderate positive effect on the Au/CeO_2 and Au/Fe_2O_3 catalysts. In addition, it was found that CO concentration greatly affected the activity of Pt/CeO_2, Au/CeO_2 and Au/Fe_2O_3 catalysts.

Our investigations on gold-based catalytic systems clearly demonstrated the Fe_2O_3 is not the most suitable supports for WGS reaction which was found by Andreeva et. al [8–10]. The catalytic activity and stability tests show that activity of the gold-containing catalysts is decreasing during the catalytic tests. The effect of addition of about 40% of H_2 into the gas mixture was also examined. A low WGS activity in the presence of H_2 is also exhibited by the Au-containing catalysts. Accordingly, the Pt supported on CeO_2 catalysts seemed to be appropriate for the WGS reaction at moderate reaction conditions and high H_2O/CO in comparison with the Au catalysts in the presence and absence of H_2.

Acknowledgements

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