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Low-temperature preferential oxidation of CO in a hydrogen rich stream (PROX) over Au/TiO_2: Thermodynamic study and effect of gold-colloid pH adjustment time on catalytic activity

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Abstract

By simulating CO and H_2 oxidations at thermodynamic equilibrium and studying the catalytic oxidations over Au/TiO_2, preferential oxidation of CO in a H_2 rich stream (PROX) was investigated. During the simulation, at least two cases under different gaseous feeds, $H_2/CO/O_2/N_2 = 50/1/0.5/48.5$ or 50/1/1/48 (vol.%) were examined under the assumption of an ideal gas and one atmosphere pressure in the reactor. It was found that the addition of 1% O_2 (the latter case) effectively reduced CO concentration to less than 100 ppm in the temperature range between 0 and 90 °C. This range narrowed to between 0 and 50 °C with the addition of 3% H_2O and 15% CO_2 in the feed. The thermodynamic study suggests that 1% CO in a H_2 rich system can be decreased to below 100 ppm within those low temperature ranges, if there is no substantial adsorptions onto the catalyst surface and the reactions rapidly reach equilibrium. During the catalysis reaction study, a well-pH adjusted Au/TiO_2 catalyst was found very active for PROX. CO conversions at the reactor outlet were close to those at equilibrium. Au/TiO_2 used in this work was prepared via deposition-precipitation (DP) method. The influence of gold colloid pH (at 6) adjustment time on gold loading, gold particle size and chloride residue on TiO_2 surface was detected by atomic absorption (AA), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). A pH adjustment time of at least 6 h for the preparation of gold colloids at room temperature was demonstrated to be essential for the high catalytic activity of Au/TiO_2. This was attributed to the smaller gold particle and the less chloride residue on the catalyst surface.

Keywords: PROX; Preferential oxidation of CO; Gold; Au/TiO_2; TiO_2; pH adjustment time

1. Introduction

Proton exchange membrane fuel cells (PEMFC) have drawn substantial attention for their various advantages in applications, such as high efficiency, high power density and low operating temperatures (Song, 2002). In terms of a safety perspective the method of on-board hydrogen production is more promising than that of hydrogen storage and consequently steam reforming, partial oxidation or autothermal reforming of liquid fuel (e.g., methanol) is typically used to supply hydrogen (Choudhary and Goodman, 2002; Ghenciu, 2002; Song, 2002; Trimm and Önsan, 2001). CO in the reformate can further react with H_2O via a water gas shift reaction (WGSR) to generate more hydrogen. Due to the thermodynamic limitation of WGSR (Corti *et al.*, 2005) the concentration of CO still remains *ca.* 0.5–1% in the outlet stream. CO would be adsorbed onto the Pt anode and decrease the cell efficiency (Cameron *et al.*, 2003). The maximum tolerable concentration of CO in the reformate for PEMFC was reported to be 100 ppm (Trimm and Önsan, 2001) and therefore further removal of CO at low temperatures is an important issue for PEMFC application.

In comparison with other approaches, for the removal of CO, such as membrane separation and methanation, the oxidation of CO in a H_2 rich stream (PROX) has been suggested to be preferentially more practical. That is, PROX excels in not only keeping the cost low but also decreasing CO to the desired level without excess hydrogen consumption (Song, 2002). Three kinds of catalysts have been currently introduced in PROX: platinum, copper and gold. Gold had higher activity in CO oxidation, making it possible to perform better than platinum and copper at low temperatures. Moreover, gold showed more

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Nomenclature

K_1	equilibrium constant of CO oxidation
K_2	equilibrium constant of H_2 oxidation
P_{CO}	partial pressure of CO (atm)
P_{CO_2}	partial pressure of CO_2 (atm)
P_{H_2}	partial pressure of H_2 (atm)
P_{H_2O}	partial pressure of H_2O (atm)
S	selectivity for PROX
X	equilibrium conversion for PROX

Greek symbols

ΔP_{CO}	pressure consumption of CO (atm)
ΔP_{H_2}	pressure consumption of H_2 (atm)

economic competitiveness than platinum (Cameron *et al.*, 2003; Corti *et al.*, 2005). Thus, Au/TiO_2, because of its extremely high activity in CO oxidation (Boccuzzi and Chiorino, 2000; Tsubota *et al.*, 1991; Yu *et al.*, 2005), was used in this research.

It has been presented in our past work (Lin *et al.*, 2002; Lin and Wan, 2003, 2004; Chen *et al.*, 2005) that Au/Y (Y represents Y-type zeolite) prepared from a gold colloid at pH 6 (pH adjusted at room temperature) possesses a better catalytic activity than those with colloids adjusted at the other pH's. Therefore, a deposition-precipitation (DP) method was used for the preparation of Au/TiO_2 in this work. $NaOH_{(ag)}$ was applied to adjust the pH of the gold colloid to 6, before the addition of TiO_2 into the solution. During the pH adjustment, the chloride coordinated to Au is gradually replaced by a hydroxide ion and the formation of gold oligomers occurs by the dehydration reactions. The chloride residue is detrimental to the catalytic activity of supported gold (Haruta, 1997; Oh *et al.*, 2002). Although the influence of different pH of $HAuCl_{4(aq)}$ on the deposition, on the size of gold particles as well as on CO oxidation activity has been extensively studied (Chang *et al.*, 1998; Haruta, 1997; Lee and Gavriilidis, 2002; Lin and Wan, 2003; Moreau *et al.*, 2004, 2005; Wolf and Schüth, 2002), the importance of the effect of the process of gold colloid pH adjustment has never received much attention. Therefore, the effect of pH-adjustment time on Au/TiO_2 is studied in this research.

In this paper, the thermodynamic simulations were introduced to examine the validity of PROX in H_2 rich stream and to picture the temperature dependence of equilibrium conversions of CO and H_2. From a comparison between the catalysis results and the results from the equilibrium study, the high activity of Au/TiO_2 for PROX was discussed. Meanwhile, the effect of gold-colloid-pH-adjustment time on the catalytic activity of Au/TiO_2 was investigated in PROX as well as in CO oxidation.

2. Experimental

2.1. Preparation of Au/TiO_2

An aqueous solution of chloroauric acid ($HAuCl_4 \cdot 3H_2O$; 1.72 mM; 230 mL; Merck) was used as gold precursor, which was prepared following the same procedures reported in our previous study (Yu *et al.*, 2005). The details are as follows: A suitable amount of $HAuCl_4 \cdot 3H_2O$ was dissolved in 230 mL deionized water to prepare gold solution with concentration of 1.72×10^{-3} M. Different pH adjustment times ranged from 0.2 to 24 h were used for preparing a series of gold colloid. NaOH $(0.1\ M)_{(aq)}$ (Acros) was used for adjusting pH of the solution to 6 in all the cases. Initially, within the first 2 h, the pH had to be constantly adjusted to 6. After this, due to a very slow decrease of pH, the pH of the solution was adjusted only every half an hour. After the pH adjustment, TiO_2 powder (JRC-TIO-4, a Japanese reference catalyst, 2.0 g) was added to the solution. It was then heated (80 °C, 1 h), cooled, filtered, washed with deionised water (500 mL) and dried at room temperature in air. The resulting samples are designated as Au/TiO_2-x, where x represents the pH adjustment time (in hours).

2.2. Catalyst characterization

The gold loading in each sample was determined using a GBC 906 atomic absorption unit. The morphology of the gold catalyst was examined by transmission electron microscopy (TEM) using a Hitachi H7100 electron microscope operated at 75 kV while the amount of chloride was determined by SEM (Hitachi S-2400) with a Kevex Delta 80000 EDS. The measurements of catalytic activity were carried out in a packed bed within a shell and tube quartz reactor (7 mm i.d.) under atmospheric pressure. The temperature of the reactor was controlled by a fluid in the shell flowing from/to a thermostat. For CO oxidation, the reaction temperature was at 0 °C. Only 0.6 mg gold in each sample was used for the test. The feed was 1% CO in air with total flow rate 33 mL min^{-1}. For PROX reactions, 40 mg of Au/TiO_2 mixed with 0.2 g of silicon carbide (SiC, Strem Chemical) were used for the tests. The reactor temperatures were controlled between 0 and 80 °C. The feed ratio was $CO/O_2/H_2/N_2 = 1/1/50/48$(vol.%) with total flow rate of 110 mL min^{-1} (space velocity = 165000 h^{-1} mL g-cat^{-1}). No catalyst pretreatment process was applied before all the reaction tests. The concentrations of CO, CO_2 and O_2 in the effluent gas were analyzed by two gas chromatographs (Shimadzu GC-8A with a Carboxen™ 1000 column and Shimadzu GC-14A with a Molecular sieve 5A column). The minimum CO concentration detected was less than 80 ppm.

3. Results

3.1. Thermodynamic equilibrium calculation

In the beginning of the thermodynamic simulation, the idealized H_2 rich stream composed of H_2, CO, O_2, and N_2 was studied for the sake of simplifying calculations. The effects of CO_2 and H_2O, that existed in the realistic reformate stream, would be examined at a later stage. Therefore, four reactions were taken into account as summarized below:

CO oxidation:

$$CO + \tfrac{1}{2}O_2 \rightleftharpoons CO_2 \qquad (1)$$

H_2 oxidation:

$$CO + \tfrac{1}{2}O_2 \rightleftharpoons H_2O \tag{2}$$

Methanation of CO:

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \tag{3}$$

Water-gas shift reaction (or WGSR):

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{4}$$

Reactions (1) and (4) are desired because either of them could decrease the CO content; although more H_2 can be produced from reaction (4). Reactions (2) and (3), however, are not desired due to H_2 consumption. The equilibrium constants (Kp) at the different temperatures were calculated according to van't Hoff's equation from the necessary thermodynamic data given in the reference (Bakker *et al.*, 1977). Because the reactions under consideration are all exothermic (Fig. 1), all of the equilibrium constants decrease with the increase of reaction temperature. The sequence of the values of equilibrium constants is: CO oxidation > H_2 oxidation ≫ methanation of CO > WGSR. The results verify that preferential oxidation of CO (PROX) is practical from a thermodynamic perspective, because the equilibrium constant of CO oxidation is larger than that of H_2 oxidation.

3.2. Equilibrium conversion study

Within reactions (1); (2) and (4), only two of these three reactions are independent. In other words, the results calculated from the reactions (1) and (2), at equilibrium, can represent that from reaction (4). Moreover, the equilibrium constants of CO and H_2 oxidations (reactions (1) and (2)) are much larger than those for the generation of methane (reaction (3)), and no methane formation was found in the later experiments. Consequently only CO and H_2 oxidations (reactions (1) and (2)) were taken into consideration for the following calculations.

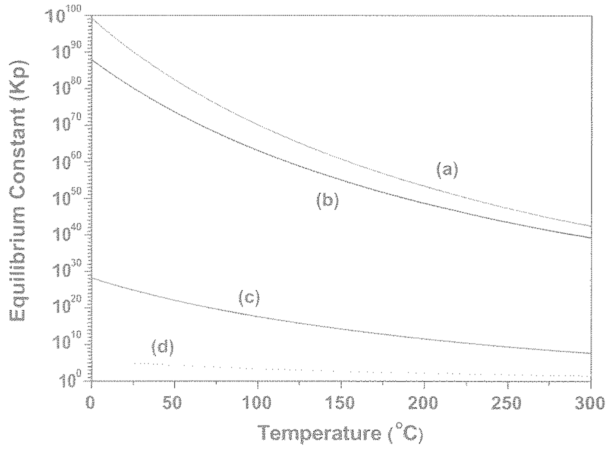

Fig. 1. The equilibrium constants (K_p) of the reactions which may occur in PROX at different temperatures under 1 atm pressure. (a) $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$. (b) $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)}$. (c) $CO_{(g)} + 3H_{2(g)} \rightarrow CH_{4(g)} + H_2O_{(g)}$. (d) $CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)}$.

For CO oxidation:

$$\frac{(P_{CO_2} + \Delta P_{CO})}{(P_{CO} - \Delta P_{CO})(P_{O_2} - \frac{1}{2}\Delta P_{CO} - \frac{1}{2}\Delta P_{H_2})^{1/2}} = K_1 \tag{5}$$

For H_2 oxidation:

$$\frac{(P_{H_2O} + \Delta P_{H_2})}{(P_{H_2} - \Delta P_{H_2})(P_{O_2} - \frac{1}{2}\Delta P_{CO} - \frac{1}{2}\Delta P_{H_2})^{1/2}} = K_2 \tag{6}$$

where P_{CO}, P_{H_2}: the reactant partial pressure of CO and H_2 in the feed, respectively; P_{CO_2}, P_{H_2O}: the product partial pressure of CO_2 and H_2O, respectively; ΔP_{CO}, ΔP_{H_2}: the pressure consumption of CO and H_2, respectively; K_1, K_2: the equilibrium constants of CO and H_2 oxidation, respectively.

Two cases with different feed conditions, $H_2/CO/O_2/N_2$ = 50/1/0.5/48.5 or 50/1/1/48 (vol.%) were studied under the assumption of ideal gas and at one atmosphere total pressure. The system consisted of two independent equations (Eqs. (5) and (6)) and two unknowns (ΔP_{CO}, ΔP_{H_2}) that were solved using the mathematics calculation software, Maple 8. The solutions with complex numbers or negative values were discarded. Thus, the temperature dependence of the equilibrium conversions of CO, H_2 and selectivity in PROX can be examined. For the practical application, CO conversion must be above 99% to ensure that the concentration of CO is decreased to less than 100 ppm. The selectivity is defined as the ratio of O_2 consumed by CO to the total amount of O_2 consumed. The higher value of selectivity is preferred because it represents the preferential oxidation of CO in these two main reactions. The calculated results of equilibrium conversion of CO as well as the selectivity at different temperatures are summarized (Table 1) (Fig. 2). It can be seen that, because of the huge equilibrium constants, O_2 conversions in both cases are at 100% at any temperature. Moreover, CO conversions decrease and H_2 conversions increase with an increase of temperature, that results in the decrease of selectivity. For the case of O_2/CO = 0.5/1 in the feed (the stoichiometric ratio for CO oxidation), the CO conversion can reach 99% and the selectivity is close to 1.0, when the reaction temperature approaches 0 °C. On the other hand, for the case of O_2/CO = 1/1, while the oxygen concentration is doubled, the temperatures for CO conversion above 99% can extend to a range from 0 to 90 °C, despite the selectivity being lowered to 0.5. This significant effect of additional O_2 in the system for CO conversions is shown (Fig. 2(a)). Despite the drawback of lower selectivity, the corresponding H_2 conversion did not exceed 2% at the temperatures equal to, or lower than, 90 °C. Hence, the ratio of O_2/CO = 1/1 is theoretically sufficient for PROX and set as the standard ratio in the following equilibrium study.

The influence of CO_2 and H_2O were investigated further to understand how PROX behaved in the realistic reformate condition. The amount of CO_2 and H_2O in the feed stream were 15% and 3%, respectively and the results are shown (Fig. 3). It can be seen that if only H_2O is present, the highest temperature for a CO conversion greater than 99% is increased to 125 °C; if only

Table 1
CO equilibrium conversion and selectivity for PROX at different temperatures under various feed conditions, obtained from thermodynamic equilibrium calculation

Temperature (°C)	Feed conditions (vol.%)									
	$CO/O_2/H_2/N_2$ = 1/0.5/50/48.5		$CO/O_2/H_2/N_2$ = 1/1/50/48		$CO/O_2/H_2/H_2O/N_2$ = 1/1/50/3/45		$CO/O_2/H_2/CO_2/N_2$ = 1/1/50/15/33		$CO/O_2/H_2/CO_2/H_2O/N_2$ = 1/1/50/15/3/30	
	Xco[a]	S[b]	Xco	S	Xco	S	Xco	S	Xco	S
0	99.0	0.99	100	0.50	100	0.50	99.8	0.50	100	0.50
10	98.6	0.99	100	0.50	100	0.50	99.7	0.50	99.9	0.50
20	98.1	0.98	100	0.50	100	0.50	99.4	0.50	99.9	0.50
30	97.5	0.97	99.9	0.50	100	0.50	99.0	0.49	99.7	0.50
40	96.7	0.97	99.9	0.50	100	0.50	98.3	0.49	99.6	0.50
50	95.8	0.96	99.8	0.50	100	0.50	97.2	0.49	99.3	0.50
60	94.8	0.95	99.7	0.50	99.9	0.50	95.7	0.48	98.9	0.49
70	93.6	0.94	99.6	0.50	99.9	0.50	93.5	0.47	98.3	0.49
80	92.2	0.92	99.4	0.50	99.8	0.50	90.5	0.45	97.5	0.49
90	90.6	0.91	99.1	0.50	99.8	0.50	86.6	0.43	96.3	0.48
100	88.8	0.89	98.7	0.49	99.7	0.50	81.6	0.41	94.7	0.47
125	83.6	0.84	97.0	0.49	99.2	0.50	64.0	0.32	88.2	0.44
150	77.4	0.77	94.2	0.47	98.5	0.49	38.8	0.19	76.6	0.38
175	70.4	0.7	89.9	0.45	97.1	0.49	6.1	0.03	58.1	0.29
200	62.8	0.63	84.2	0.42	95.0	0.48	–	–	31.6	0.16
250	47.6	0.48	69.6	0.35	88.1	0.44	–	–	–	–
300	34.0	0.34	53.8	0.27	77.5	0.39	–	–	–	–

[a] Equilibrium conversion of CO for PROX, expressed in percentage.
[b] Selectivity for PROX, expressed in ratio.

CO_2 is present, however, it decreases to 30 °C. This means that the influence of CO_2/H_2O addition is negative/positive for PROX, which corresponds to *Le Chatelier's Principle*. Therefore, when both CO_2 and H_2O are present, CO conversions greater than 99% are within the temperature range between 0 and 50 °C.

From the thermodynamic simulation it can be suggested, if no substantial adsorptions occur on the catalyst surface and if the reactions rapidly reach equilibrium, the preferential oxidation of 1% CO in H_2 rich stream should be carried out under the following conditions: the ratio of O_2 to CO in the feed

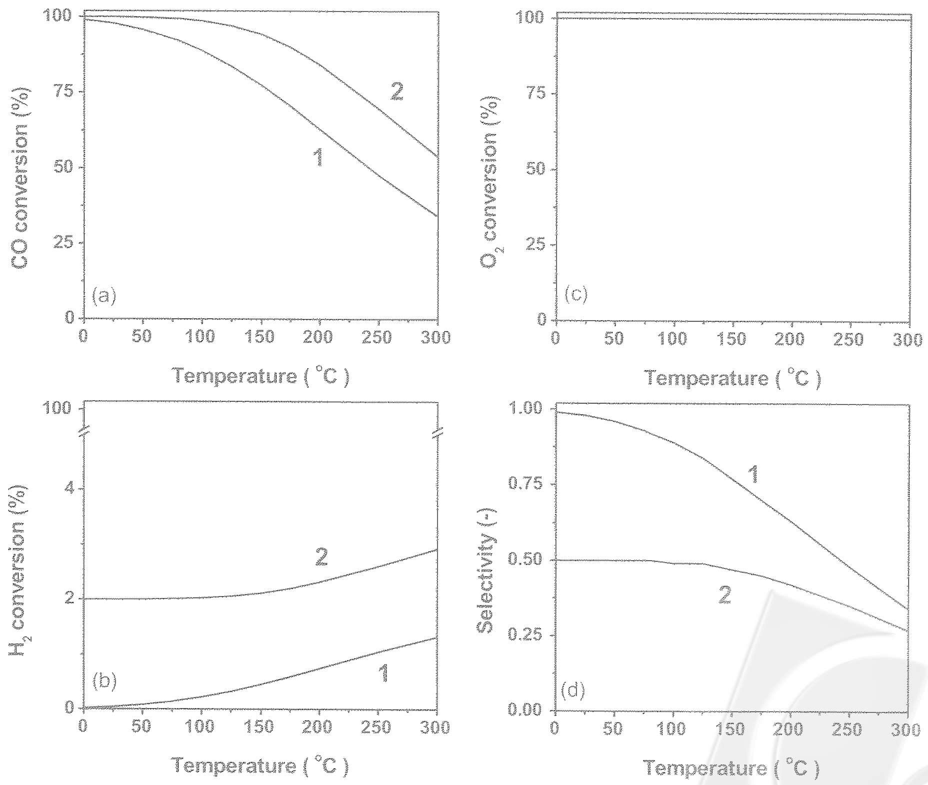

Fig. 2. Effects of O_2/CO ratio on equilibrium conversions of (a) CO; (b) H_2; (c) O_2 and (d) selectivity under 1 atm pressure. (1) $CO/O_2/H_2/N_2$ = 1/0.5/50/48.5 (vol.%). (2) $CO/O_2/H_2/N_2$ = 1/1/50/48 (vol.%).

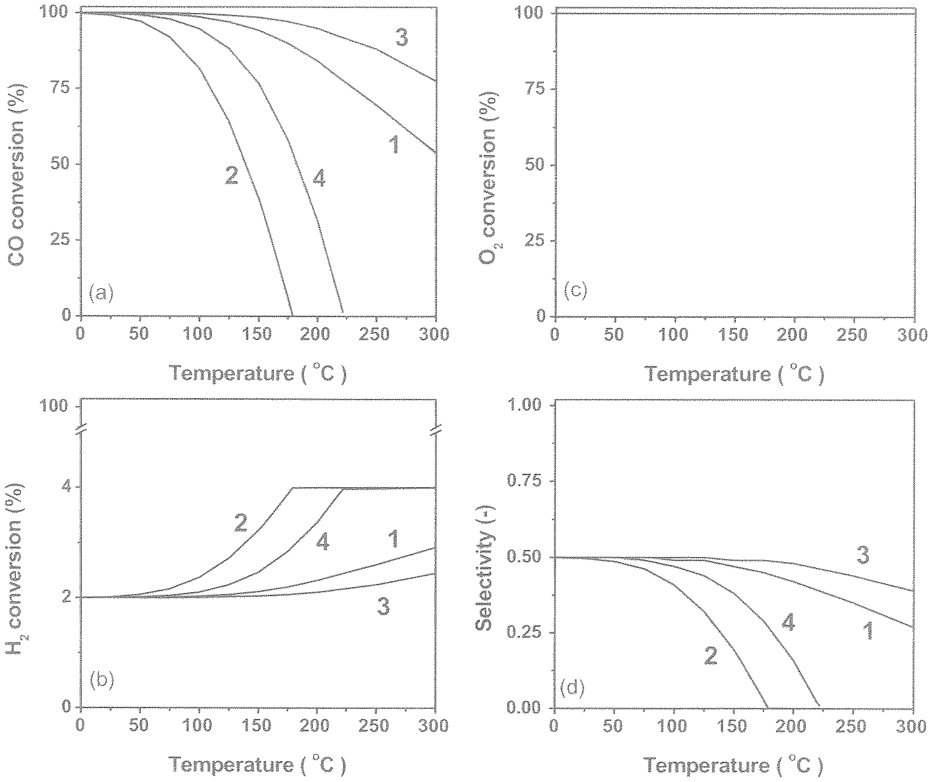

Fig. 3. Effects of H_2O and/or CO_2 addition on equilibrium conversions of (a) CO; (b) H_2; (c) O_2 and (d) selectivity under 1 atm pressure. (1) $CO/O_2/H_2/N_2$ = 1/1/50/48 (vol.%). (2) $CO/O_2/H_2/CO_2/N_2$ = 1/1/50/15/33 (vol.%). (3) $CO/O_2/H_2/H_2O/N_2$ = 1/1/50/3/45 (vol.%). (4) $CO/O_2/H_2/CO_2/H_2O/N_2$ = 1/1/50/15/3/30 (vol.%).

is 1 to 1; the reaction temperature is between 0 and 90 °C (without the presence of CO_2 and H_2O) and between 0 and 50 °C (with the presence of 15% CO_2 and 3% H_2O).

3.3. Au/TiO_2 for PROX and the effect of gold colloid pH adjustment time on catalytic activity

Fig. 4 shows the experimental results of PROX with several different Au/TiO_2 catalysts. The effects of reaction temperature and gold colloid pH adjustment time on the reaction activity are presented. The composition ratios in the feed to the reactor were $H_2/CO/O_2/N_2 = 50/1/1/48$. The catalyst activities can be classified into two groups. One is from the catalysts prepared from the gold colloid with pH adjustment time equal to or longer than 6 h (denoted as catalyst group A). The other is from those prepared from the colloid with pH adjustment time equal to or shorter than 1 h (denoted as catalyst group B). The catalysts from group A had extremely high activity, while those from group B had activity very close to zero. The catalytic activity of Au/TiO_2 for PROX, therefore, is highly relevant to the duration of pH adjustment time.

Fig. 4 also shows the dependence of the catalytic activities of group A on the reaction temperatures. It can be seen that the results were close to those of the equilibrium conversions of CO presented in the previous section, although the temperature range for removing CO (with a greater than 99% conversion) was narrower. That is, CO conversions above 99% only occurred between 25 and 50 °C, in contrast to those between 0 and 90 °C from the equilibrium study. It is noticed in Fig. 4(d), that the selectivity at the lower temperature range (between 0 and 50 °C) remained greater than 0.5, in contrast to those lower than 0.5 in the other temperature range. However, the value of the selectivity at the temperatures lower than 90 °C, obtained from the thermodynamic equilibrium study, is always 0.5. This reveals that within the lower temperature range, the oxidation of CO over Au/TiO_2 is preferred to that of H_2. The reactions were in the kinetic region, although the results were close to the equilibrium. On the other hand, when the reaction proceeded at a higher temperature range (from 50 to 80 °C), a decrease of CO conversion and an increase of H_2 conversion (Fig. 4(b)) were observed. The results suggest again that the reactions were still in the kinetic region. In other words, the rate of H_2 oxidation over Au/TiO_2 increased faster than that of CO oxidation at higher temperatures, which consumed more oxygen and caused CO to have less chance to be oxidized.

For catalyst of group B, almost no activity was observed, because CO conversion never exceeded 25% at all reaction temperatures. Nevertheless, the selectivity for catalyst of group B slightly increased with the increase of reaction temperatures. All the reaction results, however, were vastly different to those at equilibrium. These facts suggest that different reaction mechanisms occurred on the surface of the catalysts (group A) after longer pH adjustment time and on the surface of those (group B) resulting from shorter pH adjustment time.

The effect of CO_2 and H_2O (which exist in a realistic reformate stream) on PROX over Au/TiO_2 of group A has been

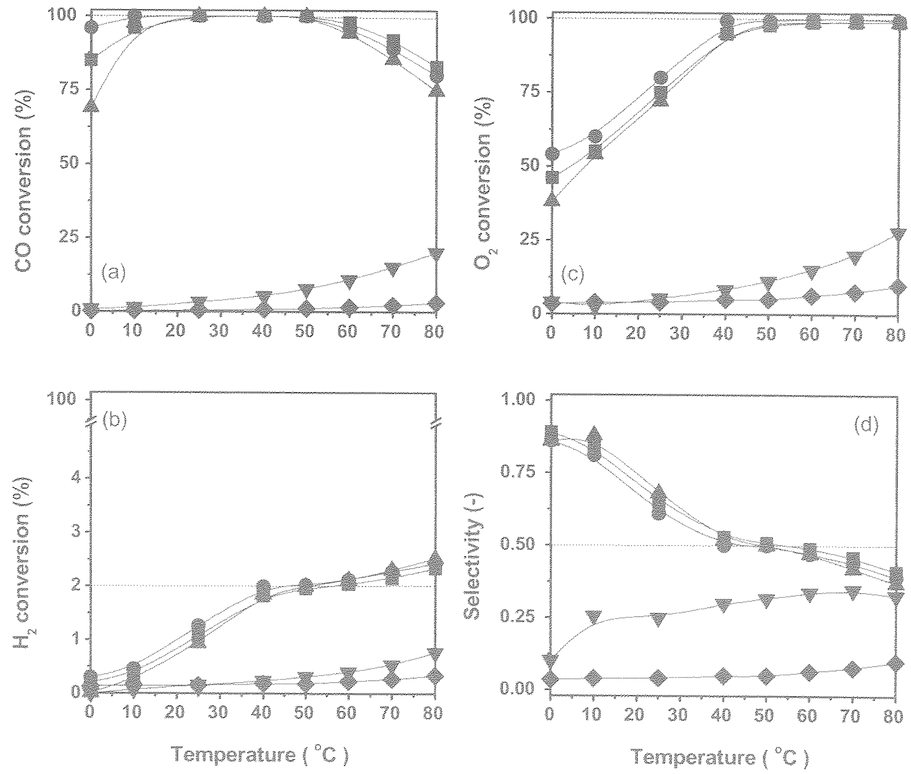

Fig. 4. Preferential oxidation of CO over 0.04 g Au/TiO_2 catalysts prepared with various pH adjustment time ((◆): Au/TiO_2-0.2; (▼): Au/TiO_2-1; (▲): Au/TiO_2-6; (●): Au/TiO_2-16; and (■): Au/TiO_2-24; (- - -) thermodynamic equilibrium) at different temperatures. (a) CO; (b) H_2; (c) O_2 conversions and (d) selectivity. Feed condition: $CO/O_2/H_2/N_2$ = 1/1/50/48 (vol.%), total flow rate = 110 mL min^{-1}.

examined and discussed in our previous work (Yu *et al.*, 2005). The decrease of CO conversions due to the presence of H_2O or CO_2 was generally similar to that presented by Daté and Haruta (2001) and Daté *et al.* (2004). Nevertheless, it should be noted that the decrease of activity in the presence of H_2O is different from the trend obtained from the thermodynamic equilibrium study obtained in this research. This may be due to the substantial coverage of the adsorbed water onto Au/TiO_2 surface in the reactor.

3.4. Catalyst characterization

A summary of the amount of $NaOH_{(aq)}$ added during the gold colloid pH adjustment process, gold loading and energy dispersive spectroscopy (EDS) results of the catalysts prepared in this work is listed (Table 2). Although all pHs of the colloids from different pH adjustment time were ensured to be at 6 before the addition of TiO_2, different amounts of $NaOH_{(aq)}$ were used for the adjustment. The relevance of gold loading and pH adjustment time was not monotonic. Furthermore, the amount of $NaOH_{(aq)}$ used was not directly proportional to the pH adjustment time. The difference in the amount of $NaOH_{(aq)}$ added was found to be less when the pH adjustment time was longer than 6 h. These results imply different chemical reactions with hydroxide at different reaction rates occur during the pH adjustment process. Moreover, almost no chloride residue was detected for the catalysts in group A, though chloride was observed from the catalysts in group B by

Table 2
Amount of 0.1 M $NaOH_{(aq)}$ added for pH adjustment, pH values of gold colloid at different preparation stages, gold loading and Cl/Au ratio in Au/TiO_2

Catalysts	pH adjustment time (h)	pH changes[a]			Total amount of 0.1 M $NaOH_{(aq)}$ added (g)	Gold loading in Au/TiO_2 (wt.%)[b]	Ratio of Cl/Au in Au/TiO_2[c]
		pH_I	pH_{II}	pH_{III}			
Au/TiO_2-0.2	0.2	3.65	3.05	3.38	10.05	1.7	0.71
Au/TiO_2-1	1	5.79	4.35	4.60	16.18	2.7	0.40
Au/TiO_2-6	6	6.54	5.45	5.98	19.22	3.4	0.05
Au/TiO_2-16	16	6.98	6.05	6.37	19.32	3.0	0.06
Au/TiO_2-24	24	7.00	6.15	6.47	20.38	2.8	0.07

[a] The initial pH of gold colloid solution (1.72 mM; 230 mL) was *ca.* 2.4, and then adjusted to pH 6 by adding 0.1 M $NaOH_{(aq)}$. pH_I, pH_{II}, pH_{III}: the pH values (I) after TiO_2 addition; (II) after heating to 80 °C and cooling to room temperature; and (III) of filtrate, respectively.

[b] Determined by atomic absorption (AA).

[c] Obtained from energy dispersive spectroscopy (EDS).

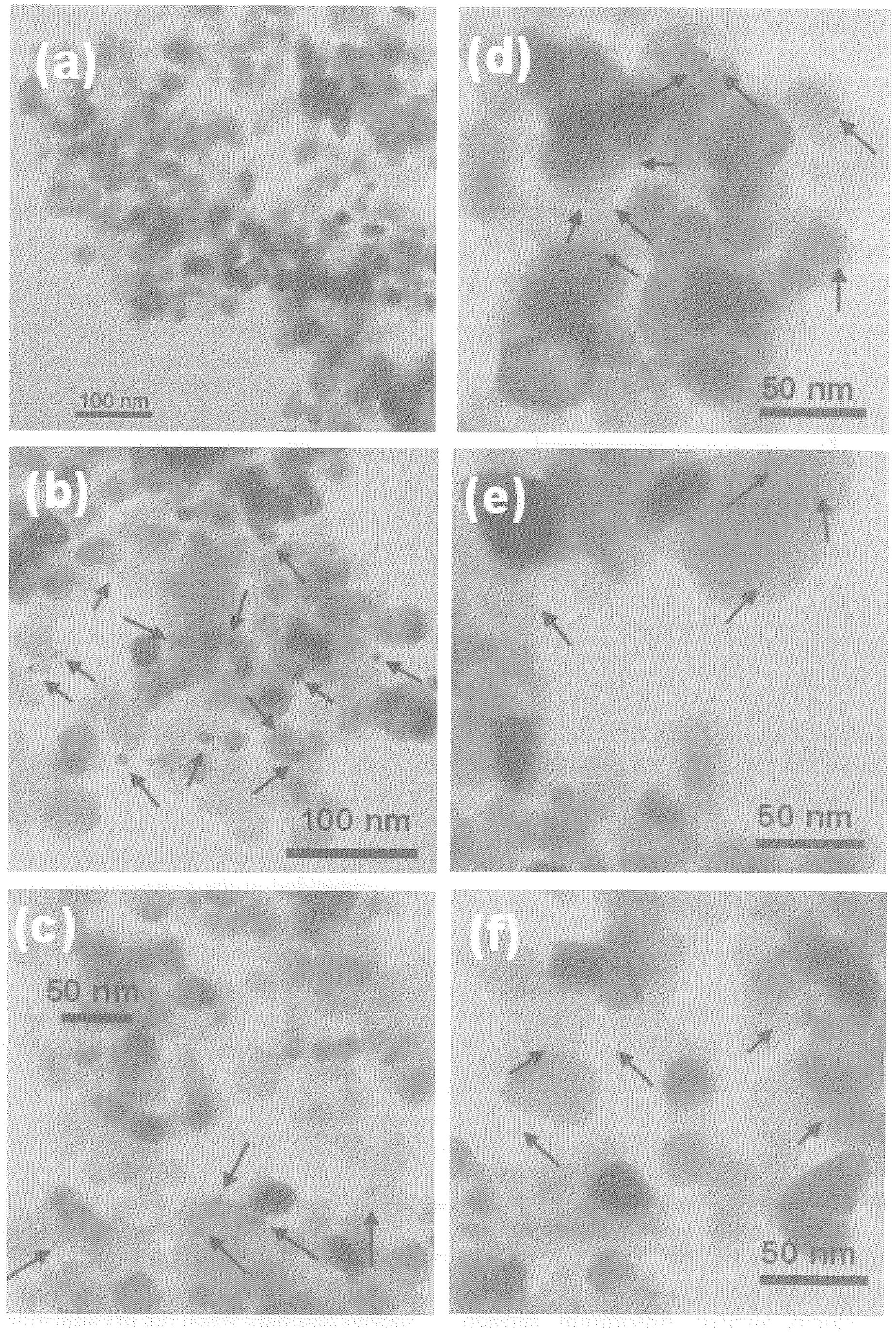

Fig. 5. TEM images of (a) TiO_2 powders; (b) Au/TiO_2-0.2; (c) Au/TiO_2-1; (d) Au/TiO_2-6; (e) Au/TiO_2-16; and (f) Au/TiO_2-24; while (b) and (c) belong to the samples of group B; and (d), (e), and (f) belong to those of group A.

EDS. Therefore, the residue of chloride on the catalyst surface could be correlated to the pH adjustment time. The TEM images of TiO_2 powder as well as those of the catalysts in group A and B are shown (Fig. 5(a)–(f)). Almost no gold particles were seen on the catalysts of group A (Fig. 5(d)–(f)). The size of the gold particles on the catalysts of group B, however, was seen to be equal, or larger than 5 nm. Thus, the larger gold particles appearing on the TiO_2 surface may be due to the chloride residue. Similar chloride effects on gold particle size and on the catalytic activity of nano-gold supported on Al_2O_3 were reported by Oh *et al.* (2002). Furthermore, CO oxidation without the presence of H_2, CO_2 or H_2O was carried out on different Au/TiO_2 catalysts, each with 0.6 mg gold in the reactor. The results are presented in Fig. 6. The purpose of these experiments was to characterize the catalytic activity based on the same weight of nano-gold. It was found that the catalytic activities of the samples from group A were still much higher than those from group B—an identical trend as observed with PROX. Therefore, from the EDS results, TEM pictures and CO oxidation test, the colloid with sufficient pH adjustment time

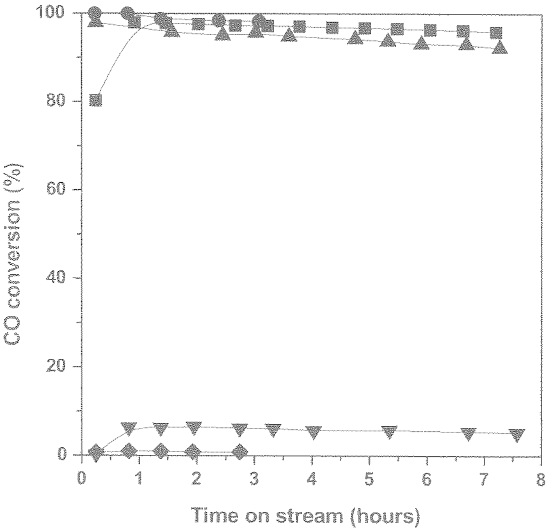

Fig. 6. CO oxidation over Au/TiO_2 catalysts prepared with various gold colloid pH adjustment time ((◆): Au/TiO_2-0.2; (▼): Au/TiO_2-1; (▲): Au/TiO_2-6; (●): Au/TiO_2-16; and (■): Au/TiO_2-24) vs. time on stream at 0 °C under 1 atm pressure. Feed condition: 1% CO in air with total flow rate 33 mL/min. Each sample contained 0.6 mg gold.

(more than 6 h) was shown to be a requirement for the Au/TiO_2 catalyst with less chloride residue, smaller gold particles on the surface and with higher catalytic activities for PROX or CO oxidation.

4. Discussion

4.1. PROX reaction and PROX on Au/TiO_2

According to the thermodynamic equilibrium studies, CO can be preferentially oxidized with little H_2 consumption at temperatures lower than 90 °C. The catalysts used in PROX, therefore, should be chosen to be capable of promoting the reactions as close to the equilibrium state as possible. Nevertheless, the mass transfer and the catalytic reactions, that involve adsorption, surface reaction and desorption on the surface of the catalysts, might alter the experimental results of PROX from the equilibrium conversions simulated in this research. In this work, the issue of mass transfer can be omitted, due to the high space velocity applied. Adsorption, surface reaction and desorption, however, would associate with the surface properties of the catalysts. In contrast to the heavy adsorption of CO on Pt surface, the surface of Au/TiO_2 is proposed to give a moderate adsorption of CO, O_2 and H_2, as indicated from the much lower ignition temperature than that of Pt catalysts (Kahlich *et al.*, 1997). This ignition temperature, that is defined as the temperature of maximum gradient in a plot of CO conversion versus temperature, combined with O_2 conversion and selectivity for PROX, can reflect the situations in the adsorption and/or desorption of reactants. Unlike Pt catalysts, more space is available for O_2 to be adsorbed, instead of being fully adsorbed by CO, on the surface of Au/TiO_2 at low temperatures. Higher priority for CO oxidation as thermodynamics suggest or the adequate distribution of CO and H_2 on the surface proposed from the properties of Au/TiO_2 ensures that CO has more opportunities to react with O_2, resulting in the high CO conversion, accompanied with high selectivity at low temperatures. As the reaction temperature increases, the probability of CO adsorption may start to decrease, which causes the probability of H_2 oxidation to increase. This assumption could be verified by the decreasing selectivity at high temperatures and can be supported by the density functional calculations (Kandoi *et al.*, 2004).

The thermodynamic simulation also suggests H_2 oxidation would become intense as the temperature increases, even if the variation in the proportion of reactants adsorbed on the catalyst surface is small. The values of the selectivity from the experiments, however, continue to decrease and even become lower than those obtained from the equilibrium study as further increase in reaction temperature. There might be two reasons for this outcome. First, the increase of the activity in H_2 oxidation with the increase of reaction temperature is faster than that in CO oxidation on the active site of Au/TiO_2. Second, insufficient reaction time is available for H_2O on the surface, which comes from H_2 oxidation, to react with CO to produce H_2 and CO_2 via the water gas shift reaction. In other words, infinite time is not given for the reactions to reach equilibrium state. Furthermore, this fact might indicate that gold catalysts are not suitable for WGSR at the temperatures lower than 80 °C. In reality, the experimental results from PROX with the catalysts in group A are roughly close to those at thermodynamic equilibrium. Therefore, PROX catalyzed by Au/TiO_2 is recommended at the temperatures lower than 80 °C.

4.2. Effect of pH adjustment time on Au/TiO_2

Sufficient pH adjustment time (equal to or longer than 6 h) for a gold colloid is found to be essential for the preparation of gold catalysts with suitable property for PROX; that is, high CO conversion and high selectivity at the temperatures lower than 80 °C. The extremely slow reaction in gold solution could be inferred from comparing the increment of $NaOH_{(aq)}$ addition, which is, initially, relatively large. According to the rate in pH decrease in a gold solution, the addition of base is proposed to be responsible for the rapid neutralization of protons in the first stage. The base then reacts slowly with gold chloro-hydroxy species and only when the pH adjustment time is long enough, does the replacement of chloride by hydroxide occur. For catalysts prepared with insufficient pH adjustment time (equal to or shorter than 1 h), a preliminary substitution of chloride in chloroauric acid is achieved. This is supported by the fact that the color of the solution is still golden after pH adjustment and a large amount of chloride remains. Furthermore, since the reaction of the replacement of chloride by hydroxide ion is slow, the corresponding slow response in pH value could be expected, resulting that the disguised end point of pH adjustment occurred. However, the subsequent hydrolysis of chloroauric acid or other reactions is indicated to progress and this can be supported by the fact that lower pH values of the gold colloid solution were recorded at the latter several preparation stages (after TiO_2 addition; after cooling from

80 °C; the filtrate after the filtration) (Table 2). Optimum pH adjustment time, however, seems to exist by analyzing the gold loading and the activity performance. When pH adjustment time is too long, it may result in the aggregation of the gold species (e.g., oligomerization of gold hydroxyl monomers by dehydration reaction) in the gold colloid solution. This might cause a lesser amount of gold to be deposited on the TiO_2 surface, as demonstrated from the comparison of gold loadings in Au/TiO_2-6, Au/TiO_2-16 and Au/TiO_2-24 samples listed in Table 2.

Certain extremely slow but crucial chemical reactions have occurred in the gold colloid during the pH adjustment steps, as indicated from the comparison between the two samples: Au/TiO_2-6 (pH adjusting for 6 h) and Au/TiO_2-16 (pH adjusting for 16 h). It should be realized that the amount of $NaOH_{(aq)}$ added for the catalyst Au/TiO_2-6 is almost the same as that for Au/TiO_2-16. The degree of chloride replaced by hydroxide is supported by the EDS results. Nevertheless, the activity of Au/TiO_2-16 for PROX at the temperatures close to 0 °C is substantially better than that of Au/TiO_2-6, as shown in Fig. 4(a), with an experimental error of no more than 10% from repeated measurements. Therefore, different gold species in the solution are believed to exist—a point that is also sustained by the pH records for different preparation stages (Table 2). This suggests that the significance of pH adjustment time should not be neglected because the activity of gold catalyst is highly related to the gold species in the solution and this is reflected in the pH of the solutions and in the catalytic activity for PROX.

5. Conclusion

(1) In the presence of 1% CO and the absence of H_2O and CO_2 in a hydrogen rich feed stream, PROX is suggested, from the thermodynamic equilibrium study, to be carried out in the presence of 1% O_2 and at the temperatures equal to or lower than 90 °C. Under these conditions, CO oxidation is preferred and CO concentration can be decreased to less than 100 ppm. On the other hand, in the presence of H_2O and CO_2 in the hydrogen rich feed stream, PROX is suggested to be carried out at the temperatures equal to, or lower than, 50 °C.

(2) Au/TiO_2 possesses good catalytic activity for PROX between 25 and 50 °C, which is close to the temperature range obtained from the thermodynamic equilibrium study.

(3) The selectivity for CO oxidation over Au/TiO_2 at the temperatures lower than 50 °C was higher than the selectivity at equilibrium; in contrast, that at the temperatures higher than 50 °C was lower than the selectivity at equilibrium.

(4) For the preparation of Au/TiO_2, pH adjustment time for gold colloid solution is significantly relevant to the performance of the catalysts. Sufficient pH adjustment time (more than 6 h) can avoid substantial amount of chloride residue, hence can result in active Au/TiO_2 for PROX and for CO oxidation.

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Au/TiO_2 於低溫下催化富氫氣體中一氧化碳的選擇性氧化反應: 熱力學模擬及金溶液酸鹼值調整時間對觸媒活性的效應

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摘　要

本研究藉由熱力學模擬及 Au/TiO_2 的催化反應研究富氫氣體中一氧化碳的選擇性氧化反應。在假設氣體為理想氣體且反應總壓是一大氣壓的條件之下，先針對不同的氣體進料比例 H_2 / CO / O_2 / N_2 = 50 / 1 / 0.5/ 48.5 or 50 / 1 / 1 / 48 (vol.%) 作一熱力學反應平衡研究。模擬結果發現 1%氧氣進料在反應達到平衡時，能較有效的降低一氧化碳濃度低於 100 ppm 以下，其適當的反應溫度操作範圍應是在 0 到 90 °C 之間；若進料氣體內再加入 3% 水氣 及 15% 二氧化碳，反應溫度則縮小至 0 到 50 °C 間。熱力學模擬的結果顯示，如果觸媒表面沒有大量的吸附問題並且反應能夠快速達到平衡，在低溫富氫氣體中的 1%一氧化碳應能降低至 100 ppm 以下。在 Au/TiO_2 觸媒催化活性方面，本研究發現經酸鹼值調整程序所製得的觸媒具有極高的活性，能催化富氫氣體中一氧化碳的氧化反應接近平衡轉化率。本研究是以沉澱沉積法製備 Au/TiO_2，並藉由原子吸收光譜 (AA)、穿透式電子顯微鏡 (TEM)、及能量分散光譜儀 (EDS) 來鑑定金溶液酸鹼值 (pH 設定為 6) 的調整時間對載體表面上金載負量、金顆粒大小、及氯殘留量所造成的影響。研究結果顯示，在室溫下金溶液酸鹼值的調整時間至少需六小時才能使 Au/TiO_2 表面有較小的金顆粒和較少的氯殘留，因而具有極高的催化活性。