Graphical abstract

Kinetic Characteristics of Oxygen-Enhanced Water Gas Shift on CeO₂-Supported Pt-Cu and Pd-Cu Bimetallic Catalysts

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Abstract

Our laboratory has developed a new approach to enhance water gas shift (WGS) at low temperature by adding a small amount of O_2 over CeO_2 -supported bimetallic catalysts, which is called oxygen-enhanced water gas shift (OWGS). In the present study, the activities of bimetallic and monometallic catalysts were comparatively evaluated and the origin for better performance in the bimetallic catalysts was sought by a kinetic study. The CeO_2 -supported Pt-Cu and Pd-Cu catalysts showed not only higher activity, but also higher stability for about 70 hours under practical OWGS condition, which was corroborated by little change in FT-IR spectra of surface species before and after the long-duration reaction. In the kinetic analysis, O_2 addition to WGS significantly increased the reaction order in CO for all the catalysts tested while the reaction order in H_2O changed little upon O_2 addition to WGS. The catalysts with relatively low CO order such as Pt or Pd had relatively high H_2O order while the catalysts with high CO order such as Cu had low H_2O order. Such a trend shows that the reaction rate is determined by the balance between the two reactants on the surface and O_2 addition to the feed changes this balance by removing some CO to make more sites open for H_2O adsorption and activation. In the presence of the product gases, H_2O activation becomes more rate-limiting, so that the combination of noble metal and copper on CeO_2 is more effective with the use of added oxygen to remove the CO strongly adsorbed on the active sites.

Key words: Oxygen-enhanced Water Gas Shift (OWGS), Water Gas Shift (WGS), Pd, Cu, Metal Catalyst, CeO_2 -supported Pd-Cu, Bimetallic catalyst

1. Introduction

Water gas shift (WGS) is one of the critical steps in fuel processing for H_2 production for low-temperature fuel cell applications. Cu supported on zinc-alumina oxide has traditionally been used for this reaction, but the activity is not sufficient and the high Cu loading causes the catalyst to be pyrophoric [1, 2]. Over the past 20 years, attention has shifted towards CeO_2 -supported metal catalysts due to its desirable oxygen storage and release properties [3]. Our group has been developing CeO_2 -supported Pt-Cu and Pd-Cu bimetallic catalysts specifically for the oxygen-enhanced water gas shift (OWGS) where a small amount of O_2 is added to promote WGS at low temperature [4-6].

The WGS activity of CeO_2 -supported catalysts largely depends on their metal component. For instance, Pd and Ni are much more active than Co or Fe [7]. Rh and Ru are both active for WGS, but they also produce methane, which significantly reduces H_2 production [8]. Pt has been reported to be the most active component, but due to the high cost for Pt, the loading should be minimized [9]. Cu/ CeO_2 is the most active among inexpensive base-metal catalysts. Since Cu inherently has pyrophoric nature and sinters easily, high Cu loading needs to be avoided [1]. Although a Cu/ CeO_2 catalyst with low Cu loading has been reported to be non-pyrophoric [10], Cu is not tolerant to water vapor. At a low temperature and high H_2O concentration, Cu surface is fully hydrated and oxidized, resulting in a loss of activity [11]. Its activity is also lower than a commercial Cu-Zn-Al oxide catalyst depending on the reaction condition [12]. Therefore, alloying Cu with noble metal would be one of the solutions to overcome these drawbacks of Cu.

The deactivation pattern and its cause are also dependent on metal species supported on CeO_2 . While the deactivation of Cu-based catalysts is primarily caused by an oxidation of Cu surface during WGS, the deactivation of CeO_2 -supported catalysts has been attributed to several causes such as over-reduction of ceria, carbonate formation, and metal agglomeration. Pt/ CeO_2 catalyst was reported to deactivate through over-reduction of CeO_2 based on the observation of strong dependence of deactivation rate on the presence/absence of H_2 in the feed [13]. Meanwhile, another group reports the main cause for deactivation is carbon deposition based on a temperature-programmed oxidation (TPO) experiment before and after an exposure to CO [14]. The authors observed a deposition of carbon, whose amount far exceeded the number of Pt surface sites but occupied only 6.5% of CeO_2 surface, leading to the argument that an active portion of support is limited to the vicinity of Pt and such a portion of CeO_2 surface enables oxygen diffusion to Pt sites to ease the reaction with CO. On the other hand, Pd/ CeO_2 was reported to deactivate through a metal agglomeration based on Pd dispersion measurements before and after the accelerated

aging in CO atmosphere [15]. The authors correlated WGS activity to metal surface area. Their observation indicated the entire surface of Pd could be effective in catalyzing WGS if the rate of oxygen transfer from CeO₂ to Pd is comparable to the overall reaction rate. Au/CeO₂ catalyst was reported to deactivate through carbonate or formate deposition in a CO/H₂ condition, but the activity is recoverable upon heating up in the air [16]. Another group reported Au/CeO₂ has no deactivation during WGS. The activity was even improved after the WGS reaction which was related to a re-dispersion of gold particles regardless of increased CeO₂ crystallite size [17]. The authors found the lower gold loading shows a better activity and this seems in good agreement with the report by Fu et al. that gold in an ionic form determines the WGS rate [18]. These reports show the cause of deactivation, reaction pathway, and active sites are mutually related.

While deactivation and kinetics of monometallic catalysts on CeO₂ has been studied in detail, little attention has been drawn for bimetallic catalysts. Literature exists for the alloy formation for Pt-Cu and Pd-Cu supported on alumina or zeolites [19, 20], but CeO₂-supported bimetallic catalysts in relation to OWGS and WGS activities were little studied. In our previous paper, it was reported that both Pt-Cu and Pd-Cu form alloy and their structures influence catalyst properties and activity [21]. The study showed Pd is highly dispersed in Cu and the Pd strongly interacts with Cu to impact positively on OWGS activity. As for kinetic aspect, there is only one report mentioning that the CO oxidation rate on Pd-Cu/(Ce, Zr)O_x is governed by the Cu/(Ce, Zr)O_x character as an active site and Pd is only involved in a CO activation process [22].

In the present study, the activity and kinetic characteristics of Pt-Cu and Pd-Cu bimetallic catalysts in an OWGS condition were compared to those of monometallic catalysts. A kinetic study was conducted to identify the effect of O₂ addition to WGS as well as to extract the reaction pathway and possible active sites from different kinetic behaviors on various metals supported on CeO₂. The influence of the product gases (H₂ and CO₂) were also discussed in relation to the reaction pathway. The cause of deactivation on each catalyst was discussed from FT-IR spectra before and after reaction.

2. Experimental

The supported metal catalysts were prepared by incipient wetness impregnation of aqueous solution of tetra-ammine platinum (IV) hydroxide, copper (II) nitrate hemipentahydrate, acetone solution of palladium (II) acetate on cerium oxide and aluminum oxide. Co-impregnation was carried out using

acetone solution for Pd-Cu bimetallic catalyst and sequential impregnation was carried out using aqueous solution for Pt-Cu bimetallic catalyst due to immiscibility of the Pt and Cu salts in aqueous solution. The employed supports were CeO₂ obtained from Rhodia (HSA, 155 m²/g of specific surface area) and Al₂O₃ obtained from Sasol (TH100/150, 150 m²/g). The platinum and palladium loadings were 1 wt% while that of copper was 5 wt% unless otherwise specified. All the catalysts were calcined at 450°C for 5 hours.

The methods for catalytic activity test and kinetic analysis are described elsewhere [21], so the procedure is described briefly here. Activity and stability for OWGS were evaluated using a quartz fixed-bed down-flow reactor with 4 mm of inner diameter (aspect ratio = ~1.5). About 0.1 g of catalyst (sieved into 0.25 to 0.50 mm in diameter) was packed in the reactor. The feed gas composition was 9.7% CO / 22.8% H₂O / 6.3% CO₂ / 37.9% H₂ / 6.9% air / argon balance (O₂/CO = 0.14). The space velocity was around 64,400 h⁻¹ (dry, excluding air and argon). In kinetic study, 0.015g of catalyst was diluted with SiC of the same particle size to attain 0.065 ml of total bed volume. The gas composition in the kinetic study was 9.8% CO / 23.0% H₂O / 6.9% air / N₂ balance. Prior to the catalytic reaction, the catalyst was reduced in-situ in 7.5% H₂/N₂ flow at 260°C for 1 h.

The CO chemisorption measurements were conducted on a Micromeritics Autochem 2910 TPD/TPR equipped with a TCD detector. After the sample was reduced in 5% H₂/argon flow at 225°C for 15 min, the residual H₂ was flushed for 15 min by helium followed by cooling down to the sample temperature to -30 ± 3°C. 10% CO/helium pulses were then sent to the sample and CO uptake was calculated from the TCD signal. The CO pulse was generated by 0.518 ml of loop volume (heated at 110°C) connected to an automated 6-way valve. The data were successfully reproduced a couple of times. The same equipment was used for transient pulse studies. The responses of multiple reactant and product gases were simultaneously monitored by an Ametek Dycor Dymaxion mass spectrometer DM200M.

The surface species on the catalyst was analyzed by in-situ Fourier transform infrared spectroscopy (FT-IR) with diffuse reflectance mode using a Nexus 470 spectrometer with a Smart Collector environmental chamber. ZnSe was used as a window material. The sample was mounted on the chamber and heated under H₂ flow (30 ml/min of total flow rate) to 260°C followed by switching to CO/H₂ flow (44 ml/min of total flow rate) and collecting diffuse reflectance data. OMNIC ver. 7 was used for data acquisition and conversion to absorbance unit by the Kubelka-Munk function.

3. Results and Discussion

3-1. Activity and stability of bimetallic catalysts in OWGS

3-1-1. Catalytic tests

Effects of metal species and support material on OWGS activity and stability were investigated in a model reformat gas containing CO, H₂O, CO₂, and H₂. A small amount of oxygen, O₂/CO = 0.14 was added to the feed. The CO conversions in time on stream on various catalysts were measured for 50 to 70 hours and the results of CeO₂-supported 1wt% Pd, 5wt% Cu, 1wt% Pd – 5wt% Cu, and 2wt% Pd – 5wt% Cu catalysts are compared in Fig. 1, the results of CeO₂-supported 1wt% Pt, 5wt% Cu, and 1wt% Pt – 5wt% Cu catalysts in Fig. 2, and the results of CeO₂-supported and Al₂O₃-supported 1wt% Pd – 5wt% Cu catalysts in Fig. 3. As shown in the figures, the order of activity was as follows:

$$\text{Pd(2)Cu(5)/CeO}_2 > \text{Pd(1)Cu(5)/CeO}_2 > \text{Pt(1)Cu(5)/CeO}_2 \sim \text{Cu(5)/CeO}_2 > \text{Pt(1)/CeO}_2 > \\ \text{Pd(1)Cu(5)/Al}_2\text{O}_3 \sim \text{Pd(1)/CeO}_2$$

The improved catalytic performance by increasing Pd loading from 1 wt% to 2 wt% indicates Pd in Pd-Cu particles forms active sites. In our previous EXAFS study, the Pd was found to be highly dispersed in Cu (The coordination numbers were $N_{\text{Pd-Pd}} = 1.4$ and $N_{\text{Pd-Cu}} = 7.1$ for CeO₂-supported 2 wt% Pd – 5 wt% Cu catalyst [21]). Such a structure of Pd-Cu suppresses H₂ oxidation activity that is inherent to Pd [23] and to promote CO shift. The Cu-containing bimetallic catalysts also showed more stable activity compared to monometallic Pt or Pd catalysts. The copper species on CeO₂ are thus resistant towards oxidation even in the OWGS condition. Also from our previous report that the presence of Cu makes catalyst retain less CO and CO₂ on the surface (less CO adsorption and faster CO₂ desorption) [21], the stable activity would be ascribed to suppressed accumulation of CO and CO₂ as carbonate-like species. Meanwhile, Pt and Pd monometallic catalysts showed large activity loss in the initial several hours and the subsequent slow deactivation. These catalysts have a large CeO₂ surface free from metal species (see the high hydroxyl bands in the FT-IR spectra in Fig. 4) in addition to the strong CO chemisorption on noble metal, and therefore the deactivation could be due to the reduction of surface oxygen of ceria by CO to form carbonate-like species which is not re-oxidized by H₂O. The deactivation pattern was similar to what Zalc et al. observed in their stability test of Pt/CeO₂ where a rapid deactivation in an initial period of few hours was followed by a slower deactivation with a constant rate [13]. It is plausible that progressive reduction of ceria accompanies carbonate accumulation. Meanwhile, Hilaire et al. pointed out that the surface of

metal-ceria catalysts are rather completely saturated with carbonate in a WGS condition [7] ascribing the deactivation to a metal sintering. Deactivation cause could depend on metal species and reaction conditions. The deactivation pattern of Al_2O_3 -supported catalyst was different from CeO_2 -supported Pt and Pd. It was monotonic without rapid deactivation in the initial hours, indicating certain continuous structural change of the catalyst.

3-1-2. Diffuse reflectance FT-IR

To investigate the surface species on the various metal catalysts, FT-IR spectra were taken in-situ in H_2 and CO/H_2 atmospheres at 260°C in a diffuse reflectance mode. The results are shown in Figs. 4 and 5, respectively. In the H_2 condition, CeO_2 -supported Pt and Pd single metal catalysts had different feature from Cu-containing samples. Although hydroxyl bands (bidentate OH at 3650 cm^{-1} and unidentate OH at 3710 cm^{-1} [24], broad peaks of tridentate OH [25] and hydrogen-bonded H_2O [26, 27] at around 3500 cm^{-1}) were observed for all the samples, the absorbance of hydroxyl groups was stronger on Pt and Pd catalysts reflecting their large CeO_2 surface free from metal. A very weak hydroxyl band on the Cu-containing samples, on the other hand, indicates that the ceria surface is considerably covered by copper. The broad absorbance of hydrogen-bonded H_2O at around 3500 cm^{-1} also suggests that Cu addition makes the catalyst surface more hydrophilic. The absorbance of carbonate at $1300 - 1600\text{ cm}^{-1}$ [28] was weaker on Pt/ CeO_2 than the other catalysts due to the low reducibility of this catalyst, which was shown in our previous temperature-programmed reduction (TPR) study [21]. In fact, the OCO bands of this sample developed when reduction temperature was raised from 260 to 350°C (not shown in the figure). The Cu-containing catalysts showed a different OCO band structure from those of Pt and Pd catalysts.

Carbonyl bands (1800 to 2100 cm^{-1} [23, 29]) were observed on the Pt and Pd catalysts while no clear corresponding peak was observed on the other catalysts. The carbonyls on Pt and Pd seem to originate from carbonate decomposition in the H_2 atmosphere [30]. These carbonyls consisted of two peaks, suggesting two different configurations. The peaks above 2000 cm^{-1} and those below 2000 cm^{-1} are commonly attributed to linearly-bonded CO and bridged-bonded CO, respectively. The band of CO adsorbed on a dispersed Pt appears at $\sim 1975\text{ cm}^{-1}$ [31] for the Pt case. The lower wavenumber bands arise for CO adsorbed on small Pt due to electronic effects, surface energetics, or the formation of Pt-carbonyl complexes. This band region was also assigned to CO adsorbed on a metal-support interface site [32]. For CO-Pd^0 absorbance, there are several types of bridging carbonyl, i.e. $\text{Pd}_2(\text{CO})$, $\text{Pd}_2(\text{CO})_2$ reported to

appear below 2000 cm^{-1} [33], and 3-fold $\text{Pd}_3(\text{CO})$ below 1900 cm^{-1} [34]. The observed peaks in the present study are therefore assigned to the stretching modes of those bridged CO on Pd.

On Pd catalyst, vibrational modes of bidentate and bridged C-H bond stretching of formate species at 2820 and 2940 cm^{-1} [35] were clearly observed together with formate OCO bands in the finger print region. This suggests that Pd catalyst retains CO_2 adsorbed in the ambient condition as these surface species at an elevated temperature. It could be related to high hydrogenation activity of Pd.

Introducing CO in the H_2 flow changed surface species in IR spectra. The hydroxyl band at 3650 cm^{-1} decreased a little, but significant change was observed in the tridentate OH and hydrogen-bonded H_2O at around 3500 cm^{-1} , which indicates CO changes structure of surface H_2O species. The formate C-H stretchings at 2840 and 2940 cm^{-1} were observed on all the catalysts upon introducing CO. The order of its intensity was $\text{Pd} > \text{Pt} > \text{Pt-Cu}$, $\text{Pd-Cu} > \text{Cu}$. The strong formate peak on Pt and Pd catalysts is consistent with the fact that the larger amount of hydroxyl is available to react with CO to form formate. The stronger formate peak on Pt-Cu and Pd-Cu than Cu alone is consistent with the fact that more CO is chemisorbed on noble metal to react with hydroxyl to form formate. However, irrelevance of formate band intensity to catalytic activity suggests that formates are not pivotal intermediates in the present condition.

The bands in the OCO region significantly increased upon introducing CO. According to literature, the bands at 1590 and 1370 cm^{-1} are assigned to OCO asymmetric and symmetric stretching vibrations mainly of formates and the bands at 1335 (the shoulder of the formate band) and 1470 cm^{-1} are unidentate carbonate OCO [7, 25, 36]. The peaks at 1560 and 1280 cm^{-1} are bidentate carbonate OCO. The peaks at 1080 , 1045 , and 1010 cm^{-1} are assigned to polydentate, unidentate, and bidentate carbonates, respectively [26]. The peak at 854 cm^{-1} is also of carbonates [28]. Similarly to the case of formate bands, Pd/ CeO_2 showed the largest intensity in the carbonate bands. However, the order of intensity of carbonate band for other catalysts was not correlated to the order of activity so the carbonate is not the critical intermediate either.

Carbonyl bands increased and shifted to higher frequency upon introducing CO. There were three absorbance peaks at 2055 , 2035 , and 1953 cm^{-1} for Pt and two peaks at 2034 and 1917 cm^{-1} for Pd, suggesting multiple configurations of chemisorbed CO on each metal. The peaks at higher frequency would be the on-top site CO and the others would be CO adsorbed on dispersed Pt [29, 31] and the bridged (2-fold) CO on Pd [34, 37, 38]. The on-top site CO on Pt includes CO adsorbed on metallic Pt with PtO_x neighbor, CO on the step site, and CO on the terrace site [25]. On Pt-Cu and Pd-Cu catalysts, only the high-frequency peak was observed, probably because both Pt and Pd form alloys with Cu and the bridged and 3-fold CO sites are lost. The intensity of the CO peak of on-top site was lower on Pd-Cu than Pt-Cu, reflecting better alloy formation and stronger interaction of the two components in Pd-Cu than

Pt-Cu, which are consistent with the previous EXAFS and TPR results [21]. The CO adsorption on Cu/CeO₂ was hardly visible because Cu barely chemisorbs CO [39].

To identify the cause of deactivation in OWGS, FT-IR spectra of the sample before and after a long-term reaction were taken in-situ in CO atmosphere in the diffuse reflectance mode. The results are shown in Fig. 6. Pd-Cu/Al₂O₃ catalyst experienced severe changes in spectra before and after the reaction. The IR band below 1200 cm⁻¹ on this sample is related to bare surface of Al₂O₃ [40, 41] and the absorbance was significantly retarded after the long-hour OWGS test. Correspondingly, the absorbance of hydroxyl group at 3750 cm⁻¹ and formate band at 1380 and 1590 cm⁻¹ significantly decreased after the reaction test. These results indicate a destruction of surface structure of the Al₂O₃ support occurred during OWGS. The intensity of carbonyl band at 2050 cm⁻¹ also decreased, suggesting a metal structure change was accompanied by the destruction of support surface. On Pt/CeO₂, the intensity of carbonate and formate increased and the hydroxyl band decreased after OWGS reaction. The increased carbonates would be due to the deepened reduction of support and concomitant retention of CO₂. The depletion of hydroxyl band at 3650 cm⁻¹ is also the sign of accumulation of these intermediates covering ceria surface. Carbon formation is also conceivable as reported in literature [14], but those were not visible in the IR spectrum. The change in carbonyl band was relatively small, but a close investigation (the magnification of the spectra in the inset of Fig. 6) showed decreases in less saturated sites on Pt leaving a flat surface (terrace sites) unchanged.

Pd/CeO₂ exhibited different changes in infrared spectrum from Pt/CeO₂ although the deactivation patterns looked similar on these two samples in Figs. 1 and 2. After the test, the intensity of carbonate region did not change much, but the C-H stretching mode of formate at 2840 cm⁻¹, the asymmetric and symmetric OCO modes of formate at 1590 and 1370 cm⁻¹ were slightly depleted. The carbonyl band at 2034 cm⁻¹ was completely lost, meaning significant change in metal structure. The result suggests sintering of Pd is the main cause of deactivation on Pd/CeO₂. Wang et al. have also reported sintering of Pd is the main cause of deactivation [15]. A transmission electron microscope was not be useful for confirming metal sintering due to the similar image contrasts between CeO₂ and Pd. The carbonate structure also changed, i.e. relative intensity of bidentate carbonate at 1010 cm⁻¹ decreased while those of unidentate and polydentate species at 1045 and 1080 cm⁻¹ increased after the reaction. Thus, carbonates cannot be excluded from deactivation cause. Cu-containing bimetallic catalysts, on the other hand, showed fewer changes in IR spectra before and after the reaction, that is well consistent with their stable activity for long hours shown in Figs. 1 and 2. Recently, specific interfacial carbonates, potentially bidentate and tridentate, were identified as the intermediates for WGS on an inverse CeO₂/CuO catalyst in an isotopic

exchange study of carbonate species and product CO₂ to reactant ¹²CO/¹³CO [42, 43]. The stability of Cu-containing bimetallic catalysts may come from smooth decomposition of carbonates.

3-2. Kinetic study of bimetallic catalysts

3-2-1. CO chemisorption

CO chemisorption measurement was conducted at -30°C for the samples used in activity tests and kinetic studies to evaluate the turnover rate of OWGS. Table 1 lists the CO uptake, metal dispersion calculated with an assumption of 1:1 of CO:M stoichiometry, and metal particle size estimated from Equation 1:

$$d_p = 3 a / D \quad (\text{Equation 1})$$

where d_p is the diameter of metal particle, D is the metal dispersion, and a is the lattice constant of metal species. The lattice constant of alloy was assumed to be proportional to the alloy composition (Vegard's law). The order of CO uptake was Pd(1), Pd(1)Cu(5), 62~63 > Pt(1), Pt(1)Cu(5), 31~34 > Cu(5), 12 (The number is CO uptake in the unit of $\mu\text{mol/g-catalyst}$). The Pd and Pt monometallic catalysts showed higher CO uptake on the total metal basis than the Cu-containing bimetallic catalysts. About twice of CO uptake by Pd catalyst compared to Pt catalyst led to a similar metal dispersion (60~70%) for these two catalysts. Cu catalyst showed about a quarter of the CO uptake of the noble metals despite its higher loading than Pt and Pd, leading to a significantly lower metal dispersion in appearance. The metal particle size of Cu catalyst calculated from its metal dispersion was more than 100 nm which is far overestimated than the value estimated from Cu K-edge EXAFS (4 nm), indicating CO does not much chemisorb on Cu surface [39, 44] even in the low temperature around -30°C while Pt or Pd surface irreversibly chemisorbs CO. A surface enrichment by Cu in the bimetallic catalysts is also possible since the surface free energy of metal is in the order of Cu << Pd < Pt [45]. Transmission electron microscope was not useful for size estimation again from the image contrast issue.

3-2-2. Effect of metal species on OWGS kinetics

To investigate how O₂ addition and choice of metal components are related to the catalytic performance of CeO₂-supported metal catalysts, kinetic analysis was conducted in a CO-H₂O-O₂

condition. The space velocity was set carefully to highlight the effect of O₂ on H₂ production, i.e. the GHSV was set so that O₂ is completely consumed, but CO conversion was still far below equilibrium. The mass transport limitation was small enough to ignore. The effectiveness factor for 250 – 300 °C of reaction temperature was 0.9948 – 0.9998 if the intrinsic rate of CO oxidation is assumed to be 100 per site per second (20 – 200 per site per second of rate attainable at 250 – 300°C on Pd/CeO₂ with 10% Pd dispersion [46]). The H₂ production rates as functions of CO and H₂O partial pressures are shown in Fig. 7. The reaction orders were calculated from the slope of the graph based on the following equations:

$$R(\text{OWGS}) = k \cdot P(\text{CO})^\alpha \cdot P(\text{H}_2\text{O})^\beta \quad \text{or alternatively}$$

$$\log R(\text{OWGS}) = \log k + \alpha \log P(\text{CO}) + \beta \log P(\text{H}_2\text{O}) \quad (\text{Equation 2})$$

where R(OWGS) is the reaction rate, k is the rate constant, P(CO) and P(H₂O) are the partial pressures of CO and H₂O, respectively, and α and β are the reaction orders in CO and H₂O, respectively. The figure showed strong dependency of the H₂ production rate on CO partial pressure in OWGS on all the CeO₂-supported catalysts. The high reaction order in CO means that CO is more sensitively reacting with coreactant (H₂O), which further means that more H₂O is available or activated on the catalyst surface. O₂ addition enhances the participation of H₂O into the reaction probably through removing CO which covers active sites by forming CO island structures [47]. Although all the catalysts showed similarly high reaction order in CO, Pt and Pd catalysts showed slight level-off of the H₂ production rate at high CO partial pressure. This further indicates the surface of these catalysts tends to saturate with CO more easily than Cu-containing catalysts due to the nature of noble metal that chemisorbs CO strongly. The highly saturated surface with CO in spite of O₂ addition would block H₂O adsorption and the subsequent processes (H₂O dissociation and reaction with chemisorbed CO). Interestingly, Pd-Cu supported on low surface area CeO₂ (2 m²/g) also showed similar reaction order in CO to Pd-Cu with high surface area CeO₂. Chemistry of H₂O activation seems independent of surface area of CeO₂ and O₂ addition seems to increase the site number for initial H₂O adsorption by removing CO on the surface. Meanwhile, Pd-Cu/Al₂O₃ showed low CO order compared to the CeO₂-supported counterpart. It is inferred that metal-Al₂O₃ lacks the strong H₂O activation sites which metal-CeO₂ has, and thus the rate is not sensitive to CO partial pressure even if O₂ addition increases the sites for H₂O adsorption. Though Barbier and Duprez claimed OWGS takes place in two steps on Pt/CeO₂-Al₂O₃, CO oxidation first and followed by WGS [48], it should be noted that the H₂O/CO ratio in the feed is 2.3 for the present study which is far lower than 12.5 for their test condition.

Contrary to the high reaction order in CO in OWGS, the reaction order in H₂O was small for all the catalysts. The catalysts with relatively high reaction order in H₂O such as Pt and Pd catalysts tend to have relatively low reaction order in CO while the catalysts with low reaction order in H₂O such as Cu catalyst tend to have high reaction order in CO (Table 2 and Fig. 9). This inverse trend in CO and H₂O fractional orders shows the reaction rate is determined by the balance of surface reactants (chemisorbed CO and H₂O). Similar characteristics of reaction kinetics has been reported by Grenoble et al. who developed a kinetic model of bifunctional reaction pathway where CO adsorbs on metal and H₂O adsorbs on alumina [49]. Considering that H₂O order was obtained at 9.8% of CO concentration where Pt or Pd surface is almost saturated with CO, the observed larger H₂O order for the Pt and Pd catalysts would be due to the limited adsorption of H₂O (limited accessibility to the active sites). On the other hand, Pt-Cu, Pd-Cu, and Cu catalysts would have enough CO-free sites for H₂O adsorption and therefore H₂O order is smaller. The Al₂O₃-supported and low surface area CeO₂-supported Pd-Cu would not have enough ability and quantity to activate H₂O, respectively, and thus the balance of activated H₂O and chemisorbed CO is more weighed on the latter leading to relatively high H₂O fractional order.

The order of H₂ production rate in OWGS (Pt > Pt-Cu > Pd-Cu > Pd > Cu, see Table 3 also) strongly reflects the property of noble metal rather than that of Cu. H₂O adsorption is thus sufficient in the present OWGS condition. The turnover frequency was 6.1 s⁻¹ for Pt, 1.6 s⁻¹ for Pd, and 0.51 s⁻¹ for Pd-Cu if Pd-Cu particle size was assumed to be 4 nm, which are comparable or higher than the value reported in literature [48]. Note that the order of apparent activation energy (Pt-Cu < Pt < Cu < Pd-Cu < Pd, see Table 4) shows that the presence of Cu in catalyst reduces activation energy, which further indicates that Pt and Pd have a large site number while Cu more involves energetics possibly increasing the adsorption enthalpy of the reactants (providing less stable surface reactants).

3-2-3. Effect of metal species on WGS kinetics

To compare with the OWGS kinetics, the kinetic study of WGS was also conducted. H₂ production rates in WGS were plotted as functions of CO and H₂O partial pressures in Fig. 8. In WGS, the reaction order in CO was much smaller than the case of OWGS. It was only under 0.6 for WGS against 1.5 for OWGS and it varied from -0.1 to 0.6 depending on metal species. The trend of reaction order in CO was Cu > Pt-Cu, Pd-Cu > Pd > Pt, inversely reflecting the strength of CO chemisorption. Both Pt and Pd showed negative or zero order kinetics in CO, suggesting that the surface of these metals is fully saturated with CO [39]. The combination of Pt or Pd with Cu led to a higher CO order than Pt and Pd catalysts due to the lower CO coverage caused by Cu. The Al₂O₃-supported Pd-Cu showed lower CO dependency

compared to the CeO₂-supported counterpart, similarly to the OWGS case. This would be due to the lack of activation of H₂O on the Al₂O₃-supported catalyst. The higher rate for Cu(5)/Al₂O₃ than Pd(2)Cu(5)/Al₂O₃ in contrast to the trend for CeO₂-supported counterparts in Fig. 8 demonstrates that the active sites are essentially different between these catalysts with CeO₂ and Al₂O₃. Support does not simply add H₂O activation sites and it changes metal properties.

The reaction order in H₂O again showed an inverse trend to the CO order in WGS, i.e. Pt > Pd > Pt-Cu, Pd-Cu > Cu (Table 3 and Fig. 9). This evidences that the reaction rate is determined by the balance of the two reactants on the surface. The H₂O order in WGS was slightly higher than that in OWGS, but the trend among the five different catalysts was same, which confirms that chemistry in H₂O activation is not changed by O₂ addition to WGS, but only the H₂O adsorption (accessibility to the surface for H₂O) increased. The order of H₂ production rate (Pd-Cu > Pt-Cu > Cu ~ Pt > Pd) reflects synergy in the combination of noble metal and Cu. Comparing with the order of OWGS rate (Pt > Pt-Cu > Pd-Cu > Pd > Cu) which strongly reflects the property of noble metal, the order of WGS rate more reflects the effect of Cu to modify active noble metal (to decrease CO coverage to increase H₂O activation sites) in this condition.

The kinetic data were fitted to a Langmuir-Hinshelwood (L-H) model and redox model using software DataFit ver. 9 (Oakdale Engineering). In the former mechanism, adsorption of CO and H₂O occurs on the same site and adsorption/desorption of the reactants is in equilibrium. With the assumption that H₂O dissociates to hydroxyl and atomic hydrogen upon adsorption, the rate is determined by surface CO coverage and H₂O coverage:

$$\theta_{\text{CO}} = K_{\text{CO}} P_{\text{CO}} / (1 + K_{\text{CO}} P_{\text{CO}} + (K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^{1/2}) \quad (\text{Equation 3})$$

$$\theta_{\text{H}_2\text{O}} = (K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^{1/2} / (1 + K_{\text{CO}} P_{\text{CO}} + (K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^{1/2}) \quad (\text{Equation 4})$$

$$\text{rate} = k \theta_{\text{CO}} \theta_{\text{H}_2\text{O}} = k K_{\text{CO}} P_{\text{CO}} (K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^{1/2} / (1 + K_{\text{CO}} P_{\text{CO}} + (K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^{1/2})^2 \quad (\text{Equation 5})$$

where θ_{CO} and $\theta_{\text{H}_2\text{O}}$ are the surface coverages of the two reactants, K_{CO} and $K_{\text{H}_2\text{O}}$ are the equilibrium constants for adsorption/desorption of the reactants, P_{CO} and $P_{\text{H}_2\text{O}}$ are the partial pressures, respectively. In the latter mechanism, the rate of CO oxidation by surface oxygen is assumed to equal to the rate of reoxidation of the surface by H₂O:

$$k_{\text{CO}} [\text{O}] P_{\text{CO}} = k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} (1 - [\text{O}]) \quad \text{or} \quad [\text{O}] = k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / (k_{\text{CO}} P_{\text{CO}} + k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}) \quad (\text{Equation 6})$$

$$\text{rate} = k_{\text{CO}} P_{\text{CO}} k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / (k_{\text{CO}} P_{\text{CO}} + k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}}) \quad (\text{Equation 7})$$

where k_{CO} and $k_{\text{H}_2\text{O}}$ are the rate constants for oxidation of CO and ceria reoxidation by H_2O , respectively. In the case of OWGS, for both models, P_{CO} was replaced by $P_{\text{CO}} - 2 P_{\text{O}_2}$ to consider the loss of the reactant CO by O_2 addition. The $K_{\text{H}_2\text{O}}$ in L-H model was fixed to unity to simplify the calculation for all the catalysts. Otherwise the results did not converge to the proper range. The fitted parameters are summarized in Table 5. The comparison of simulated and experimental data for Pd(1)Cu(5)/CeO₂ catalyst are also shown in Fig. 10. The experimental data were well fitted to both models, but they were better fitted to the L-H model. The significant decrease in K_{CO} by O_2 addition to WGS on Pd and Pd-Cu catalysts shows blockage of active surface by CO is severe in WGS and O_2 addition frees up the active sites. It has been reported that strongly chemisorbed CO creates island structure on the surface which prevents the coreactant to associate with chemisorbed CO [47]. The concomitant increase of k shows the reaction rate increased not only through H_2O adsorption on such vacant sites, but also through an increased probability of association of the two reactants, i.e. a larger number of adjoining pairs of CO and H_2O on the surface, and an enhanced exponential factor due to an increase of local temperature by the exothermic oxidation reaction. The fitting to the redox model showed an exclusive promotion in the reoxidation of ceria by H_2O upon O_2 addition to WGS. The better fit to the L-H model than redox model suggests that the kinetic behavior of OWGS is more likely explained by the O_2 role to change the balance of surface reactants.

3-2-4. Effect of product gases on OWGS and WGS kinetics

In Fig. 11, comparison was made for H_2 production rates in the two WGS conditions, CO- H_2O and CO- H_2O -CO₂- H_2 conditions. The H_2 production rate was much higher in the former condition, but the order of activity was somewhat similar to each other except Cu:

$$\begin{array}{ll} \text{CO-}\text{H}_2\text{O condition} & : \text{Pd-Cu} > \text{Pt-Cu} > \text{Pt} > \text{Cu} > \text{Pd} \\ \text{CO-}\text{H}_2\text{O-CO}_2\text{-}\text{H}_2 \text{ condition} & : \text{Pd-Cu} > \text{Cu} > \text{Pt-Cu} > \text{Pt} > \text{Pd} \end{array}$$

The role of Cu becomes more dominant in the latter condition. This indicates Cu has less reaction inhibition by the product gases which originates from its high tolerance to H_2 [50] and CO₂ [21]. Pd-Cu was still better than Cu in the latter condition in contrast to Pt-Cu which falls below Cu probably because Pd-Cu combination offers more interaction between Pd and Cu to form active sites with less inhibition by the product gases [21, 51]. The stronger interaction comes from more uniformly dispersed Pd in Pd-Cu

alloy than Pt in Pt-Cu alloy shown in our previous EXAFS data ($N_{\text{Pd-Pd}} = 1.4$, $N_{\text{Pd-Cu}} = 7.1$ for 2 wt% Pd – 5 wt% Cu on CeO_2 and $N_{\text{Pt-Pt}} = 3.0$, $N_{\text{Pt-Cu}} = 5.8$ for 1 wt% Pt – 5 wt% Cu on CeO_2). The Pd in the Pd-Cu alloy was more surrounded by Cu than the Pt in the Pt-Cu alloy.

Fig. 12 compares OWGS rates in $\text{CO-H}_2\text{O-O}_2$ and $\text{CO-H}_2\text{O-CO}_2\text{-H}_2\text{-O}_2$ conditions. Note the double scale of y-axis (H_2 production rate) in Fig. 12 compared to that in Fig. 11. The order of H_2 production rate among the five catalysts drastically changed in the presence of the product gases showing a large reaction inhibition by the product gases:

$\text{CO-H}_2\text{O-O}_2$ condition	: Pt > Pt-Cu > Pd-Cu > Pd > Cu
$\text{CO-H}_2\text{O-CO}_2\text{-H}_2\text{-O}_2$ condition	: Pd-Cu > Pt-Cu > Cu > Pt > Pd

The trend in the $\text{CO-H}_2\text{O-CO}_2\text{-H}_2\text{-O}_2$ condition resembled that of the WGS conditions where Cu functions positively. Cu was least active in the $\text{CO-H}_2\text{O-O}_2$ condition, but it was more active than Pt or Pd catalysts in the $\text{CO-H}_2\text{O-CO}_2\text{-H}_2\text{-O}_2$ condition. This would be again due to a low reaction inhibition originating from the nature of Cu which does not much adsorb CO, and does not retain CO_2 [21] and H_2 [50]. In contrast, the Pt catalyst showed the best performance in the $\text{CO-H}_2\text{O-O}_2$ condition, but it showed poor activity in $\text{CO-H}_2\text{O-CO}_2\text{-H}_2\text{-O}_2$ condition. The Pt-Cu and Pd-Cu showed better activity than monometallic catalysts by the complementary role of each component.

Pd preferred oxidation of H_2 over oxidation of CO [23], resulting in loss of H_2 in OWGS as shown in Fig. 12. However, the combination of Pd with Cu suppressed H_2 oxidation on Pd to improve OWGS performance significantly. Therefore, the dispersed Pd in Pd-Cu prevents H_2 activation inherent to Pd. It creates highly active sites for CO shift resistant to reaction inhibition, and prevents H_2 activation to bring a synergistic effect on increasing OWGS rate.

In summary in the kinetic study, O_2 addition increases the reaction order in CO while it does not the reaction order in H_2O , which suggests O_2 removes CO to free up the sites for H_2O adsorption and it does not change chemistry in H_2O activation. This was supported by kinetic simulation. The inverse trend in CO order and H_2O order shows the rate is determined by the balance of surface reactants. The Pt-Cu and Pd-Cu bimetallic catalysts have an advantage in OWGS or WGS in the presence of product gases. The noble metal alloyed with copper chemisorbs CO moderately and activates H_2O where the copper modifies the noble metal property for lower CO coverage and for less reaction inhibition by the product gases to secure the active sites.

3-2-5. Transient response study

To understand the influence of metal species on the H₂O activation step, a study of pulse response was performed. Figs. 13 – 15 show the response signals to CO/D₂O, CO, D₂O pulses in 5% H₂/argon flow at different temperatures on Pd-Cu/CeO₂, Cu/CeO₂, and Pd/CeO₂ catalysts. All the signals were monitored in real-time by a quadrupole mass spectrometer. With CO/D₂O pulses in a H₂ flow, WGS (reaction of CO and D₂O) and hydrogen isotopic exchange between H₂ and D₂O were observed at the same time. Meanwhile, D₂O pulses in H₂ flow were used for observing only the latter reaction (isotopic exchange) and CO pulses were used for observing reaction of CeO₂ surface oxygen with CO or adsorption of CO on the surface. The signal of m/z = 44 (CO₂) was interpreted as the response from WGS and the signal of m/z = 2 (H₂), 3 (HD), and 4 (D₂) were interpreted as the responses from both WGS and H₂-D₂O isotopic exchange as expressed below:

Upon eight consecutive CO/D₂O pulses in H₂/argon flow, the peaks of m/z = 28 (unreacted CO), 18 (unreacted D₂O, HDO, and H₂O), 44 (product CO₂), 2 (H₂), 3 (HD), 4 (D₂) were observed. Each CO/D₂O pulse produced a sharp H₂ peak together with a CO₂ peak, both of which come from WGS. The detection of H₂ peak instead of HD or D₂ peak is probably because of the fast diffusion of hydrogen, i.e. the catalyst behaves like a pool for hydrogen and the sites for D₂O dissociation and H₂ generation could be apart. These m/z = 2 peaks also include the D⁺ fragments from HD or D₂ molecules although the contribution of D⁺ seems to be minor [52, 53]. The HD peak which is the indicator of cleavage of D-O bond in D₂O to exchange deuterium with H₂ showed a long tail and accompanied the corresponding negative H₂ peak with a long tail. The similar time constant of decay for HD or D₂ peaks in contrast to the sharp H₂ peak (See the magnification of the signals in Fig. 13) indicates that the isotopic exchange is not involved in WGS. There is no hydrogen diffusion and thus the isotopic exchange takes place via molecularly adsorbed D₂O or hydroxyls on CeO₂ support. When temperature was increased from 210°C to 350°C, the peak intensity of H₂ and CO₂ increased while those of HD and D₂ were kept almost unchanged, which is another evidence that the WGS and the isotopic exchange are irrelevant. Much smaller CO₂ and H₂ peaks upon individual CO and D₂O pulses shows the two reactants or intermediates are not retained for a long time. These observations indicate the reaction is superficial and it proceeds via a Langmuir-Hinshelwood type route in

the present pulse (low surface coverage) condition. The slight formation of CO_2 upon these individual pulses would be due to decomposition of carbonate by D_2O pulses or oxidation of CO by CeO_2 surface. The relatively high H_2 formation on Cu/CeO_2 upon CO pulses indicates Cu can retain water and this pre-adsorbed water can react with the CO pulse to produce hydrogen. The smaller CO_2 and H_2 responses to $\text{CO/D}_2\text{O}$ pulses on Pd/CeO_2 are consistent with its lower WGS activity than the other two catalysts.

The above results show the two reactants need to associate in a relatively short time for WGS to occur. WGS involves dissociation of water at metal sites and/or periphery of metal (so-called metal-ceria interface).

4. Conclusions

The CeO_2 -supported Pt-Cu and Pd-Cu bimetallic catalysts were demonstrated to have high activity for OWGS and to retain their initial activity for at least 70 hours on stream while Pt, Pd, and Al_2O_3 -supported Pd-Cu catalysts gradually lost their initial activity along the elapsed time. The in-situ FT-IR spectra before and after the long-duration test suggested that the major cause of deactivation differs by metal composition in catalyst. The Pt catalyst deactivates through both a progressive reduction of ceria accompanying carbonate formation and a change in metal surface structure. Pd/CeO_2 deactivates mainly through a metal sintering. Al_2O_3 -supported Pd-Cu catalyst deactivates through a destruction of the surface structure of Al_2O_3 accompanying a change in metal structure.

The reason for the better activity of bimetallic catalysts was analyzed by a kinetic study. The much larger reaction order in CO (above 1.0) for OWGS than that for WGS (-0.1 to 0.6) in contrast to similar reaction order in H_2O in OWGS and WGS shows that the active sites for H_2O adsorption are significantly blocked by strongly chemisorbed CO in WGS and that O_2 addition to the feed removes some CO to free up the sites for H_2O to participate in the reaction. From the inverse trend of H_2O fractional order to CO fractional order, i.e. the relatively lower CO order on Pt and Pd in contrast to the relatively higher H_2O order on these catalysts and the higher CO order on Cu in contrast to the lower H_2O order on Cu, it was confirmed that O_2 addition increases the reaction rate by changing the balance of surface reactants. The presence of product gases significantly inhibited the reaction, resulting in a shift of rate-limiting factor towards H_2O activation. Copper addition was shown to prevent reaction inhibition by product gases to enhance H_2O activation and to mitigate CO saturation on the noble metal to keep the active sites accessible for H_2O . Pd-Cu exhibited the highest activity under realistic OWGS conditions due to a

synergy of two metals that originates from the structure of highly dispersed Pd in Pd-Cu alloy and strong interaction of Pd with Cu.

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Tables

Table 1 Physicochemical properties of CeO₂-supported bimetallic and monometallic catalysts.

Me/CeO ₂	BET surface area (m ² /g)	pore volume (ml/g)	average pore diameter (nm)	CO uptake (μmol/g)	metal dispersion (%) [*]	particle size of metal (Å) ^{**}
Pt(1)	152	0.145	3.8	31.4	61	19
Pd(1)	148	0.147	4.0	63.0	67	17
Cu(5)	136	0.134	3.9	11.9	1.5	718
Pt(1)Cu(5)	129	0.121	3.8	34.0	4.1	271
Pd(1)Cu(5)	132	0.130	3.9	62.1	7.1	156
Pd(2)Cu(5)	115	0.124	4.2	81.2	8.3	133
Pd(2)Cu(5) on CeO ₂ -LS	2	--	> 70	20.6	2.1	525
Pd(2)Cu(5) on Al ₂ O ₃	123	0.900	29.1	109	11.2	99

^{*} Metal dispersion was calculated assuming 1:1 of CO:M stoichiometry (M = metal atom on the surface).

^{**} Particle size of metal was calculated from metal dispersion using Equation 1.

Table 2 Reaction orders in CO and H₂O for CeO₂-supported bimetallic and monometallic catalysts.

catalyst	WGS		OWGS	
	CO order	H ₂ O order	CO order	H ₂ O order
Pt(1)/CeO ₂	-0.1	0.7	1.2	0.5
Pd(1)/CeO ₂	0.1	0.5	1.1	0.4
Pd(1)Cu(5)/CeO ₂	0.4	0.3	1.4	0.3
Pt(1)Cu(5)/CeO ₂	0.4	0.3	1.5	0.2
Cu(5)/CeO ₂	0.6	0.2	1.3	0.1
Pd(2)Cu(5)/CeO ₂	0.4	0.3	1.6	0.2
Pd(2)Cu(5)/CeO ₂ -LS	--	--	1.6	0.5
Pd(2)Cu(5)/Al ₂ O ₃	0.2	-0.3	0.9	0.5

Condition: 4.8-12.5% CO / 23.0% H₂O / 1.4% O₂ / N₂ balance for obtaining reaction order in CO and 9.8% CO / 12.3-27.7% H₂O / 1.4% O₂ / N₂ balance for obtaining reaction order in H₂O (O₂ was replaced by N₂ in the feed gas for WGS); Temperature: 260°C; Total gas flow rate: 132.5 ml/min; Catalyst weight: 0.015g diluted by SiC to attain 0.065 ml of bed volume. The reaction order was obtained from the minimum square root of four points of log (rate) – log (partial pressure) plot in Figs. 7 and 8.

Table 3 H₂ production rates in OWGS on CeO₂-supported bimetallic and monometallic catalysts.

catalyst	rate-A ($\mu\text{mol/g/s}$)	rate-B ($\mu\text{mol/g/s}$)
Pt(1)/CeO ₂	193	16
Pd(1)/CeO ₂	99	-18
Cu(5)/CeO ₂	79	19
Pt(1)Cu(5)/CeO ₂	160	21
Pd(1)Cu(5)/CeO ₂	122	38
Pd(2)Cu(5)/CeO ₂	163	45
Pd(2)Cu(5)/CeO ₂ -LS	20	-10
Pd(2)Cu(5)/Al ₂ O ₃	45	-13

Temperature: 260°C; Gas composition: 9.8% CO / 23.0% H₂O / 1.4% O₂ (0.015g catalyst + SiC dilution) for rate-A, 9.8% CO / 23.0% H₂O / 1.4% O₂ / 6.3% CO₂ / 37.9% H₂ (0.1g catalyst) for rate-B; Total gas flow rate was 132.5 ml/min for both conditions.

Table 4 Apparent activation energy for OWGS on CeO₂-supported bimetallic and monometallic catalysts.

catalyst	apparent activation energy (kJ/mol)
Pt(1)/CeO ₂	30.2
Pd(1)/CeO ₂	57.2
Cu(5)/CeO ₂	34.3
Pt(1)Cu(5)/CeO ₂	23.7
Pd(1)Cu(5)/CeO ₂	41.2
Pd(2)Cu(5)/CeO ₂	29.0
Pd(2)Cu(5)/CeO ₂ -LS	87.0
Pd(2)Cu(5)/Al ₂ O ₃	41.6

Condition: 9.8% CO / 23.0% H₂O / 1.4% O₂ / N₂ balance; Temperature: 220 – 260°C; Total gas flow rate: 132.5 ml/min; Catalyst weight: 0.015g diluted by SiC to attain 0.065 ml of bed volume.

Table 5 Fitted kinetic parameters of Langmuir-Hinshelwood model and redox model.

catalyst	parameter (L-H)	WGS		OWGS	
		value	error	value	error
Pd(1)Cu(5) /CeO ₂	k	1415	63	4188	918
	K _{CO}	8.05	1.09	2.23	0.61
	K _{H₂O}	1	--	1	--
Pd(1)/CeO ₂	k	296	6	1618	390
	K _{CO}	18.81	2.53	5.98	2.61
	K _{H₂O}	1	--	1	--
Cu(5)/CeO ₂	k	816	62	2371	428
	K _{CO}	4.70	0.67	2.81	0.68
	K _{H₂O}	1	--	1	--
catalyst	parameter (redox)	WGS		OWGS	
		value	error	value	error
Pd(1)Cu(5) /CeO ₂	k _{CO}	2003	329	1975	50
	k _{H₂O}	971	175	3680	463

L-H model: $\text{rate} = k K_{\text{CO}} (P_{\text{CO}} - 2P_{\text{O}_2}) (K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^{1/2} / (1 + K_{\text{CO}} (P_{\text{CO}} - 2P_{\text{O}_2}) + (K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^{1/2})^2$, $K_{\text{H}_2\text{O}}$ was assumed to be unity for all the catalysts both in OWGS and WGS. Redox model: $\text{rate} = k_{\text{CO}} P_{\text{CO}} k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / (k_{\text{CO}} P_{\text{CO}} + k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})$. Experimental data: 4.8-12.5% CO / 12.3-27.7% H₂O / 1.4% O₂ (or N₂) / N₂ balance for OWGS (or WGS), Temperature: 260°C, Total gas flow rate: 132.5 ml/min, Catalyst weight: 0.015g (35-60 mesh) diluted with SiC particles of the same size to attain 0.065 ml of the catalyst bed volume.

Figure Captions

Fig. 1 Long duration OWGS performance on CeO₂-supported Pd-Cu bimetallic catalysts and monometallic catalysts.

Feed: 9.7% CO / 22.8% H₂O / 6.3% CO₂ / 37.9% H₂ / 6.9% Air (1.4% O₂) / argon balance; Temperature: 260°C; GHSV: 64,400h⁻¹(dry). The two sets of data (square and star symbols) are of the Pd(1)Cu(5) catalysts prepared in different batches. The activity of the former was closer to those in our previous reports.

Fig. 2 Long duration OWGS performance on CeO₂-supported Pt-Cu bimetallic catalysts and monometallic catalysts.

Feed: 9.7% CO / 22.8% H₂O / 6.3% CO₂ / 37.9% H₂ / 6.9% Air (1.4% O₂) / argon balance; Temperature: 260°C; GHSV: 64,400h⁻¹(dry).

Fig. 3 Long duration OWGS performance on Pd-Cu bimetallic catalysts supported on CeO₂ and Al₂O₃.

Feed: 9.7% CO / 22.8% H₂O / 6.3% CO₂ / 37.9% H₂ / 6.9% Air (1.4% O₂) / argon balance; Temperature: 260°C; GHSV: 64,400h⁻¹(dry). The comments on the two data sets of Pd(1)Cu(5) are same as in **Figure 1**.

Fig. 4 Diffuse reflectance FT-IR spectra of various CeO₂-supported catalysts reduced in H₂ at 260°C.

Condition: 100% H₂, 30 ml/min, ca. 50 mg catalyst.

Fig. 5 Diffuse reflectance FT-IR spectra of various CeO₂-supported catalysts in the presence of CO at 260°C.

Condition: CO/H₂/He = 0.9/35/8.1 in the unit of ml/min, ca. 50 mg catalyst.

Fig. 6 Diffuse reflectance FT-IR spectra of samples before and after long duration OWGS reaction at 260°C.

Condition: CO/H₂/He = 0.9/35/8.1 in the unit of ml/min, 260°C, ca. 50 mg catalyst. Upper black spectrum: after OWGS for 70 h, lower blue spectrum: fresh sample. No pretreatment was carried out for the used samples.

Fig. 7 Effect of CO and H₂O partial pressures on H₂ production rate in OWGS.

CeO₂-supported Pt(1): open circle; Pd(1): open diamond; Cu(5): filled triangle; Pt(1)Cu(5): filled diamond; Pd(1)Cu(5): filled square; Pd(2)Cu(5): cross; Pd(2)Cu(5) on low surface area CeO₂: star; Pd(2)Cu(5) on Al₂O₃: plus; Gas composition: 4.8-12.5% CO / 23.0% H₂O / 1.4% O₂ / N₂ balance for obtaining reaction order in CO and 9.8% CO / 12.3-27.7% H₂O / 1.4% O₂ / N₂ balance for obtaining reaction order in H₂O; Temperature: 260°C; Total gas flow rate: 132.5 ml/min; Catalyst weight: 0.015g (35-60 mesh) diluted with SiC particles of the same size to attain 0.065 ml of the catalyst bed volume.

Fig. 8 Effect of CO and H₂O partial pressures on H₂ production rate in WGS.

CeO₂-supported Pt(1): open circle; Pd(1): open diamond; Cu(5): filled triangle; Pt(1)Cu(5): filled diamond; Pd(1)Cu(5): filled square; Pd(2)Cu(5): cross; Pd(2)Cu(5) on low surface area CeO₂: star; Pd(2)Cu(5) on Al₂O₃: plus; Gas composition: 4.8-12.5% CO / 23.0% H₂O / N₂ balance for obtaining reaction order in CO and 9.8% CO / 12.3-27.7% H₂O / N₂ balance for obtaining reaction order in H₂O; Temperature: 260°C; Total gas flow rate: 132.5 ml/min; Catalyst weight: 0.015g (35-60 mesh) diluted with SiC particles of the same size to attain 0.065 ml of the catalyst bed volume.

Fig. 9 Comparison of fractional orders in CO and H₂O on various CeO₂-supported metal catalysts in OWGS and WGS.

CO order in OWGS: open square; H₂O order in OWGS: open circle; CO order in WGS: filled square; H₂O order in WGS: filled circle. The fractional orders were obtained from linear fits of log (rate) – log (partial pressure) within the gas compositions: 4.8-12.5% CO / 12.3-27.7% H₂O / 6.9% Air (1.4% O₂) / N₂ balance for OWGS and 4.8-12.5% CO / 12.3-27.7% H₂O / N₂ balance for WGS.

Fig. 10 Fittings of H₂ production rates to Langmuir-Hinshelwood (L-H) model and redox model.

Red square: OWGS data; blue circle: WGS data; solid red: OWGS L-H fitting; solid blue: WGS L-H fitting; dotted red: OWGS redox fitting; dotted blue: WGS redox fitting. L-H model: $\text{rate} = k K_{\text{CO}} (P_{\text{CO}} - 2P_{\text{O}_2}) (K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^{1/2} / (1 + K_{\text{CO}} (P_{\text{CO}} - 2P_{\text{O}_2}) + (K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^{1/2})^2$ ($k, K_{\text{CO}}, K_{\text{H}_2\text{O}}$) = (4188, 2.23, 1.00) for OWGS, ($k, K_{\text{CO}}, K_{\text{H}_2\text{O}}$) = (1415, 8.05, 1.00) for WGS. Redox model: $\text{rate} = k_{\text{CO}} P_{\text{CO}} k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / (k_{\text{CO}} P_{\text{CO}} + k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})$ ($k_{\text{CO}}, k_{\text{H}_2\text{O}}$) = (1975, 3680) for OWGS, ($k_{\text{CO}}, k_{\text{H}_2\text{O}}$) = (2003, 971) for WGS. The experimental data were from Fig. 7 and Fig. 8, Temperature: 260°C, Catalyst: Pd(1)Cu(5)/CeO₂.

Fig. 11 Difference in H₂ production rate in WGS at 260°C with and without product gases.

Condition: 9.8% CO / 23.0% H₂O / N₂ balance (0.015g catalyst + SiC dilution, dotted bar) and 9.7% CO / 22.8% H₂O / 6.3% CO₂ / 37.9% H₂ / Ar balance (0.1g catalyst, solid bar); Total gas flow rate: 132.5 ml/min for both conditions; Catalyst: Me/CeO₂.

Fig. 12 Difference in H₂ production rate in OWGS at 260°C with and without product gases.

Condition: 9.8% CO / 23.0% H₂O / 1.4% O₂ / N₂ balance (0.015g catalyst + SiC dilution, dotted bar) and 9.7% CO / 22.8% H₂O / 1.4% O₂ / 6.3% CO₂ / 37.9% H₂ / Ar balance (0.1g catalyst, solid bar); Total gas flow rate: 132.5 ml/min for both conditions; Catalyst: Me/CeO₂.

Fig. 13 Responses to CO/D₂O, CO, D₂O pulses on Pd(1)Cu(5)/CeO₂ catalyst.

A: 10 CO/D₂O (8.2/8.2 μmol) pulses; B: 10 CO (16.4 μmol) pulses; C: 10 D₂O (8.2 μmol) pulses; Carrier flow: 5% H₂/Ar 50 ml/min; Catalyst weight: 0.1g. The H₂/Ar carrier gas was continuously supplied to the catalyst during the heating period.

Fig. 14 Responses to CO/D₂O, CO, D₂O pulses on Cu(5)/CeO₂ catalyst.

A: 10 CO/D₂O (8.2/8.2 μmol) pulses; B: 10 CO (16.4 μmol) pulses; C: 10 D₂O (8.2 μmol) pulses; Carrier flow: 5% H₂/Ar 50 ml/min; Catalyst weight: 0.1g. The H₂/Ar carrier gas was continuously supplied to the catalyst during the heating period.

Fig. 15 Responses to CO/D₂O, CO, D₂O pulses on Pd(1)/CeO₂ catalyst.

A: 10 CO/D₂O (8.2/8.2 μmol) pulses; B: 10 CO (16.4 μmol) pulses; C: 10 D₂O (8.2 μmol) pulses; Carrier flow: 5% H₂/Ar 50 ml/min; Catalyst weight: 0.1g. The H₂/Ar carrier gas was continuously supplied to the catalyst during the heating period.

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Figure

Fig. 1 Long duration OWGS performance on CeO_2 -supported Pd-Cu bimetallic catalysts and monometallic catalysts. Feed: 9.7% CO / 22.8% H_2O / 6.3% CO_2 / 37.9% H_2 / 6.9% Air (1.4% O_2) / argon balance; Temperature: 260°C; GHSV: 64,400 h^{-1} (dry). The two sets of data (square and star symbols) are of the Pd(1)Cu(5) catalysts prepared in different batches. The activity of the former was closer to those in our previous reports.

Fig. 2 Long duration OWGS performance on CeO_2 -supported Pt-Cu bimetallic catalysts and monometallic catalysts. Feed: 9.7% CO / 22.8% H_2O / 6.3% CO_2 / 37.9% H_2 / 6.9% Air (1.4% O_2) / argon balance; Temperature: 260°C; GHSV: 64,400 h^{-1} (dry).

Fig. 3 Long duration OWGS performance on Pd-Cu bimetallic catalysts supported on CeO₂ and Al₂O₃. Feed: 9.7% CO / 22.8% H₂O / 6.3% CO₂ / 37.9% H₂ / 6.9% Air (1.4% O₂) / argon balance; Temperature: 260°C; GHSV: 64,400h⁻¹(dry). The comments on the two data sets of Pd(1)Cu(5) are same as in **Figure 1**.

Fig. 4 Diffuse reflectance FT-IR spectra of various CeO₂-supported catalysts reduced in H₂ at 260°C. Condition: 100% H₂, 30 ml/min, ca. 50 mg catalyst.

Fig. 5 Diffuse reflectance FT-IR spectra of various CeO₂-supported catalysts in the presence of CO at 260°C. Condition: CO/H₂/He = 0.9/35/8.1 in the unit of ml/min, ca. 50 mg catalyst.

Fig. 6 Diffuse reflectance FT-IR spectra of samples before and after long duration OWGS reaction at 260°C. Condition: CO/H₂/He = 0.9/35/8.1 in the unit of ml/min, 260°C, ca. 50 mg catalyst. Upper black spectrum: after OWGS for 70 h, lower blue spectrum: fresh sample. No pretreatment was carried out for the used samples.

Fig. 7 Effect of CO and H₂O partial pressures on H₂ production rate in OWGS.

CeO₂-supported Pt(1): open circle; Pd(1): open diamond; Cu(5): filled triangle; Pt(1)Cu(5): filled diamond; Pd(1)Cu(5): filled square; Pd(2)Cu(5): cross; Pd(2)Cu(5) on low surface area CeO₂: star; Pd(2)Cu(5) on Al₂O₃: plus; Gas composition: 4.8-12.5% CO / 23.0% H₂O / 1.4% O₂ / N₂ balance for obtaining reaction order in CO and 9.8% CO / 12.3-27.7% H₂O / 1.4% O₂ / N₂ balance for obtaining reaction order in H₂O; Temperature: 260°C; Total gas flow rate: 132.5 ml/min; Catalyst weight: 0.015g (35-60 mesh) diluted with SiC particles of the same size to attain 0.065 ml of the catalyst bed volume.

Fig. 8 Effect of CO and H₂O partial pressures on H₂ production rate in WGS.

CeO₂-supported Pt(1): open circle; Pd(1): open diamond; Cu(5): filled triangle; Pt(1)Cu(5): filled diamond; Pd(1)Cu(5): filled square; Pd(2)Cu(5): cross; Pd(2)Cu(5) on low surface area CeO₂: star; Pd(2)Cu(5) on Al₂O₃: plus; Gas composition: 4.8-12.5% CO / 23.0% H₂O / N₂ balance for obtaining reaction order in CO and 9.8% CO / 12.3-27.7% H₂O / N₂ balance for obtaining reaction order in H₂O; Temperature: 260°C; Total gas flow rate: 132.5 ml/min; Catalyst weight: 0.015g (35-60 mesh) diluted with SiC particles of the same size to attain 0.065 ml of the catalyst bed volume.

Fig. 9 Comparison of fractional orders in CO and H₂O on various CeO₂-supported metal catalysts in OWGS and WGS. CO order in OWGS: open square; H₂O order in OWGS: open circle; CO order in WGS: filled square; H₂O order in WGS: filled circle. The fractional orders were obtained from linear fits of log (rate) – log (partial pressure) within the gas compositions: 4.8-12.5% CO / 12.3-27.7% H₂O / 6.9% Air (1.4% O₂) / N₂ balance for OWGS and 4.8-12.5% CO / 12.3-27.7% H₂O / N₂ balance for WGS.

Fig. 10 Fittings of H₂ production rates to Langmuir-Hinshelwood (L-H) model and redox model.
 Red square: OWGS data; blue circle: WGS data; solid red: OWGS L-H fitting; solid blue: WGS L-H fitting;
 dotted red: OWGS redox fitting; dotted blue: WGS redox fitting.
 L-H model: $\text{rate} = k K_{\text{CO}} (P_{\text{CO}} - 2P_{\text{O}_2}) (K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^{1/2} / (1 + K_{\text{CO}} (P_{\text{CO}} - 2P_{\text{O}_2}) + (K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^{1/2})^2$
 $(k, K_{\text{CO}}, K_{\text{H}_2\text{O}}) = (4188, 2.23, 1.00)$ for OWGS, $(k, K_{\text{CO}}, K_{\text{H}_2\text{O}}) = (1415, 8.05, 1.00)$ for WGS.
 Redox model: $\text{rate} = k_{\text{CO}} P_{\text{CO}} k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / (k_{\text{CO}} P_{\text{CO}} + k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})$
 $(k_{\text{CO}}, k_{\text{H}_2\text{O}}) = (1975, 3680)$ for OWGS, $(k_{\text{CO}}, k_{\text{H}_2\text{O}}) = (2003, 971)$ for WGS.
 The experimental data were from Fig. 7 and Fig. 8, Temperature: 260°C, Catalyst: Pd(1)Cu(5)/CeO₂.

Fig. 11 Difference in H₂ production rate in WGS at 260°C with and without product gases. Condition: 9.8% CO / 23.0% H₂O / N₂ balance (0.015g catalyst + SiC dilution, dotted bar) and 9.7% CO / 22.8% H₂O / 6.3% CO₂ / 37.9% H₂ / Ar balance (0.1g catalyst, solid bar); Total gas flow rate: 132.5 ml/min for both conditions; Catalyst: Me/CeO₂.

Fig. 12 Difference in H₂ production rate in OWGS at 260°C with and without product gases.
 Condition: 9.8% CO / 23.0% H₂O / 1.4% O₂ / N₂ balance (0.015g catalyst + SiC dilution, dotted bar)
 and 9.7% CO / 22.8% H₂O / 1.4% O₂ / 6.3% CO₂ / 37.9% H₂ / Ar balance (0.1g catalyst, solid bar);
 Total gas flow rate: 132.5 ml/min for both conditions; Catalyst: Me/CeO₂

Fig. 13 Responses to CO/D₂O, CO, D₂O pulses on Pd(1)Cu(5)/CeO₂ catalyst.

A: 10 CO/D₂O (8.2/8.2 μmol) pulses; B: 10 CO (16.4 μmol) pulses; C: 10 D₂O (8.2 μmol) pulses;

Carrier flow: 5% H₂/Ar 50 ml/min; Catalyst weight: 0.1g.

The H₂/Ar carrier gas was continuously supplied to the catalyst during the heating period.

Fig. 14 Responses to CO/D₂O, CO, D₂O pulses on Cu(5)/CeO₂ catalyst.

A: 10 CO/D₂O (8.2/8.2 μ mol) pulses; B: 10 CO (16.4 μ mol) pulses; C: 10 D₂O (8.2 μ mol) pulses;

Carrier flow: 5% H₂/Ar 50 ml/min; Catalyst weight: 0.1g.

The H₂/Ar carrier gas was continuously supplied to the catalyst during the heating period.

Fig. 15 Responses to CO/D₂O, CO, D₂O pulses on Pd(1)/CeO₂ catalyst.

A: 10 CO/D₂O (8.2/8.2 μmol) pulses; B: 10 CO (16.4 μmol) pulses; C: 10 D₂O (8.2 μmol) pulses;

Carrier flow: 5% H₂/Ar 50 ml/min; Catalyst weight: 0.1g.

The H₂/Ar carrier gas was continuously supplied to the catalyst during the heating period.