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Preferential oxidation of CO in H_2-rich gases over Co-promoted Pt-γ-Al_2O_3 catalyst

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Carbon monoxide is a poison to the Pt anode in proton exchange membrane fuel cell (PEMFC). Preferential oxidation (PROX) is an effective method to reduce CO in hydrogen-rich gas streams to a tolerant level. In the present work, the effect of adding cobalt to Pt/γ-Al_2O_3 on the PROX of CO was investigated. Our results showed that the addition of Co to Pt/γ-Al_2O_3 could not only improve the low-temperature activity but also reduce significantly the loading of Pt in the catalysts. Over the catalyst 3%Co/1%Pt/γ-Al_2O_3 the conversion of CO was close to 100% at 90 °C and space velocity of 8000 mL g^{-1} h^{-1}. In addition, the Co-promoted Pt/γ-Al_2O_3 catalyst showed good resistance to H_2O and CO_2 and could be operated in a wide range of space velocity. At temperatures above 90 °C, the existence of H_2O in the feed increased the conversion and broadened the operating temperature range without worsening the selectivity. When space velocity was changed from 8000 to 80,000 mL g^{-1} h^{-1} and temperatures was kept between 120 and 160 °C, the conversion of CO was always over 99% and the decrease in O_2 selectivity did not exceed 10%. Furthermore, a strong opposite effect of the ratio of O_2 to CO on the conversion of CO and the selectivity of O_2 was observed. However, at the O_2/CO ratio of 1.0 and temperatures between 120 and 160 °C, a satisfied balance between conversion and selectivity could be obtained.

KEY WORDS: preferential oxidation of CO; hydrogen; Pt catalyst; promoter; cobalt; PEMFC.

1. Introduction

Methanol steam reforming has been used in on-board manufacturing of hydrogen for fuel cell vehicle application. Usually, after the steps of steam reforming and water gas shift reaction, about 1 vol% of CO remain unchanged in the reformate. Since the anode platinum catalyst in proton exchange membrane fuel cell (PEMFC) is very sensitive to the poisoning by CO, the concentration of CO has to be reduced to a level of below 50 ppm [1], typically below 10 ppm. Preferential oxidation (PROX) and membrane separation were proposed for removing CO from hydrogen-rich gas streams. However, PROX of CO is advantageous over membrane separation technology due to its reaction at relative low temperature and atmospheric pressure. Therefore, PROX of CO is more attractive [2].

So far, Pt group metals are regarded as the most practical catalysts for PROX of CO [3–13]. However, the reported operating temperature at around 200 °C [3–5] seemed too high to match the subsequent reaction in PEMFC, which is usually at 50–125 °C [2]. On the other hand, the loading of Pt in the catalyst is currently in the range of 2–6 wt% [4–11], which needs to be lowered and the resistance of Pt catalyst against H_2O and CO_2 should be improved further [12,13].

Dabill *et al.* [14] reported that in a mixture of H_2, CO and O_2 no reaction could occur until sufficient adsorbed carbon monoxide was removed from the surface of catalyst to allow the dissociative adsorption of oxygen. This is because of the strong adsorption of CO on Pt at low temperature. Accordingly, in order to initiate the oxidation reaction, a partial amount of CO should be desorbed by increasing the reaction temperature for vacating active sites for the dissociative adsorption of O_2. However, the most desirable alternative may be the modification of surface composition to create the active sites for the dissociative adsorption of O_2 [15].

It is known that cobalt oxides are very active for the deep oxidation of CO [15,16] and CoO_x could serve as O-supplier [16]. Cobalt ion may also promote the adsorption of O_2 on Pt by an increased electron back donation into the anti-bonding orbital of molecularly adsorbed O_2. Therefore, the promotional effect of cobalt on the PROX of CO is worthy of exploration.

Epling *et al.* [13] have investigated the PROX of CO over Pt/Co/TiO_2 catalyst and obtained an almost complete conversion of CO at 30 °C. However, with the increase of reaction temperature the conversion of CO decreased rapidly and both CO_2 and H_2O showed a detrimental effect on the activity of Pt/Co/TiO_2. Teng *et al.* [17] found that in the absence of water vapor the

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conversion of CO over CoO catalyst reached near 99% at 100 °C, but in the presence of 3% H_2O in feed the catalytic activity was inhibited and the conversion of CO was low even at 130 °C.

Recently, Farrauto and coworkers [6,18] investigated the effect of adding iron oxide to Pt/γ-Al_2O_3 on the PROX of CO. They found that a 100% conversion of CO could be obtained at 90 °C and the iron oxide provided active oxygen to the CO oxidation. However, the loading of Pt in the catalyst was high (5 wt%).

In the present work, the effect of adding Co to a Pt/γ-Al_2O_3 catalyst with a low loading of Pt (1.0 wt%) on the PROX of CO was investigated and the behavior of the co-promoted Pt/γ-Al_2O_3 catalyst in the co-existence of H_2O and CO_2 was examined.

2. Experimental

Chloroplatinic acid ($H_2PtCl_66H_2O$, analytical reagent, Shanghai No. 1 Factory of Chemical Reagents) was impregnated over a γ-Al_2O_3 support (specific surface area: 106 m^2/g, Shandong Aluminum Industry Corp.) using the incipient wetness method. The loading of Pt was 1 wt% based on the weight of support. The catalysts were dried at 100 °C for 12 h, calcined in air at 500 °C for 2 h, and reduced in a stream of 20%H_2/N_2 at 350 °C for 2 h. Then, a solution of cobalt nitrate ($Co(NO_3)_26H_2O$, analytical reagent, Shanghai No. 2 Factory of Chemical Reagents) was impregnated over the reduced Pt/γ-$A1_2O_3$ catalyst and the loading of Co was 3 wt%. The Co/Pt/γ-$A1_2O_3$ catalysts were dried at 80 °C for 12 h and calcined in air at 400 °C for 2 h. Prior to each run of experiment, the catalyst was reduced *in situ* in the reactor at 350 °C for 2 h. In order to make comparison, Pt/γ-Al_2O_3 and Co/γ-Al_2O_3 catalysts were prepared in the same procedure.

A fixed-bed flow reactor (a stainless steel tube with a diameter of 12 mm and a length of 380 mm) was used for the oxidation reaction. In each measurement, a 0.5 g of catalyst with the size of 10–20 meshes was diluted with two-times volume of quartz sand (10–20 meshes). The length of the packed bed was 18.8 mm. The temperature was measured in the center of the bed using a K-type thermocouple and the difference of the measured temperature to the hot spot, which located at ca. 1/4 upside of the bed, was within 5 °C depending on the reaction temperature. The reaction temperature was varied from 90 to 230 °C and was maintained at each set point for 2 h. The feed gas was composed of 1.1%CO, 67%H_2, 20%CO_2, 0.55–1.98%O_2, 9%H_2O (if need) and N_2 balanced. Except for the experiments of investigating space velocity, the total gas flow rate was 340 mL/min, corresponding approximately to a gas hourly space velocity (GHSV) of 40,000 mL g^{-1} h^{-1}.

The concentration of the components in inlet and outlet gas streams was analyzed by a gas chromatograph with a thermal conductivity detector (TCD) and a flame-ionized detector (FID). A carbon molecular sieve (TDX-01) column was used to separate O_2, N_2, CO and CO_2. The separated CO and CO_2 were further converted into CH_4 in a methanation reactor and analyzed by FID.

The selectivity of O_2 in this paper was defined as follows:

$$O_2 \text{ selectivity } (\%)\ S = \frac{0.5 \times (C_{CO}^{in} - C_{CO}^{out})}{C_{O_2}^{in} - C_{O_2}^{out}} \times 100\%$$

3. Results and discussion

3.1. Comparison of catalytic activity

Figure 1 shows the conversion of CO and the selectivity of O_2 as a function of reaction temperature over 3%Co/γ-Al_2O_3, 1%Pt/γ-Al_2O_3, and 3%Co/1%Pt/γ-Al_2O_3. It is evident in figure 1a that a significant improvement of activity was resulted by introducing Co into the Pt/γ-Al_2O_3 catalyst. The conversion of CO over the catalyst 3%Co/1%Pt/γ-Al_2O_3 was already near 90% at 90 °C and reached a maximum of 99.9% at 120 °C. However, over the non-promoted Pt/γ-Al_2O_3 catalyst

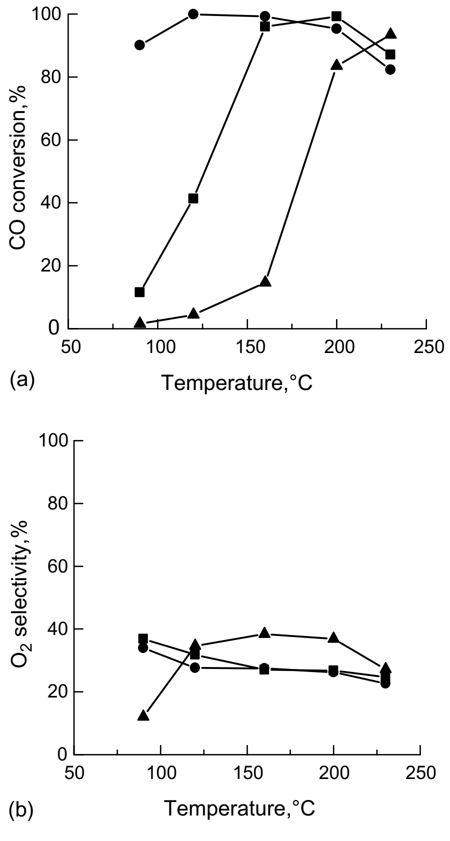

Figure 1. Effect of temperature on CO conversion (a) and O_2 selectivity (b). ■: 1%Pt/γ-Al_2O_3, ▲: 3%Co/γ-Al_2O_3, ●: 3%Co/1%Pt/γ-Al_2O_3 (feed: O_2/CO = 1.8, $\varphi_{CO} = 1.1\%$, $\varphi_{H_2} = 67\%$, $\varphi_{CO_2} = 20\%$, $\varphi_{H_2O} = 9\%$, N_2 balanced, GHSV = 40,000 mL g^{-1} h^{-1}).

the conversions at the above mentioned same temperatures were only 10% and 45%, respectively, and a maximum conversion of 99.8% occurred till 200 °C. In the case of 3%Co/γ-Al$_2$O$_3$, the CO conversion was not more than 20% at temperatures below 160 °C. A rapid increase in conversion was observed at 160 °C and a maximum conversion of 99% occurred at 200 °C.

It can be seen in figure 1b that for the Pt-containing catalysts the selectivity of O_2 decreased with the increase of temperature and the effect of the introduction of Co on the selectivity was negligible. The catalyst 3%Co/γ-Al$_2$O$_3$ showed different change of selectivity. At lower temperature, the selectivity was higher than that of the Pt-containing catalysts, especially at 160 °C. However, as the temperature increased up to 230 °C, the selectivity of O_2 dropped to about 30%. Taking the conversion of CO at the corresponding temperature into account, the high selectivity showed by the non-precious metal catalyst is not of practical meaning.

Combining the results of conversion and selectivity, it can be recognized that the Co-promoted Pt/γ-Al$_2$O$_3$ catalyst is not only active at low temperature but also provides a broader range of operating temperature.

The methanation of CO and CO_2 in the H_2-rich gas stream is another concern of selectivity due to the consumption of hydrogen in a molar ratio of 3–1 and 4–1, respectively. Epling *et al.* [13] reported that Co/TiO$_2$ catalyst could catalyze the formation of methane to some extent above 150 °C, but none of the Pt or Pt/Co containing catalysts was active for methanation. However, in our experiments, methane was detected over the catalyst 3%Co/1%Pt/γ-Al2O3 at temperatures above 230 °C, even though the concentration was below 200 ppm. Fortunately, the optimal working temperature of the 3%Co/1%Pt/γ-Al$_2$O$_3$ catalyst is well below 200 °C and hence, the detriment of selectivity caused by methanation could be avoided effectively.

The improvement of catalytic activity of Pt/γ-Al$_2$O$_3$ by the incorporation of cobalt may be caused by various factors, but it is evident that there is a synergistic effect between the active components Pt and Co. Cobalt cations could promote the adsorption of O_2 on Pt, serving as a short-living precursor state for dissociative adsorption of oxygen or CoO$_x$ could directly dissociate O_2 under the assistance of O-vacancies on cobalt oxides [16]. As a result, a spillover of active oxygen species from CoO$_x$ to Pt sites might be involved in the reaction course. Epling *et al.* [13] proposed another mechanism in which Pt might cause a further reduction in neighboring Co sites which adsorb more of oxygen and lend this reactant to the CO adsorption sites, most likely associated with the Pt.

3.2. *Effect of H_2O and CO_2*

Many of the previous investigations were carried out using a simplified feed composition containing only H_2, CO, O_2 and inert gas [5,10,17]. However, in a real reformation gas there is a relative high concentration of H_2O and CO_2. Therefore, the influence of H_2O and CO_2 on the PROX of CO should be examined. Korotkikh and Farrauto [6] reported that on base metal promoted 5%Pt/γ-Al$_2$O$_3$ catalyst the introduction of 3 vol% water vapor caused a decrease in the conversion of CO, but after increasing the water content to 10 vol% no further changes in the conversion and selectivity occurred. Furthermore, in their experiments, the existence of CO_2 did not show any influence on the catalytic activity. Epling *et. al.* [13] found that the addition of CO_2 and/or H_2O to the feed would cause a decrease in the CO conversion. In the present work, the effect of H_2O and CO_2 was investigated on the catalyst 3%Co/l%Pt/γ-Al$_2$O$_3$ and the results are given in figure 2.

From the results shown in figure 2, it is found that the introduction of water vapor enhanced the reaction significantly. The conversion of CO at 90 °C increased from about 90% for a dried feed to 94.7% for a feed containing 9 vol% of water vapor. The enhancive effect of water vapor was even stronger at temperatures above 120 °C. As can be seen in figure 2a, the conver-

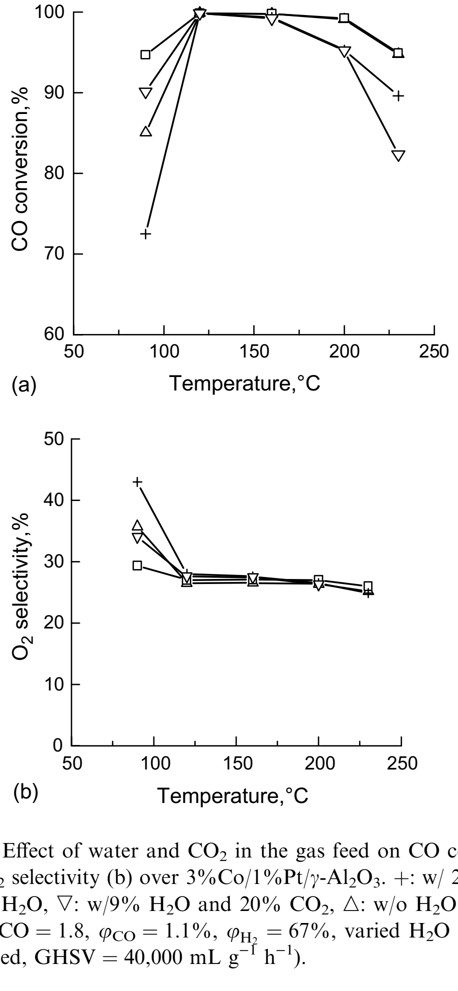

Figure 2. Effect of water and CO_2 in the gas feed on CO conversion (a) and O_2 selectivity (b) over 3%Co/1%Pt/γ-Al$_2$O$_3$. +: w/ 20% CO_2, □: w/9% H_2O, ▽: w/9% H_2O and 20% CO_2, △: w/o H_2O and CO_2 (feed: O_2/CO = 1.8, φ_{CO} = 1.1%, φ_{H_2} = 67%, varied H_2O and CO_2, N_2 balanced, GHSV = 40,000 mL g^{-1} h^{-1}).

sion kept always over 99% in a wide range of temperature as long as water existed. However, the effect of water vapor on the selectivity of O_2 was negative and at temperatures above 120 °C became insignificant (see figure 2b).

In contrast to the effect of water vapor, the existence of CO_2 in feed decreased the conversion of CO and increased the selectivity of O_2, especially at lower temperature. For example, at the reaction temperature of 90 °C, the CO conversion decreased from about 90% for a feed without CO_2 and H_2O to 72.5% for a feed containing 20 vol% CO_2. However, under the same condition, the selectivity was raised by about 10%.

Finally, the co-existence of H_2O and CO_2 showed a positive net effect on both conversion and selectivity at temperatures below 120 °C. When temperature increased further, both the conversion of CO and the selectivity of O_2 decreased and the influence was very like that of CO_2 solely.

Several models have been proposed for explaining the effect of water vapor and CO_2 on the CO oxidation. Snytnikov *et al.* [12] observed an inhibited effect of both H_2O and CO_2 over Pt/C catalyst. They proposed that adsorbed water might either block the active sites on Pt/C catalyst or form CO–H_2O surface complexes, which were less active than the adsorbed CO, while the negative effect of CO_2 could be attributed to the reverse water gas shift reaction: $CO_2 + H_2 \rightarrow CO + H_2O$. However, Manasilp and Gulari [11] observed an enhancive effect of water and suggested the explanation that the hydroxyl group formed on the catalyst upon adsorbed water is a better oxidant than oxygen. They further proposed that the negative effect of CO_2 could be caused by the reverse water gas shift reaction, the formation of carbonates, or the dissociative adsorption of CO_2. Schubert *et al.* [19] contributed the promotional effect of water to the interaction between hydroxylated $A1_2O_3$ support and CO adsorbed on Pt. As a result, the formation of formate species on the support consumes Pt-bonded CO, vacating free Pt-sites for the adsorption/dissociation of O_2.

In order to clarify the effect of CO_2 in the present work, the reverse water gas shift reaction was investigated over the 3%Co/1%Pt/γ-Al_2O_3 catalyst and the results are shown in figure 3. The following feed composition was used in the experiment: CO_2 20%, H_2 70% and balanced with N_2. It is found that the reverse water gas shift reaction did not occur at temperatures below 120 °C. The formation of CO at 160 °C was below 0.01% and increased to 0.05% at 200 °C. The results indicate that reverse water gas shift reaction could cause negative effect only at temperatures above 160 °C and the inhibition by CO_2 at lower temperatures may follow different mechanism.

The contribution of water gas shift reaction to the enhancive effect of water vapor was examined over the 3%Co/1%Pt/γ-Al_2O_3 catalyst and the results are shown in figure 4. The feed was composed of 1.1%CO, 9%H_2O and balanced with N_2. Conversion of CO was not detected at temperatures below 160 °C. However, at higher temperature WGS reaction occurred and the conversion of CO was 3% and 12% at 200 and 230 °C, respectively. Obviously, the contribution of WGS was significant only at temperatures above 200 °C and the enhancive effect of water vapor at lower temperature would be caused by other mechanism.

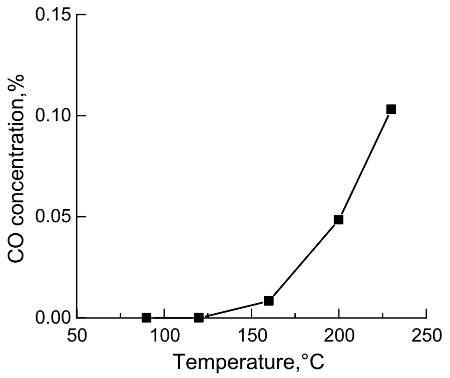

Figure 3. CO formed by reverse water gas shift reaction over 3%Co/1%Pt/γ-Al_2O_3. Feed: $\varphi_{H_2} = 67\%$, $\varphi_{CO_2} = 20\%$, N_2 balanced, GHSV = 40,000 mL g^{-1} h^{-1}.

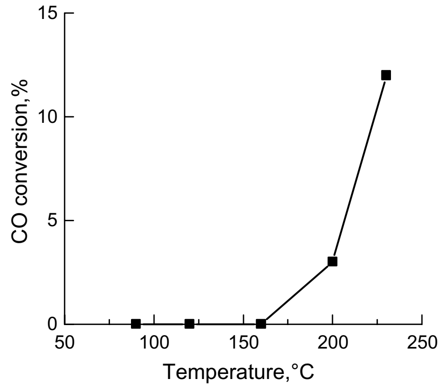

Figure 4. CO conversion via water gas shift reaction over 3%Co/1%Pt/γ-Al_2O_3. Feed: $\varphi_{CO} = 1.1\%$, $\varphi_{H_2O} = 9\%$, N_2 balanced, GHSV = 40,000 mL g^{-1} h^{-1}.

3.3. *Effect of O_2/CO ratio*

Figure 5 shows the conversion of CO and the selectivity of O_2 as a function of O_2/CO ratio. Raising the ratio of O_2/CO from 0.31 to 1.0 affected both the conversion and the selectivity significantly. At 120 °C, the conversion was increased from 57% to 99.9% and the selectivity decreased from 87% to 48%. When the O_2/CO ratio increased further, the conversion was not improved much, while the selectivity decreased signifi-

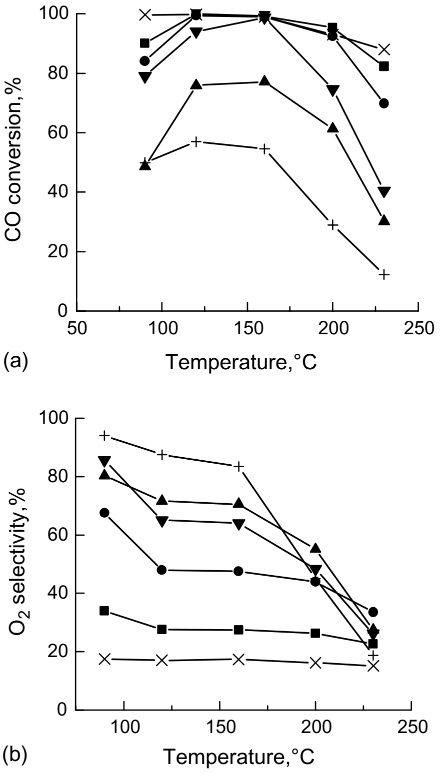

Figure 5. Effect of O_2 to CO ratio on CO conversion (a) and O_2 selectivity (b) over 3%Co/1%Pt/γ-Al_2O_3. +: O_2/CO = 0.31, ▲: O_2/CO = 0.50, ▼: O_2/CO = 0.78, ●: O_2/CO = 1.0, ■: O_2/CO = 1.8 × O_2/CO = 3 (feed: φ_{CO} = 1.1%, φ_{H_2} = 67%, φ_{CO_2} = 20%, φ_{H_2O} = 9%, varied O_2, N_2 balanced, GHSV = 40,000 mL g^{-1} h^{-1}).

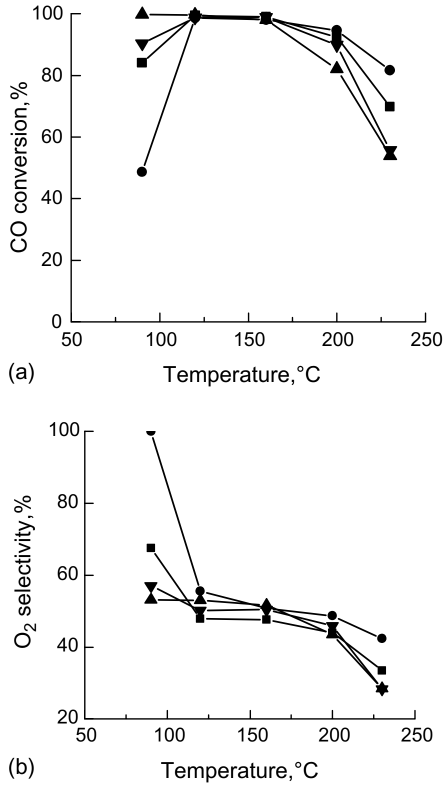

Figure 6. Effect of space velocity on CO conversion (a) and O_2 selectivity (b) over 3%Co/1%Pt/γ-Al_2O_3. ▲: GHSV = 8000 mL g^{-1} h^{-1}, ▼: GHSV = 20,000 mL g^{-1} h^{-1}, ■: GHSV = 40,000 mL g^{-1} h^{-1}, ●: GHSV = 80,000 mL g^{-1} h^{-1} (feed: O_2/CO = 1.0, φ_{CO} = 1.1%, φ_{H_2} = 67%, φ_{CO_2} = 20%, φ_{H_2O} = 9%, varied O_2, N_2 balanced).

cantly. At the O_2/CO ratio of 3.0, the conversion was nearly 100% and the selectivity was only 17%. As a whole, at the O_2/CO ratio of 1.0 a high conversion and relative high selectivity could be obtained at temperatures ranged from 120 to 160 °C.

3.4. *Effect of space velocity*

For the application of fuel cell in transportation, the output of power and thus, the hydrogen produced will be varied. Usually, a 10-fold turn-down ratio of hydrogen volume may be required. Therefore, it is necessary to investigate the effect of space velocity in a wide range. Figure 6 shows the dependence of CO conversion and O_2 selectivity on space velocity when the gas flow rate was increased for 10 times. It can be seen that at 90 °C a strong opposite effect of space velocity on conversion and selectivity existed. At the lowest GHSV of 8000 mL g^{-1} h^{-1}, almost complete conversion was obtained, while at the highest GHSV of 80,000 mL g^{-1} h^{-1}, a 100% of selectivity was reached. However, it is evident that at temperatures between 120 and 160 °C, the change in space velocity had no effect on the conversion and little influence on the selectivity. In this temperature range, the conversion and selectivity were over 99% and over 45%, respectively. When reaction temperature increased further, the effect on conversion and selectivity became significant again.

It should be noticed that the dependence of conversion on space velocity was reversed at temperatures above 160 °C, namely the lower the space velocity, the lower the conversion was. The phenomenon might be caused by reverse water gas shift reaction that occurs more readily at low space velocities and temperatures above 160 °C (see Section 3.2). Furthermore, it can be observed in figure 6 that after the temperature was raised to above 200 °C the selectivity decreased more steeply at low space velocities. This later phenomenon could be attributed to the oxidation of hydrogen that takes place more easily at higher temperature and low space velocities. On the other hand, as mentioned in Section 3.1, additional consumption of hydrogen could be caused by methanation at high temperature. Our further experimental results (see table 1) showed that this side reaction is also space velocity dependent. At the space velocity of 8000 mL g^{-1} h^{-1} the formation of methane occurred already at 90 °C and increased rapidly at temperatures above 200 °C while at the space velocity of 20,000 mL g^{-1} h^{-1}, the formation of methane at 230 °C was 330 ppm.

Table 1
Formation of CH_4 at different space velocities

GHSV (mL g^{-1} h^{-1})	Concentration of CH_4 in the outlet (ppm)				
	90 °C	120 °C	160 °C	200 °C	230 °C
8000	140	150	150	160	1760
20,000	n.d.	n.d.	n.d.	n.d.	330
40,000	n.d.	n.d.	n.d.	n.d.	70
80,000	n.d.	n.d.	n.d.	n.d.	n.d.

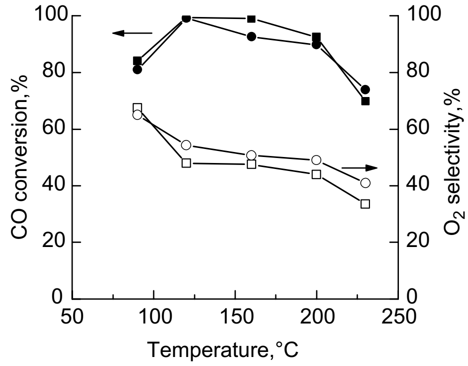

Figure 7. Hysteresis of CO conversion and selectivity over 3%Co/1%Pt/γ-Al_2O_3. ■: increasing temperature, ●: decreasing temperature (feed: $O_2/CO = 1.0$, $\varphi_{CO} = 1.1\%$, $\varphi_{H_2} = 67\%$, $\varphi_{CO_2} = 20\%$, $\varphi_{H_2O} = 9\%$, varied O_2, N_2 balanced, GHSV = 40,000 mL g^{-1} h^{-1}).

3.5. *Hysteresis phenomenon*

Hysteresis is a common phenomenon in the oxidation of CO. Wang *et al.* [20] reported that the activity of CuO/Sm-doped CeO_2 for the CO oxidation in decreasing temperature was higher than that in increasing temperature. Grisel *et al.* [21] observed also that over Au/MO_x/Al_2O_3 (M = Mg, Mn) the CO conversion in the cooling branch exceeded that of the heating branch at low temperatures. Dow and Huang [22] reported that there existed a large hysteresis loop for the CO oxidation over Pt/γ-$A1_2O_3$ and Pd/γ-Al_2O_3, while the hysteresis was small over CuO/γ-Al_2O_3. The authors attributed the differences to different mechanisms of chemisorption and different TOFs of the active sites.

In the present work, we investigated the hysteresis over the 3%Co/1%Pt/γ-Al_2O_3 catalyst by traversing the temperature range in different direction. The results are showed in figure 7. A small hysteresis was observed for both the CO conversion and O_2 selectivity. The conversion of CO was a little bit higher in the heating direction, whilst the selectivity of O_2 was increased to a small extent in the cooling direction. Obviously, the addition of Co to Pt affected significantly the chemisorption of CO and O_2 on the catalyst.

4. Conclusions

(1) The addition of cobalt to Pt/γ-Al_2O_3 catalyst improved the catalytic activity for the PROX of CO and reduced the loading of Pt significantly. Over the catalyst 3%Co/1%Pt/γ-Al_2O_3, an almost complete conversion of CO and an O_2 selectivity of over 45% could be obtained at 120 °C.

(2) At temperatures above 90 °C, the existence of H_2O in the feed could increase the conversion and broaden the operating temperature range, whilst the selectivity was not worsened.

(3) There was a strong opposite influence effect of the ratio of O_2 to CO on the conversion of CO and the selectivity of O_2. However, at the O_2/CO ratio of 1.0 and temperatures between 120 and 160 °C, a satisfied balance between conversion and selectivity could be obtained.

(4) A 10 times of change in space velocity (8000–80,000 mL g^{-1} h^{-1}) did not affect the conversion of CO and had insignificant influence on the selectivity at temperatures ranged from 120 to 160 °C.

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