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Preferential oxidation of CO over CuO/CeO_2 and $Pt\text{-}Co/Al_2O_3$ catalysts in micro-channel reactors

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Abstract

Micro-channel plates with dimension of 1 mm × 0.3 mm × 48 mm were prepared by chemical etching of stainless steel plates followed by wash coating of CeO_2 and Al_2O_3 on the channels. After coating the support on the plate, Pt, Co, and Cu were added to the plate by incipient wetness method. Reaction experiments of a single reactor showed that the micro-channel reactor coated with CuO/CeO_2 catalyst was highly selective for CO oxidation while the one coated with $Pt\text{-}Co/Al_2O_3$ catalyst was highly active for CO oxidation. The 7-layered reactors coated with two different catalysts were prepared by laser welding and the performances of each reactor were tested in large scale of PROX conditions. The multi-layered reactor coated with $Pt\text{-}Co/Al_2O_3$ catalyst was highly active for PROX and the outlet concentration of CO gradually increased with the O_2/CO ratio due to the oxidation of H_2 which maintained the reactor temperature. The multi-layered reactor coated with CuO/CeO_2 showed lower catalytic activity than that coated with Pt catalyst, but its selectivity was not changed with the increase of O_2/CO ratios due to the high selectivity. In order to combine advantages (high activity and high selectivity) of the two individual catalysts ($Pt\text{-}Co/Al_2O_3$, CuO/CeO_2), a serial reactor was prepared by connecting the two multi-layered micro-channel reactors with different catalysts. The prepared serial reactor exhibited excellent performance for PROX.

Keywords: Preferential oxidation of CO; CuO/CeO_2; $Pt\text{-}Co/Al_2O_3$; Micro-reactor; Fuel processor

1. Introduction

Hydrogen fueled proton exchange membrane fuel cell (H_2-PEMFC) has received much attention as clean and efficient power for various electrical applications especially for portable devices due to its high power density, low operating temperature and rapid start-up [1,2]. While hydrogen is the ideal fuel for the PEMFC, there are several problems associated with distribution and storage of hydrogen in the use of hydrogen as a fuel for PEMFC. In order to overcome these concerns, it is proposed that the hydrogen required by the fuel cell could be generated from hydrocarbon fuels such as natural gas, gasoline and methanol in an on-board fuel processor [2].

In fuel reforming processor for PEMFC, CO clean-up is an important step to avoid rapid deactivation of the platinum anode catalyst since Pt electro-catalyst is easily poisoned in the presence of only 10 ppm CO [2–4]. Among the various CO clean-up methods, preferential oxidation of CO (PROX) seems to be the most efficient and economical one compared with pressure swing adsorption (PSA) and methanation for removing CO from hydrogen-rich gas in a fuel processor [2,3,5].

Supported precious metal catalysts are well known to be highly effective for PROX [5–10]. Recently, Jung et al. [11] and Avgouropoulos and Ioannides [12] reported that CuO/CeO_2 catalyst had high activity and selectivity for PROX. Other researchers [13–15] also reported that CuO/CeO_2 catalyst showed high activity for CO oxidation. On the basis of the above results of precious metal catalyst and metal oxide catalyst, it seems interesting if these two catalysts are used together in PROX.

However, in the case of large scale PROX system, packed-bed reactors have several concerns such as pressure drop within catalyst layer, temperature gradient, and hot spots due to the high exothermicity of oxidations of CO and H_2 [16]. In

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addition, large scale packed-bed reactors are unsuitable for the use in mobile and portable devices due to their large volume of reactors. These issues are much helpful to handle in micro-reactors due to their principal benefits including fast transfers of heat and mass, high surface to volume ratio, and decrease of volume [16–18]. Micro-reactor might be efficient for selective oxidation of CO in portable fuel processors.

In the present work, the micro-channel reactors were prepared by coating various catalysts (Pt-Co/Al_2O_3, CuO/CeO_2) on micro-channels and their performances of each reactor were tested in PROX reaction conditions. In order to combine of advantages (high activity and high selectivity) of the two catalysts, the two micro-reactors with different catalysts were connected in series (the reactor with Pt-Co/Al_2O_3 catalyst was connected to the outlet of the reactor with CuO/CeO_2 catalyst), and the PROX performance of the prepared serial reactor was examined.

2. Experimental

2.1. Micro-channel reactor fabrication

Micro-channels with dimension of 1 mm × 0.3 mm × 48 mm were prepared by chemical etching of stainless steel plates followed by wash coating of CeO_2 and Al_2O_3 on the channels. Stainless steel samples were patterned with photo-resist mask and then subject to spray etching with ferric chloride ($FeCl_3$) for an optimum time. Alumina slurry was prepared by ball-milling of mixture of commercial gamma alumina (Alfa), alumina bohemite sol and PVA (organic binder) for 22 h. Ceria slurry was also prepared by same method. After coating the plate with supports, the products were dried in an oven at 100 °C for 12 h and subsequently calcined at 500 °C for 4 h. Fig. 1 shows the microscopic image of cross section of the plate with micro-channels using a digital microscope (Xi-CAM, Bestecvision). The alumina layer was uniform with good adhesion and its thickness was 200 μm.

In the case of micro-reactor coated with Pt-Co/Al_2O_3, 5 wt% Pt was added to the alumina coated plate by incipient wetness method with an aqueous solution of $H_2PtCl_6{\cdot}6H_2O$ (Aldrich).

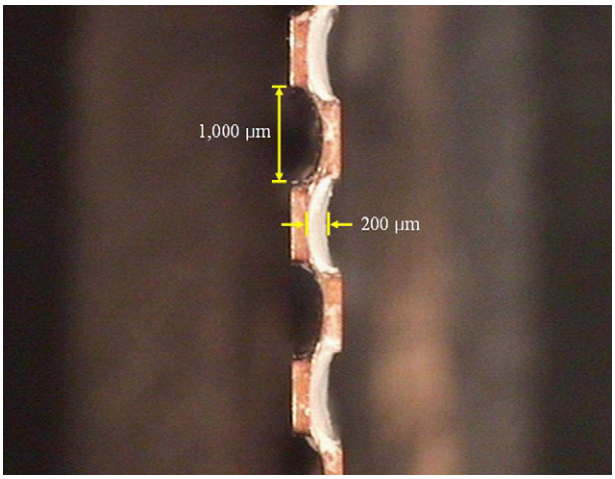

Fig. 1. Microscopic image of the cross section of plate with micro-channels.

After drying (100 °C) and calcinations (500 °C) of the product, promoter (Co) was added to the plate coated with Pt/Al_2O_3 by incipient wetness method. The weight ratio of Co/Pt was controlled to 0.9 and 1.8. The products obtained were dried overnight at 100 °C, calcined at 500 °C for 4 h and subsequently reduced at 400 °C for 2 h. The micro-reactors coated with CuO/CeO_2 were prepared by the identical procedure. 5 wt% Cu was added to the CeO_2 coated plate by incipient wetness method followed by drying (100 °C) and calcination (700 °C). The preparation procedure of micro-channel reactors coated with various catalysts is shown schematically in Fig. 2.

To enhance the efficiency and decrease the volume of reactor, the 7-layered reactor consisted of 2 end plates and 5 middle plates. The middle plates had alternative micro-channels on both sides (Fig. 1), while the end plates had channels on one side only. Single (2-layered) micro-reactor consisted of 2 end plates. The stacks of the plates were prepared by laser welding.

2.2. Activity test for preferential oxidation of CO

The catalytic activities of the 2-layered micro-reactors coated with different catalysts (Pt-Co/Al_2O_3 and CuO/CeO_2)

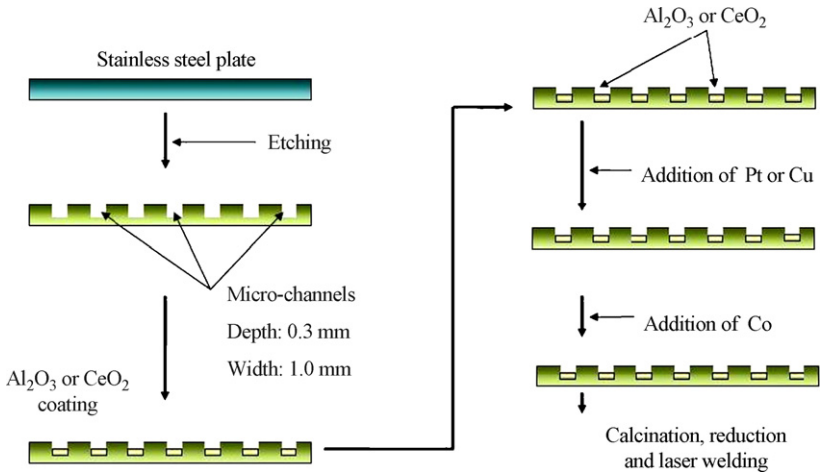

Fig. 2. Schematic preparation procedure of the micro-channel reactor.

were tested for PROX using air as an oxidant. The total flow rate of the reaction mixture was 230 ml/min and the composition of the mixture, using H_2 as balance gas, was 24.6% CO_2, 0.8% CO, and added 10% H_2O by volume (simulating methanol steam reforming gas composition) in the feed. As to addition of H_2O, the activity test started from 100 °C in order to avoid condensation of H_2O within the reactor. An excess of oxygen was used for the selective oxidation experiments ($[O_2]/[CO] = 1.5$). As for CuO/CeO_2 catalyst coated micro-reactor, the activity was tested varying O_2/CO ratio (1.5–2.5). A CO analyzer (SIEMENS) was used for the analysis of CO, and O_2 contents were analyzed by gas chromatography.

The 7-layered reactors coated with two different catalysts were prepared by laser welding and the reaction performances of each reactor were tested in the same above simulated methanol steam reforming conditions. The two reactors with different catalysts were connected in series (the reactor with Pt-Co/Al_2O_3 catalyst was connected to the outlet of the reactor with CuO/CeO_2), and the PROX performance of the prepared serial reactor was also examined. The total flow rate of the mixture gas equal to 2300 ml/min was used for each run. Fig. 3 shows the images of the substrate with micro-channel and the reactor.

The selectivity was calculated from the oxygen mass balance as follows:

$$\text{selectivity} = \frac{0.5([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100(\%)$$

3. Results and discussion

Platinum supported on γ-alumina catalyst is known to be highly active for PROX in proton exchange membrane fuel cell (PEMFC) [1,2]. However, PROX system using Pt/γ-Al_2O_3 catalyst had a problem at cold start-up since the Pt/γ-Al_2O_3 catalyst had high activity at relatively high temperatures (175–200 °C) and low one at low temperatures. Therefore, it would be better for PROX catalyst to have high activity and selectivity at a wide range of temperature. In order to increase the activity of PROX catalyst, many research groups have studied the preparation of platinum based catalysts active over a wide temperature range by addition of promoters [9,10]. For this purpose, Suh et al. reported that modification of Pt/γ-Al_2O_3 catalysts by adding various promoters enhanced their performance for PROX to a great extent. Comparing to Pt/γ-Al_2O_3 catalyst, Pt/γ-Al_2O_3 catalyst promoted with Co reduced the outlet concentration of CO to below 10 ppm in a wide temperature range of 25–175 °C [9].

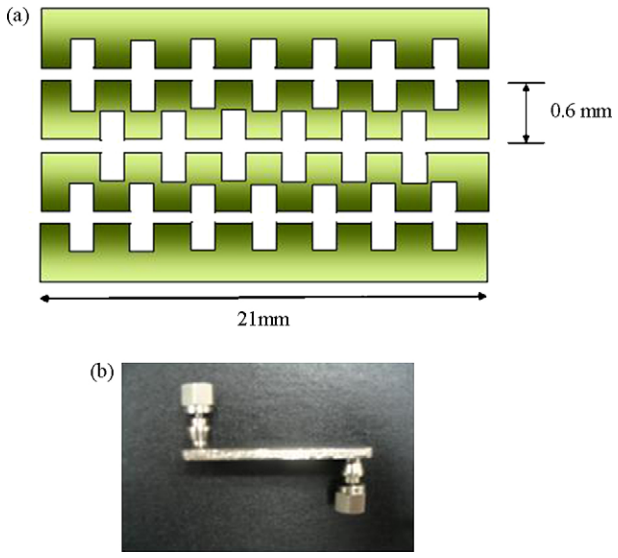

Fig. 3. Photographs of the substrate and reactor with micro-channels: (a) schematic cross section of 4-layered micro-reactor and (b) multi-layered micro-reactor.

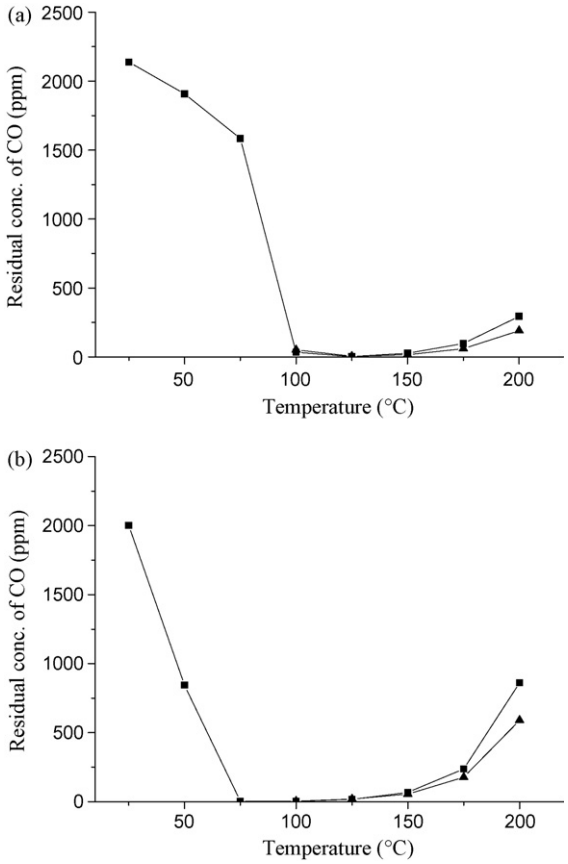

Fig. 4. Activity of Pt-Co/Al_2O_3 prepared by different Co/Pt weight ratio (a) 0.9 and (b) 1.8 as a function of reaction temperature in the absence of H_2O (■) and in the presence of H_2O (▲) for PROX.

Fig. 4 shows the catalytic activities of single (2-layered) micro-reactors coated with Pt-Co/Al_2O_3 which were prepared by different Co/Pt weight ratio (0.9 and 1.8) for PROX as a function of reaction temperature. The loading amounts of the catalysts were 0.11 g for each micro-reactor. All of them exhibited excellent performances for PROX and the activity was increased with temperature and weight ratio of Co/Pt. When the temperature was above 100 °C, all of them showed similar selectivity (~33%) since all O_2 supplied were consumed. In addition, there was little effect of water; the catalytic activities were slightly increased due to water which was also used as an oxidant. Selectivity implies the competition between CO and H_2 oxidations and it is very important in

PROX because H_2 is fuel for the fuel cell. It was very hard to reduce the outlet concentration of CO below 10 ppm because Pt catalyst had a relatively low selectivity under hydrogen-rich atmosphere at practical operating temperatures. Therefore, an excess of oxygen (O_2/CO = 1.5, ideal corresponding stoichiometry: 0.5) was used for the selective oxidation to reduce the residual concentration of CO below 10 ppm in practical conditions, which reduced selectivity. In the case of Co/Pt = 1.8, the residual concentration of CO began to decrease rapidly at 50 °C and remained below 10 ppm in the temperature range of 75–100 °C without water addition. However, the activity was decreased with increasing the weight ratio of Co/Pt at the high reaction temperature (>175 °C). The catalytic performances of coated micro-reactors obtained were influenced by the amount of promoter. Consequently, it was possible to lower the reaction temperature to achieve the same conversion level as the Co/Pt weight ratio increased. However, upon further increasing the amount of Co (Co/Pt > 1.8), the activity decreased because the excessive promoter (Co) covered active sites (Pt).

For the scale-up of micro-reactors, the 7-layered reactors coated with promoted Pt catalysts (different Co/Pt weight ratio) were prepared by laser welding and the reaction performance of each reactor was tested varying O_2/CO ratio (1.5–2.5). Fig. 5 presents catalytic performances of the 7-layered micro-reactors coated with Pt-Co/Al_2O_3 which was prepared by different Co/Pt weight ratio (0.9 and 1.8) for large scale of PROX. In contrast of the results obtained from single (2-layered) micro-reactors, as the increase of total flow rate (2300 ml/min), the temperature of micro-reactors was increased without any external heating due to the high exothermicity of oxidations of CO and H_2. The O_2/CO ratio affected the temperature of reactor, which caused a complete conversion of O_2 supplied, as shown in Fig. 5(b). As a result, the activities of the micro-reactors were decreased with increasing O_2/CO ratio since most of O_2 supplied was reacted with H_2, because H_2 oxidation is more favorable than CO oxidation at high temperature [19]. The micro-reactor coated with low weight ratio of Co/Pt (0.9) catalyst showed superior performance to the one with high weight ratio of Co/Pt (1.8) due to increase of the reactor temperature, and exhibited the minimum outlet concentration of CO (380 ppm) at O_2/CO ratio of 1.5.

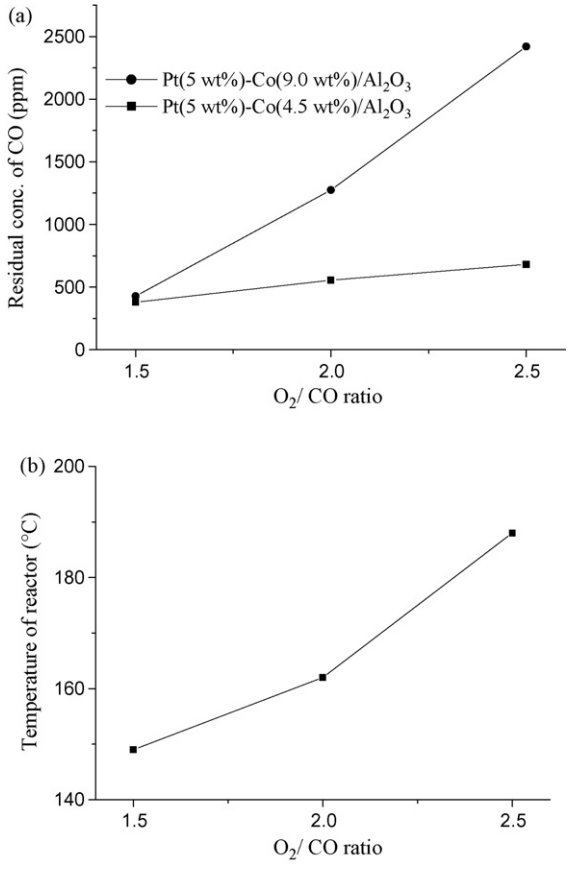

Fig. 5. (a) Activity and (b) reactor temperature of Pt-Co/Al_2O_3 prepared by different Co/Pt weight ratio (0.9 and 1.8) as a function of O_2/CO ratio for large scale of PROX.

Based on the above results, PROX activities of the reactors were greatly influenced by the amount of promoter, reaction temperature which caused feed flow rate, and O_2/CO ratio especially for scale-up. However, although promoted Pt catalyst coated micro-reactor showed excellent performances in the large scale of PROX, they could not reduce the outlet concentration of CO below 10 ppm to avoid deactivation of the platinum anode catalyst in PEMFC. Therefore, if two-stage micro-reactor is used for PROX, the concentration of CO will be easily reduced to a level less than 10 ppm. However, this is not suitable for portable fuel processor because it requires another oxidant supply device.

Recently, for the purpose of lower cost and enhanced selectivity of the catalyst, metal oxide catalysts have been studied for selective oxidation of CO [11–15]. Especially, CuO/CeO_2 catalysts exhibited excellent activity and selectivity for PROX due to a strong interaction of CuO and CeO_2 and high dispersion of CuO on the surface of CeO_2 support. In our previous works [11], we found that the PROX activity of CuO/CeO_2 was highest at CuO loading of 5 wt% and decreased with CuO loading. In addition, the catalyst calcined at 700 °C showed the best activity. Therefore, CuO loading and calcination temperature were maintained at this level.

Fig. 6 shows the activity and selectivity of single (2-layered) micro-reactor coated with CuO/CeO_2 catalyst as a function of reaction temperature and O_2/CO ratio (1.5–2.5). The loading amount of the catalyst was 0.11 g. Comparing with the results of the reactor coated with Pt-Co/Al_2O_3, CuO/CeO_2 coated micro-reactor showed relatively low activity for PROX and the activity was increased with temperature. However, in spite of high temperature, the selectivity was not changed by increasing the amount of O_2 at the same temperature in Fig. 6(b). Generally, in the case of PROX over Pt based catalysts at high temperature, H_2 oxidation is more favorable than CO oxidation. As a result, all of O_2 supplied is consumed. Therefore, if the amount of O_2 increases, the activity and selectivity of Pt based catalysts decrease since most of O_2 supplied are reacted with H_2. On the basis of the above results, CuO/CeO_2 coated micro-reactor showed good selectivity for PROX compared with modified Pt catalyst coated reactor.

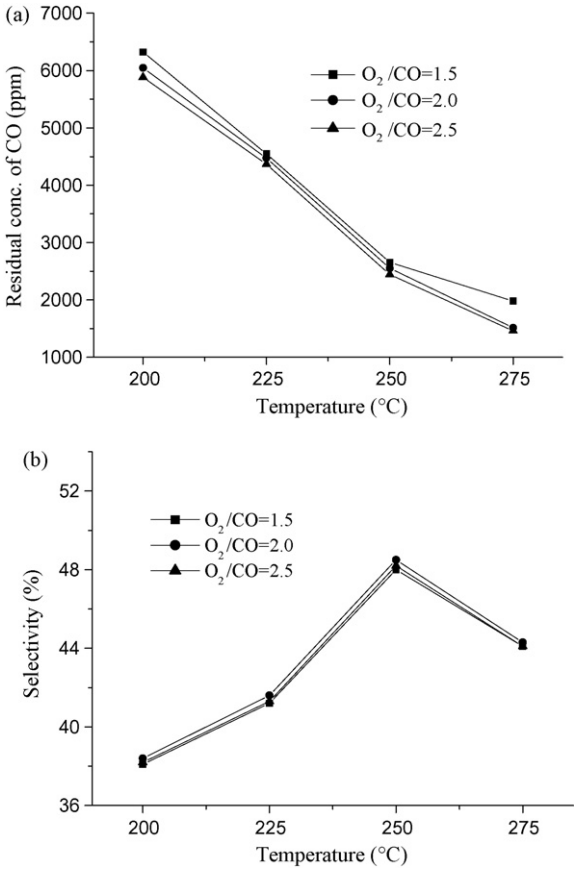

Fig. 6. Activity and selectivity of CuO/CeO_2 as a function of reaction temperature and O_2/CO ratio (1.5–2.5) for PROX: (a) activity of CuO/CeO_2 and (b) selectivity of CuO/CeO_2.

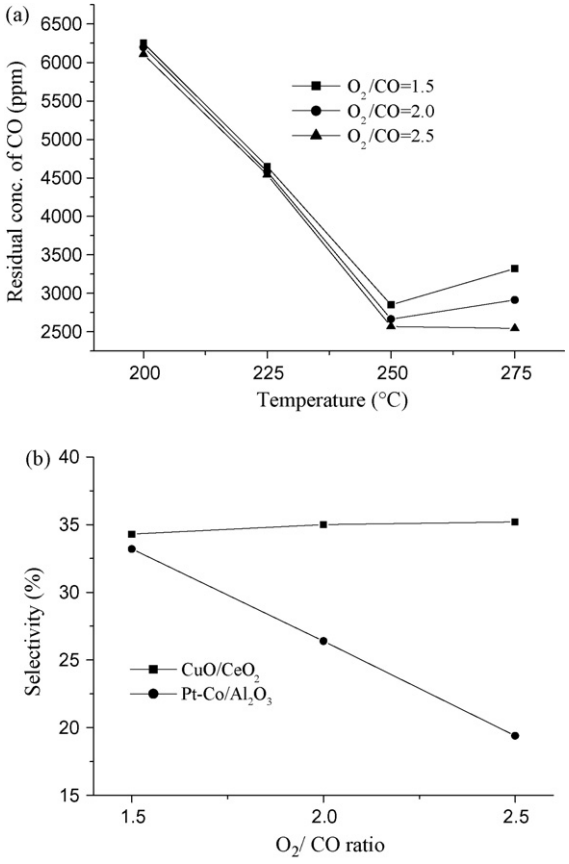

Fig. 7. Activity and selectivity of CuO/CeO_2 as a function of reaction temperature and O_2/CO ratio (1.5–2.5) for large scale of PROX: (a) activity of CuO/CeO_2 and (b) comparison of selectivity between CuO/CeO_2 and $Pt\text{-}Co/Al_2O_3$ (Co/Pt = 0.9) at 250 °C.

Fig. 7 shows the results obtained from 7-layered reactors coated with CuO/CeO_2 catalyst under large scale PROX conditions. As similar results of single micro-reactor (Fig. 5), the activity increases with temperature. Fig 7(b) shows the comparison of selectivity between CuO/CeO_2 and $Pt\text{-}Co/Al_2O_3$ (Co/Pt = 0.9) at 250 °C. The selectivity of CuO/CeO_2 was superior to that of $Pt\text{-}Co/Al_2O_3$ and was not changed with the increase of O_2/CO ratio. On the other hand, as the total flow rate (2300 ml/min) increased, the catalytic activity decreased slightly at 275 °C and the coated reactor had the best activity at 250 °C. In addition, comparing the reactor with Pt catalyst for large scale of PROX, the micro-reactor coated with CuO/CeO_2 needed external heating due to low catalytic activity, high selectivity of CO, and relative high reaction temperature.

In order to combine individual advantages (high activity and high selectivity) of the two catalysts ($Pt\text{-}Co/Al_2O_3$, CuO/CeO_2), the two micro-reactors with different catalysts were connected in series (the reactor with $Pt\text{-}Co/Al_2O_3$ catalyst was connected to the outlet of the reactor with CuO/CeO_2), and the PROX performance of the prepared serial reactor was examined. A schematic of the experimental set-up is shown in Fig. 8.

Fig. 9 shows the performance of the serial reactor prepared by connecting the two multi-layered micro-channel reactors for large scale of PROX as a function of O_2/CO ratio (1.5–2.5). The temperature of the reactor with CuO/CeO_2 was fixed at 250 °C which was the best temperature (Fig. 7) and there was no temperature control of the reactor with Pt catalyst. Without any external heating, the temperature of promoted Pt catalyst coated micro-reactor was increased with O_2/CO ratio since the first-step had a high selectivity. After selective oxidation in the first-step (CuO/CeO_2), the large amount of CO was reduced (over 65% conversion). In addition, the outlet gas involved enough amount of O_2 (over 2 of O_2/CO) due to high selectivity of CO over CuO/CeO_2 in Fig. 7(b). Therefore, the concentration of CO was easily reduced to a level less than 10 ppm in the second-step ($Pt\text{-}Co/Al_2O_3$). As a result, the prepared serial reactor by connecting the two micro-channel reactors exhibited

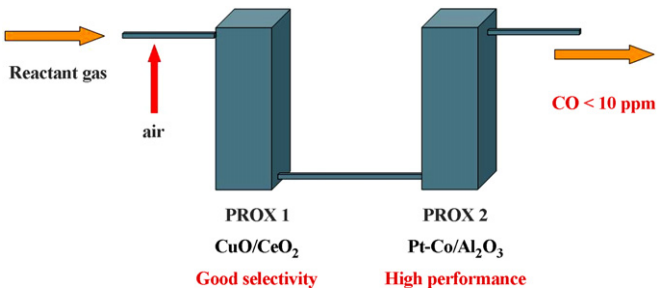

Fig. 8. Schematic of the serial reactor set-up for PROX.

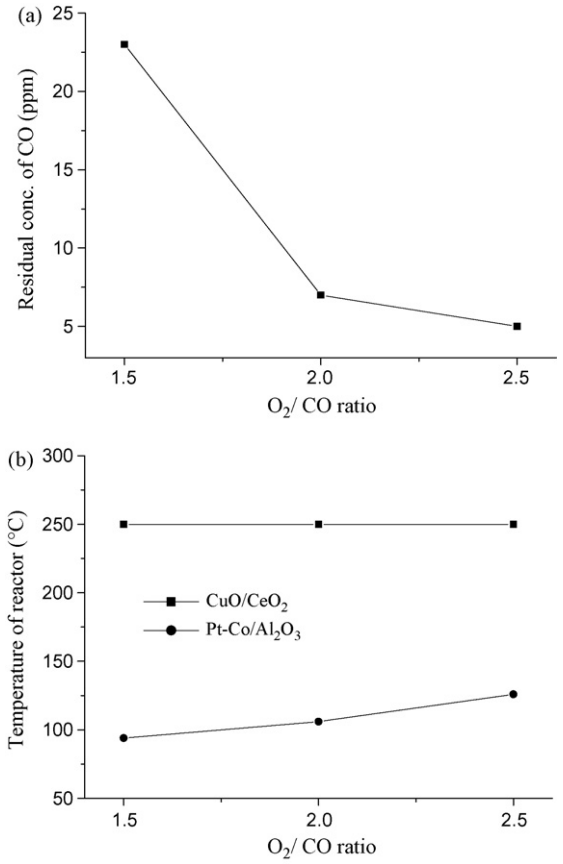

Fig. 9. (a) Activity and (b) reactor temperature of the serial reactor prepared by connecting the two micro-channel reactors as a function of O_2/CO ratio (1.5–2.5) for large scale of PROX.

excellent performance for PROX and the outlet concentration of CO was measured below 10 ppm in the O_2/CO ratio range between 2 and 2.5. The serial micro-reactor demonstrated a potential for selective oxidation of CO, and provided advantages such as low pressure drop, efficient heat and mass transfer and decrease of volume in portable fuel processor.

4. Conclusions

In this study, several different micro-channel reactors were prepared by coating various catalysts (CuO/CeO_2, Pt-Co/Al_2O_3) on micro-channels for preferential oxidation of CO. Reaction experiments of a single reactor showed that the micro-channel reactor coated with CuO/CeO_2 catalyst was highly selective for CO oxidation while the one coated with Pt-Co/Al_2O_3 catalyst was highly active. For a large scale of PROX, two 7-layered reactors coated with Pt-Co/Al_2O_3 and CuO/CeO_2 were prepared. Using the 7-layered reactor, Pt-Co/Al_2O_3 was found to be highly active for PROX and the outlet concentration of CO gradually increased with O_2/CO ratio due to H_2 oxidation which maintained the reactor temperature. CuO/CeO_2 showed similar results when using a 2-layered reactor that the activity increased with temperature and the selectivity did not change as increasing O_2/CO ratio. In order to combine both advantages (high activity and high selectivity) of the two individual catalysts (Pt-Co/Al_2O_3, CuO/CeO_2), a serial reactor was prepared by connecting the two multi-layered micro-channel reactors with different catalysts. The prepared serial reactor exhibited excellent performance for PROX due to the combination of selectivity of CuO/CeO_2 catalyst and activity of Pt catalyst.

Acknowledgements

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