

Selective oxidation of CO in hydrogen-rich mixtures and kinetics investigation on platinum-gold supported on zinc oxide catalyst

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Abstract

A series of gold zinc oxide catalysts have been prepared using a coprecipitation procedure and selective oxidation of CO in hydrogen-rich mixtures was investigated in a fixed-bed reactor in the temperature range from 313 to 393 K. The results showed that the suitable content of Au in ZnO was about 1.5 wt.% and calcined at 573 K, shortened as Au (1.5)/ZnO-573. Stability investigation, performed at 353 K and lasted for 500 h, indicated Au (1.5)/ZnO-573 catalyst activity was slightly deteriorated as time on stream was over 350 h. Investigation indicated little addition of platinum into Au (1.5)/ZnO-573 catalyst could definitely improve its stability. However, further study showed that the selectivity of removal of CO from hydrogen-rich mixtures for Au (1.5)-Pt/ZnO-573 catalyst would be decreased with increasing content of Pt on the catalyst when Pt content was over 1.0 wt.%, which indicates that the suitable content of Pt would be 1.0 wt.% and the catalyst was indicated as Au (1.5)-Pt (1.0)/ZnO-573. Kinetic experiments performed on it were carried out in an isothermal fixed-bed microreactor under intrinsic conditions.

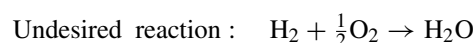
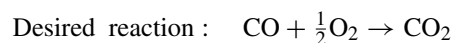
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1. Introduction

Polymeric electrolyte membrane fuel cells (PEMFCs) operate at relatively low temperatures, usually at 353–493 K [1]. This is particularly so when applied to vehicles. Pure hydrogen is an ideal fuel for PEMFCs with the advantage of simple system integration, high efficiency and zero adverse emissions. However, poor storage capacity, safety problems and lack of the necessary infrastructure associated with hydrogen use are potentially major disadvantages. Thus, on-site and perhaps on demand production of hydrogen, for example from hydrocarbons or methanol, is possibly an attractive approach to the problem. The hydrogen would then, in effect, be chemically stored in liquid hydrocarbons. When

hydrogen fuel is produced from methanol or other hydrocarbons by partial oxidation and steam reforming (POSR) combined with water gas shift (WGS) reaction process [2–4], the Pt anodes at these low temperatures are often poisoned by by-products such as CO. This reduces the overall fuel cell performance [5]. Under normal running conditions, the product hydrogen stream contains approximately 75 vol.% H₂, 25 vol.% CO₂, 0.5–1.0 vol.% CO and small amounts of water. In order to obtain optimum performance from the fuel cells, the concentration of CO in the gas stream should be reduced, if possible, to below 100 ppm. Selective oxidation of CO in hydrogen-rich mixtures is a possible solution to this issue. In the selective oxidation of CO, water is, however, formed at the expense of hydrogen production. The equations are as follows:



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Therefore, reducing water formation while maintaining a high CO oxidation rate is an important requirement of catalysts which can be used in the reaction. Given the problems associated with the other methods which have been reported for CO removal [6–8], selective oxidation of CO with molecular oxygen would appear to be a possibly more effective method for reducing the CO contamination in the hydrogen-rich gas mixtures down to the ppm-level [9]. There are several catalysts which can be used in the oxidation of CO. Mixed oxide catalyst containing copper have been used at lower temperatures but the CO would usually not be reduced to the desired ppm-level [10–12]. An example of this would be Cu-Mn-O [13]. Other catalysts reported in the literature would include platinum [14,15], ruthenium [16], rhodium [17], gold [18] and silver [19] supported on alumina or zeolites. Bracchini [20] showed that Pt and Ru supported on active carbon had higher activities in the selective oxidation CO when compared to Pt supported on alumina [21,22]. Sanchez [23] reported that Au supported on manganese oxides had performed well in terms of selective CO oxidation. As the Au catalysts are, in contrast to the Pt catalysts, intrinsically more active in terms of CO oxidation than in H₂ oxidation, and also since the catalytic activity of Au is possibly enhanced by moisture and it is almost insensitive to CO₂ [23], it has been widely investigated for possible application in selective oxidation of CO in hydrogen-rich mixture gases both concerning about its oxidation dynamics and selectivity [1,2,14,19,24,25]. For PEMFCs to be commercially viable, it would be desirable to develop catalysts which are effective at comparatively low temperatures, and in the presence of CO₂ and small amounts of water.

This paper reports the use of Au supported on zinc oxides to selectively oxidize CO within a temperature range from 313 to 493 K. The effect of adding Pt to the Au supported on the support of zinc oxides on selective CO oxidation performance is also investigated. Finally, kinetic experiments performed on desired catalyst are carried out in an isothermal fixed-bed microreactor under intrinsic conditions, i.e. in the absence of mass and heat transfer limitations, in the temperature range from 313 to 493 K, with CO and O₂ inlet partial pressures between 0.4 and 5.0 kPa, and total gas space velocity is 3.0×10^4 – 3.0×10^5 h⁻¹ with pure N₂ as the balance gas.

2. Experimental

2.1. Catalyst preparation

Gold supported on zinc oxides was prepared by coprecipitation, from an aqueous solution of HAuCl₄·3H₂O (Fluka) and Zn(NO₃)₂·6H₂O (Merk) with the aqueous solution of Na₂CO₃ (Fluka). The HAuCl₄ and Zn(NO₃)₂ solution was added into the Na₂CO₃ solution under continuously stirring condition. The coprecipitated materials were then washed several times until the pH of the resulting supernatant did not

change substantially and then filtered and dried overnight under vacuum, before finally calcining in air at 353 K about 6 h. The resulting catalyst of Au/ZnO was tagged as Au (*w*)/ZnO-*T*, where *w* = wt.% content of Au and *T* = calcining temperature, K.

Catalysts doped with Pt were prepared by impregnating Au/ZnO using an aqueous solution of H₂PtCl₆·6H₂O (Fluka). The impregnation time was over 4 h. The mixture was then filtered and the material of catalyst precursor was dried at 368 K for 6 h under vacuum and then it was calcined in air in a muffle furnace at pre-determined temperatures for 4 h. The Au-Pt/ZnO catalysts were tagged as Au (*w*₁)-Pt (*w*₂)/ZnO-*T*, where *w*₁ = wt.% content of Au, *w*₂ = wt.% content of Pt and *T* = calcining temperature, K.

2.2. Catalyst characterization

Several bulk and surface analysis methods were employed to characterize the catalysts before and after reaction. Surface area was measured using a Micromeritics ASAP 2010 BET apparatus with N₂ desorption. Scanning electron microscope (SEM) characterization was analyzed by using S-3200N HITACH apparatus. X-ray diffraction (XRD) for identification of the crystalline phases was performed in a D/Max-rA instrument using Cu K α radiation. Typical samples were determined by infrared spectroscopy with adsorption of gas mixtures containing CO, H₂ and CO₂ at room temperature, 298 K, in a Bruker IFS113V FT-IR apparatus. The catalyst compositions were determined using inductively coupled plasma (ICP).

2.3. Catalytic test

Selective CO oxidation was initially investigated using a fixed-bed flow reactor system under atmospheric pressure. The reaction chamber was made with stainless steel with 10 mm i.d. and 350 mm long. Reaction temperature was controlled using a thermocouple inserted into the center of the catalyst bed. The reaction section of the reactor was charged with 500 mg of the catalyst. Sandwiching this catalyst segment would be segments on either side comprising 500 mg of quartz chips (content of SiO₂ >99.8%, supplied by Sichuan Mineral Factory, same in the dynamic study), which have been calcined at 973 K. Prior to the experiments, the catalyst bed was flushed with N₂ (99.999%) at 393 K and gas space velocity of 3000 h⁻¹. The reactor was then cooled to the pre-determined reaction temperature with N₂. A stainless steel reactor with 6 mm i.d. and 350 mm long was used to determine the kinetics of the catalytic reactions and the former was placed in a temperature programmable tube furnace. Hundred milligrams of the catalyst with sieve size of 0.25 mm would be loaded into reactor. A similar amount of the inert quartz chips of sieve size 0.25 mm was mixed with the catalyst bed so as to dissipate heat more evenly and keep the bed isothermal. All the kinetic data were obtained in the absence of mass and heat transfer limitations, in the temperature

Table 1
Typical experimental conditions

Parameters	Conditions
Reaction temperatures (K)	313–393
Catalysts weight (mg)	100–500
Average particle size (mm)	0.25
Gas space velocity (h^{-1})	3.0×10^4 – 3.0×10^5
Gas compositions (vol.%)	H ₂ : 50–75 CO ₂ : 15–25 CO: 0.4–5 O ₂ : 0.4–5 N ₂ : balance

range from 313 to 393 K, with CO and O₂ inlet partial pressures between 0.4 and 5.0 kPa, and total gas space velocity is 3.0×10^4 – $3.0 \times 10^5 \text{ h}^{-1}$ with pure N₂ as the balance gas.

The mixtures of N₂, H₂, O₂, CO₂ and CO (all of gases purities were 99.999%) were used to evaluate the catalyst performance in the fixed-bed reactor and controlled by using mass flow controllers. The gas mixtures generated could either be sent into the reactor or diverted to the gas chromatograph for analysis. The typical reaction conditions are listed in Table 1.

2.4. Analytical methods

Quantitative analysis of H₂O, CO, CO₂, O₂, H₂ and hydrocarbons was performed by two gas chromatographs (GC 4000) with thermal conductivity detectors (TCDs) and argon as the carrier gas. One of the gas chromatograph was set up to detect CO₂ and H₂O using a polar column (Hayesep Q) at an oven temperature of 353 K. The second gas chromatograph was used to detect H₂, O₂, CO and hydrocarbons on a molecular sieve (molecular sieve 5 Å) at an oven temperature of 333 K.

The conversions of CO and O₂, and CO oxidation selectivity were defined as follows:

$$\text{CO conversion}(\%) = \frac{\Delta \text{CO}}{\text{CO}_{\text{in}}} = \frac{F_{\text{CO},\text{in}} - F_{\text{CO},\text{out}}}{F_{\text{CO},\text{in}}} \quad (1)$$

$$\text{O}_2 \text{ conversion}(\%) = \frac{\Delta \text{O}_2}{\text{O}_{2,\text{in}}} = \frac{F_{\text{O}_2,\text{in}} - F_{\text{O}_2,\text{out}}}{F_{\text{O}_2,\text{in}}} \quad (2)$$

$$\text{CO selectivity}(\%) = \frac{1}{2} \frac{\Delta \text{CO}}{\Delta \text{O}_2} = \frac{1}{2} \frac{F_{\text{CO},\text{in}} - F_{\text{CO},\text{out}}}{F_{\text{O}_2,\text{in}} - F_{\text{O}_2,\text{out}}} \quad (3)$$

where $F_{\text{CO},\text{in}}$ and $F_{\text{O}_2,\text{in}}$ are CO and O₂ molar flow rates into the reactor, respectively. $F_{\text{CO},\text{out}}$ and $F_{\text{O}_2,\text{out}}$ are CO and O₂ molar flow rates out of the reactor, respectively.

3. Results and discussion

3.1. Effect of Au content on Au/ZnO performance

Table 2 showed the XRD and BET surface area characterization results for the Au/ZnO catalysts with various Au

Table 2
XRD and BET characterization results for Au-Zn-O catalysts

Catalysts	Crystallize phase	BET surface area ($\text{m}^2 \text{ g}^{-1}$)
Au (0.5)/ZnO-423	ZnO, Zn ₅ (CO ₃) ₂ (OH) ₆	98.64
Au (1.0)/ZnO-423	Au, ZnO, Zn ₅ (CO ₃) ₂ (OH) ₆	95.32
Au (1.5)/ZnO-423	Au, Au ₂ O ₃ , ZnO, Zn ₅ (CO ₃) ₂ (OH) ₆	94.43
Au (2.0)/ZnO-423	Au, Au ₂ O ₃ , ZnO, Zn ₅ (CO ₃) ₂ (OH) ₆	87.28
Au (2.5)/ZnO-423	Au, Au ₂ O ₃ , ZnO, Zn ₅ (CO ₃) ₂ (OH) ₆	86.75
Au (3.0)/ZnO-423	Au, Au ₂ O ₃ , ZnO, Zn ₅ (CO ₃) ₂ (OH) ₆	84.32

contents. All of these were calcined at 423K. XRD analysis showed the crystalline phases in these Au/ZnO catalysts were different for the various Au contents. The crystalline phases were primarily of ZnO and Zn₅(CO₃)₂(OH)₆ when the Au content was 0.5 wt.%. From 1.0 wt.% Au content onwards, Au in the crystalline phase appeared in the Au/ZnO catalyst and from 1.5 wt.% Au content, Au₂O₃ appeared with the Au, ZnO and Zn₅(CO₃)₂(OH)₆ crystalline phases. The reason why Au or Au₂O₃ crystalline phases could not be detected when the Au content in Au/ZnO was low was probably because the Au was more uniformly dispersed in the catalyst. With increasing Au content, its status loaded on the catalysts might be varied as well as increasing particle size, thus it could be appeared the crystalline phases of Au and Au₂O₃. The presence of Zn₅(CO₃)₂(OH)₆ was because the calcining temperature used was low. BET results showed that surface area in the catalysts decreased as Au content increased, given the same calcining temperature.

Fig. 1 was the results of selective CO oxidation as catalysed by Au/ZnO-423 with various Au contents at a reaction temperature of 353 K at the following gas compositions (vol.%) 70 H₂ + 20 CO₂ + 0.4 CO + 1.0 O₂ + balance N₂ (same gas compositions of the following experiments except for the dynamic experiments). The catalytic activity of Au/ZnO-423 was improved slightly with increasing Au

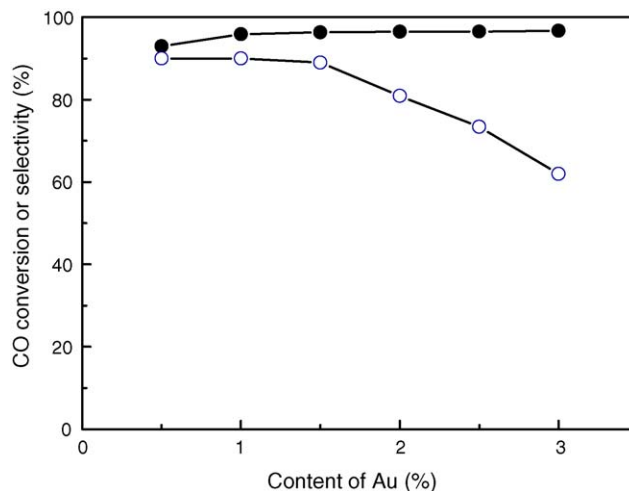


Fig. 1. The effect of content of Au on Au/ZnO-423 catalyst activity. (●) Conversion, (○) selectivity.

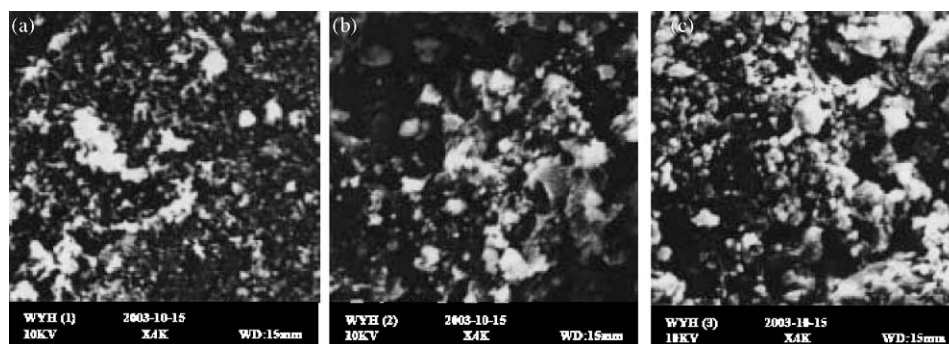


Fig. 2. SEM characterization of Au (1.5)/ZnO catalysts calcined at different temperatures. (a) 423 K, (b) 573 K, (c) 673 K.

content up till 1.5 wt.%. CO selectivity also increased initially but declined after the Au content exceeded 1.5 wt.%. It is known CO or H₂ must first be adsorbed onto the catalyst's active sites where they would then be oxidised with O₂. At the lower Au contents, the catalyst's surface would be mainly covered with CO since CO is more easily adsorbed onto the active sites than H₂. However, with increasing Au content, adsorption of H₂ would have increased. This would have interfered with selective CO oxidation.

3.2. Effect of calcining temperature on Au (1.5)/ZnO activity

Some results have shown that the calcining temperatures would greatly affect the activity of catalysts of the Au/MO_x (M, metals; x, ratio coefficient of oxygen) type [21]. The effect of calcining temperatures on Au (1.5)/ZnO catalyst structure and performance was investigated and the results showed the presence of Zn₅(CO₃)₂(OH)₆ when the calcining temperature was lower than 483 K. It, however, disappeared when the calcining temperature was equal or higher than 513 K. With higher calcining temperatures, Au₂O₃ would also disappear. The BET results indicated that surface area decreased slightly as calcining temperatures increased up till 573 K. When the calcining temperature was over 573 K, e.g. 673 K, surface area declined substantially, e.g. 94.4 m² g⁻¹ when calcined at 423 K to 74.3 m² g⁻¹ at 673 K. Compared with calcination at 423 K, catalyst surface area had declined by about 21% when it was calcined at 673 K. Fig. 2 showed the catalyst textural patterns characterized by SEM when it was calcined at 423, 573 and 673 K, respectively. It showed that it would possibly occur in the phenomenon of aggregation of particles with the increasing calcined temperature.

Fig. 3 showed the effect of calcining temperature on CO oxidation selectivity and conversion at the reaction temperature of 353 K. Selectivity slightly increased as the calcining temperature increased up to 673 K and thereafter decreased. The CO conversion increased and then decreased slightly as calcining temperatures increased. Since Au has the higher activity in selective CO oxidation, and increasing calcining temperatures would change Au₂O₃ into Au, then Au (1.5)/ZnO catalyst activity can be expected to increase with

increasing calcining temperature. But if the calcining temperature was too high (higher than 673 K in this study), the catalyst would undergo a little bit phenomenon of sintering, as shown in Fig. 2. The latter would cause the catalyst's surface area to decrease, and hence its activity to decrease as well.

3.3. Au (1.5)/ZnO-573 activity and stability

Fig. 4 showed CO conversion and selectivity for catalyst calcined at 573 K (i.e. Au (1.5)/ZnO-573) when used at reaction temperatures of 313–393 K. It showed that the activity of Au (1.5)/ZnO-573 did not vary much with the reaction temperature within the temperature range from 313 to 393 K. However, CO oxidation selectivity decreased slightly when the reaction temperature was increased beyond 353 K.

The stability for the Au (1.5)/ZnO-573 catalyst was investigated at 353 K over 500 h. It indicated that the catalyst's activity was slightly decreased when the reaction time was over 350 h. The catalyst's surface area and crystalline phases before and after reaction were investigated and the results shown in Table 3. The 500 h of reaction did not change the catalyst's crystalline phases. However, its surface area had declined noticeably from 83.56 to 68.32 m² g⁻¹

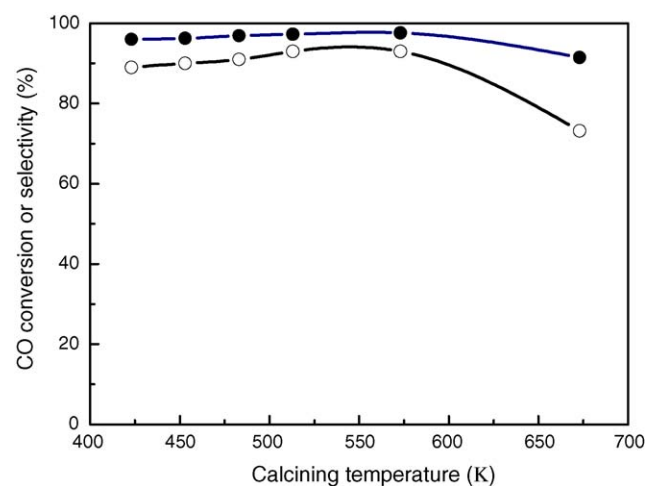


Fig. 3. The effect of calcining temperature on Au (1.5)/ZnO catalyst activity. (●) Conversion, (○) selectivity.

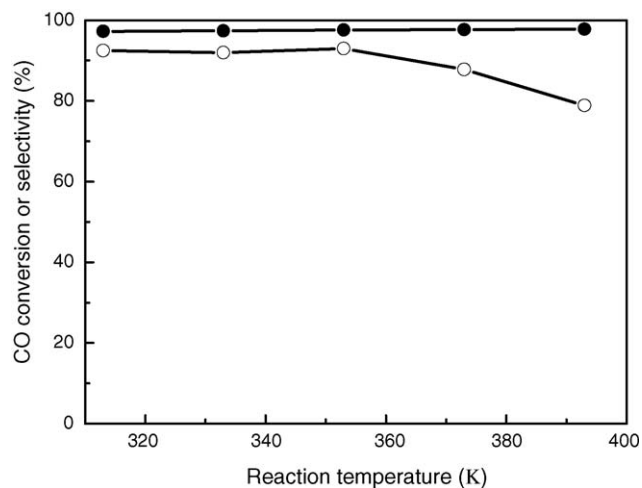


Fig. 4. The CO oxidation performance on Au (1.5)/ZnO-573 catalyst at different reaction temperature. (●) Conversion, (○) selectivity.

Table 3
XRD and BET characterizations for Au (1.5)/ZnO-573 before/after reaction

Catalysts	Crystallize phase	BET surface area ($\text{m}^2 \text{g}^{-1}$)
Au (1.5)/ZnO-573 ^a	Au, ZnO	83.56
Au (1.5)/ZnO-573 ^b	Au, ZnO	68.32

^a Before reaction.

^b After reaction.

(18% decline). This suggested the catalyst's activity would eventually be compromised by the reaction as it is catalysing.

3.4. Effect of Pt on Au (1.5)/ZnO-573 catalyst

Catalyst performance of removal of CO from rich hydrogen on Pt/ZnO-573 was shown in Fig. 5, which indicated its activity was increased with increasing its content at 353 K, however, its activity was lower than that of Au (1.5)/ZnO-573

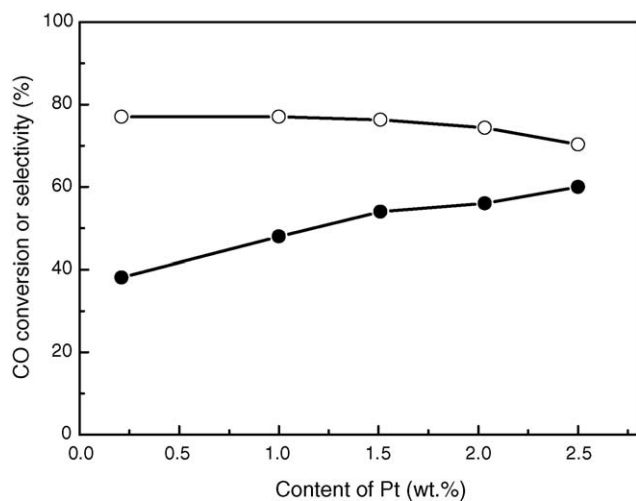


Fig. 5. The effect of content of Pt/ZnO-573 catalyst activity and selectivity. (●) Conversion, (○) selectivity.

Table 4
XRD and BET characterization results for Au-Pt-Zn-O catalysts

Catalysts	Crystallize phase	BET surface area ($\text{m}^2 \text{g}^{-1}$)
Au (1.5)-Pt (0.5)/ZnO-573	Au, ZnO	82.31
Au (1.5)-Pt (0.8)/ZnO-573	Au, ZnO	81.56
Au (1.5)-Pt (1.0)/ZnO-573	Au, PtO, ZnO	78.69
Au (1.5)-Pt (1.2)/ZnO-573	Au, PtO, ZnO	76.24
Au (1.5)-Pt (1.6)/ZnO-573	Au, PtO, ZnO	75.43

catalyst, as shown in Fig. 4, which implied that Pt/ZnO-573 catalyst could not sufficiently remove CO from rich hydrogen at mild reaction temperature. It was noticed the selectivity of Pt/ZnO-573 was almost remained constant when Pt content was below 1.5 wt.% under experimental conditions. Furthermore, research [26] also indicated supported platinum had good stability under oxidation conditions. Thus, to improve the stability of Au (1.5)/ZnO-573 catalyst, the Au (1.5)/ZnO-573 catalyst was doped with various amounts of Pt to determine if the latter can enhance the performance of the catalyst. XRD and BET characterization results of the Pt doped catalyst were shown in Table 4. When the Pt quantity was below 1.0%, PtO was not detected in the crystalline phase.

The effect of Pt on Au (1.5)-Pt/ZnO-573 catalyst oxidation CO activity and selectivity was shown in Fig. 6 where the tests had been conducted at 353 K. Catalyst activity had increased slightly with increasing Pt content in the Au (1.5)-Pt/ZnO-573 catalyst. The improvement in its selectivity was more obvious but this was up to 1.0 wt.% Pt only, following which selectivity declined. Stability of the catalyst doped with 1.0 wt.% Pt (i.e. Au (1.5)-Pt (1.0)/ZnO-573) was tested at 353 K over 500 h. The activity of Au (1.5)-Pt (1.0)/ZnO-573 catalyst was obviously stable over the entire 500 h period. The BET surface area and XRD results for the catalyst before and after it had been used were shown in Table 5. Both the crystalline phases and surface areas did not differ much. This meant that the catalyst of Au (1.5)-Pt (1.0)/ZnO-573 would

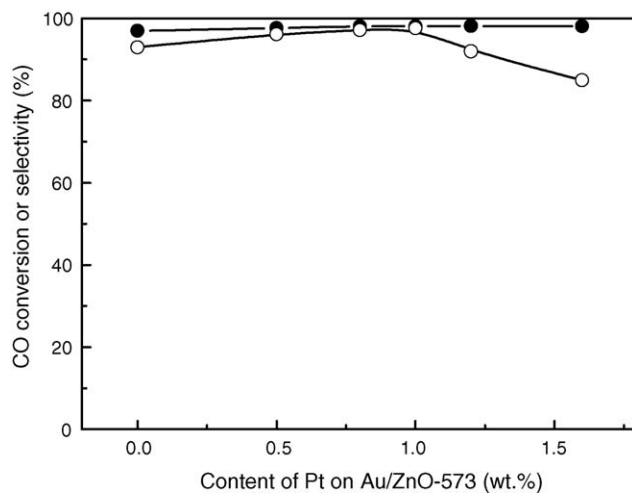


Fig. 6. The effect of content of Pt on Au (1.5)/ZnO-573 activity and selectivity. (●) Conversion, (○) selectivity.

Table 5
XRD and BET characterizations for Au (1.5)-Pt (1.0)/ZnO-573 before/after reaction

Catalysts	Crystallize phase	BET surface area (m ² g ⁻¹)
Au (1.5)-Pt (1.0)/ZnO-573 ^a	Au, PtO, ZnO	78.69
Au (1.5)-Pt (1.0)/ZnO-573 ^b	Au, PtO, ZnO	77.80

^a Before reaction.

^b After reaction.

be a promising catalyst to be used in the preferential oxidation of CO in the hydrogen-rich for the fuel cell application.

In order to clarify the promoting mechanism when platinum was added on Au (1.5)/ZnO-573 catalyst, samples were characterized using FT-IR spectra of CO, H₂ and CO₂ chemisorbed on catalysts of Au (1.5)/ZnO-573 and Au (1.5)-Pt (1.0)/ZnO-573, respectively. Samples were pretreated at 473 K for 4 h under pure nitrogen and then cooled to room temperature prior to CO, H₂ and CO₂ adsorption. According to the experimental data (not shown the figure in the text), bands at 1451 and 1640 cm⁻¹ were attributed by deposited carbonate-like species on the ZnO support, and band at 2085 cm⁻¹ was belonged to CO adsorbed on the Pt and Au mental particles. The band at 2345 cm⁻¹ was mainly caused by CO₂ adsorption on the catalytic particles. Compared to the catalyst of Au (1.5)/ZnO-573, modified catalyst, Au (1.5)-Pt (1.0)/ZnO-573, showed much CO adsorbed on the active sites and less CO₂ adsorbed on the active sites, which meant that the modified Au (1.5)/ZnO-573 catalyst had selective property of adsorption of species on its active sites. It probably seemed that it was the main reason why the Au (1.5)/ZnO-573 catalyst performance has been improved with Pt modification in this experiment. This promoting mechanism was also confirmed by Liu et al. [27], in which the catalyst of Pt supported on aluminum was promoted by ferric oxides. Other characterization should be done in the future studies to confirm this promoting mechanism.

3.5. Reaction kinetics on Au (1.5)-Pt (1.0)/ZnO-573 catalyst

For the dynamics experiments, some researches indicated that the partial pressure of carbon dioxide did not significantly affect itself production rate performed on the supported noble catalyst under the experimental conditions, however, other evidence showed that the effect of the presence of carbon dioxide on both its activity for the selective carbon monoxide oxidation, and the selectivity, is strongly dependant on the nature of the catalyst [21]. This means that the mechanism of preferential oxidation of CO in the hydrogen-rich mixtures is quite complicated on different catalysts. In this study, CO oxidation rate could be expressed as the following empirical form for the simplification reason:

$$R_{\text{CO}} = k_0 \exp\left(-\frac{E_a}{RT}\right) P_{\text{CO}}^{n_1} P_{\text{O}_2}^{n_2} \quad (4)$$

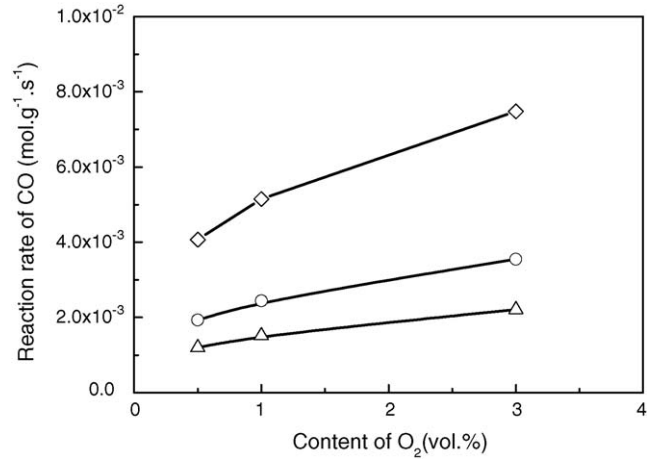


Fig. 7. Effects of oxygen concentration on reaction rate of CO conversion at 343 K. (Δ) 0.5 vol.% CO, (○) 1.0 vol.% CO, (◇) 3.0 vol.% CO.

where R_{CO} is CO reaction rate (mol g⁻¹ s⁻¹); k_0 the pre-exponential factor (mol g⁻¹ s⁻¹); E_a the apparent activation energy (J mol⁻¹); R the gas constant (J mol⁻¹ K⁻¹); T the reaction temperature (K); P_{CO} , P_{O_2} the carbon monoxide and oxygen partial pressure, respectively (kPa) and n_1 , n_2 are the exponents for carbon monoxide and oxygen partial pressure, respectively.

It should be noted the equation essentially described the observed CO oxidation rates but did not necessarily described the mechanism of the CO oxidation. The data for estimation of the kinetic constants were collected with 100 mg catalyst mixed with 100 mg inert materials, and with high gas velocity. The inert material and high gas velocity were to help dissipate the reaction heat quickly and more evenly, and so keep the catalyst bed isothermal and make the conversion ratio of CO oxidation below to 20%, respectively. A typical result was shown in Fig. 7, which was carried out at 343 K. The experimental results showed the CO oxidation rates was increased with increasing concentrations of CO and O₂ in the mixtures at same reaction temperature, as shown in Fig. 7. The other experimental results (not shown in text) indicated that reaction rate of CO conversion was increased with reaction temperature at same concentration of CO and O₂ in the mixtures. In order to determine the reaction parameters defined in the Eq. (4) by fitting the predicted values of rate model with experimental data, an objective function in terms of square sum of relative difference was defined as follows:

$$\lambda(k_0, E_a, n_1, n_2) = \sum_i \left(\frac{R_{\text{CO},i}^m - R_{\text{CO},i}^e}{R_{\text{CO},i}^e} \right)^2 \quad (5)$$

where superscripts m and e indicated model predicted and experimental rates, respectively. Nonlinear regression algorithm was used to minimize the function (5) and rate parameters involved in Eq. (4). The results of parameter estimation showed that the reaction orders with respect to CO

and O_2 were 0.68 (n_1) and 0.34 (n_2), respectively, according to the present experimental results. Apparent activation energy and pre-exponential factors were 27.0 kJ mol^{-1} and $38.6 \text{ mol g}^{-1} \text{ s}^{-1}$, respectively.

4. Conclusion

A gold zinc oxide catalyst with various pre-determined amounts of Au was prepared using a coprecipitation procedure. The results showed that the catalyst activity when oxidizing CO in hydrogen-rich mixtures in a fixed-bed reactor increased with increasing content of Au up to 1.5 wt.% Au. However, further increasing in Au beyond did not confer additional enhancement. Therefore, 1.5 wt.% Au was identified as the optimal Au content in the catalyst. The calcining temperature also had an impact on the Au (1.5)/ZnO catalyst's activity and the optimal calcining temperature was determined to be 573 K. Further increases in the calcining temperature resulted in a decline in the catalyst activity. The resulting Au (1.5)/ZnO-573 catalyst was noted to have remained largely stable in terms of its performance even when tested over 500 h, however, a slight decline in its performance after 350 h. Doping the catalyst with Pt improved the catalyst's stability. However, a limit on the quantity of Pt which can be used. When the Pt content was more than 1.0 wt.%, CO oxidation selectivity declined although catalyst activity remained largely unaffected. An appropriate catalyst composition would be Au (1.5)-Pt (1.0)/ZnO-573. Finally, the dynamic experiments were carried out on Au (1.5)-Pt (1.0)/ZnO-573 catalyst and simple power-law kinetics was applied to describe the observed CO oxidation rates. Nonlinear regression algorithm was used to determine the dynamic equation parameters, which gave the reaction orders with respect to CO and O_2 were 0.68 and 0.34, respectively, according to the present experimental results, and apparent activation energy and pre-exponential factors were 27.0 kJ mol^{-1} and $38.6 \text{ mol g}^{-1} \text{ s}^{-1}$, respectively.

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