CO selective oxidation in a microchannel reactor for PEM fuel cell

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Abstract

It is indispensable to remove CO at the level of less than 50 ppm in H_2-rich feed gas for the proton exchange membrane (PEM) fuel cells. In this paper, catalyst with high activity and selectivity, and a microchannel reactor for CO preferential oxidation (PROX) have been developed. The results indicated that potassium on supported Rh metal catalysts had a promoting effect in the CO selective catalytic oxidation under H_2-rich stream, and microchannel reactor has an excellent ability to use in on-board hydrogen generation system. CO conversion keeps at high levels even at a very high GHSV as $500\,000\,h^{-1}$, so, miniaturization of hydrogen generation system can be achieved by using the microchannel reactor.
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Keywords: Hydrogen generation; CO preferential oxidation; Microchannel reactor; Autothermal reforming; Washcoating; Carbon monoxide oxidation

1. Introduction

Automotive exhaust is currently one of the major pollution sources. As a pollution-free and energy-saving power supply for electric vehicles, the fuel cell is one of the best candidates because of its high energy conversion efficiency (50–70%) and zero or nearly zero emission. Hydrogen is the fuel for proton exchange membrane fuel cell (PEMFC). The on-board production of hydrogen from liquid alcohols and hydrocarbons, especially methanol, is the most practical way for PEMFC vehicle. Nowadays, PEMFC technology has been well developed, and is gradually in the stage of commercial application, while the hydrogen-generating technology has become the bottle-neck for the practical utilization of fuel cells. The miniaturization of hydrogen source is the prerequisite for its practical application [1,2].

Technology for converting methanol into a hydrogen-rich supply for the fuel cells is mainly based on steam reforming, partial oxidation, or a combination of both (autothermal reforming). However, due to thermodynamic constrains of methanol reforming, significant amount of CO as a poisoning impurity of platinum electro-catalyst is produced. It is necessary to reduce the level of CO in the hydrogen-rich gas to less than 50 ppm, although high CO-resistant electro-catalysts were developed [3–6].

Methods for CO removal include palladium diffusion membranes, methanation and selective catalytic oxidation. Among these methods, CO selective catalytic oxidation is regarded as the most potential and practical method. Catalyst for CO selective catalytic oxidation with high activity and selectivity should be developed to maximize the levels of CO oxidation while minimizing the extent of hydrogen oxidation.

Microchemical technology (MCT) is a new direction of chemical engineering originated in the early 1990s. This technology is focused on the study of the chemical engineering processes and principles of the micro-devices and systems whose characteristic length and time scales are less than hundreds of microns and hundreds of milliseconds, respectively. Owing to the small dimensions, the surface effect is enforced because of the increased specific area, and leads to a remarkable increase in transfer rates of transport (flow, heat transfer and mass transfer), which exceed those of conventional-sized devices by 2–3 orders of magnitude. The application of MCT can greatly improve the efficiency of systems and diminish their volumes and weights. The integration of microchannel reactor system and heat exchanger system is the main technique of the MCT. Further study of it will provide important theoretical directions for the miniaturization of fuel cell hydrogen source and accelerate its commercialization [7–10].

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As on-board fuel processor requires novel catalyst and reactor configuration, the performance of selective oxidation of CO in hydrogen-rich gas with air in microchannel reactors was mainly studied in this paper.

2. Experimental

2.1. Microchannel reactor

The chip of the microchannel reactor made by chemical etching method is shown in Fig. 1. The chip is made of stainless steel. The dimensions of the chip are summarized in Table 1. The microchannel reactor used in this work is shown in Fig. 2.

2.2. Catalyst preparation

Rh-K/Al$_2$O$_3$ catalyst on stainless steel chips was prepared as following procedure. First, stainless steel substrates were cleaned by Na$_2$SiO$_3$ solution in order to remove the oily substance, rinsed out by distilled water, and dried at 383 K for 2 h. Second, wash-coat in stainless steel was made by Al$_2$O$_3$ solution using solution coating method, dried at 393 K for 3 h, and calcined in air at 773 K for 3 h. Third, substrate coated with Al$_2$O$_3$ were dip-coated with an aqueous solution of KNO$_3$ in 5 wt.%, dried at 393 K for 2 h, and calcined in air at 773 K for 3 h. Finally, Rh-K/Al$_2$O$_3$ catalyst was prepared

Table 1
Parameters of the structure of the chip of the microreactor

H (mm)	0.34
h (mm)	0.17
L (mm)	30
w_c (mm)	0.5
w_w (mm)	0.5
W (mm)	45
n_1	48
n_2	4
V (cm^3)	0.88

H: thickness of chip, h: depth of channel, L: length of channel, w_c: width of channel, w_w: wall thickness between channels, W: width of total channels, n_1: number of channel per chip, n_2: number of chip, V: volume of microreactor including microchannels and inlet section for gas distribution.

by the incipient wetness impregnation of an aqueous solution of RhCl$_3$ in 2 wt.%, followed by drying at 383 K for 6 h, and calcined at 773 K for 3 h. The catalyst was reduced at 773 K with 10% H$_2$–N$_2$ mixture gas during 2 h prior to the activity test.

The procedure to prepare monolith catalyst was same as above [11,12].

2.3. Gas analysis

The selective catalytic oxidation of CO in hydrogen-rich gas was carried out both in a microchannel reactor and a fixed-bed flow reaction system with ceramic monolith cat-
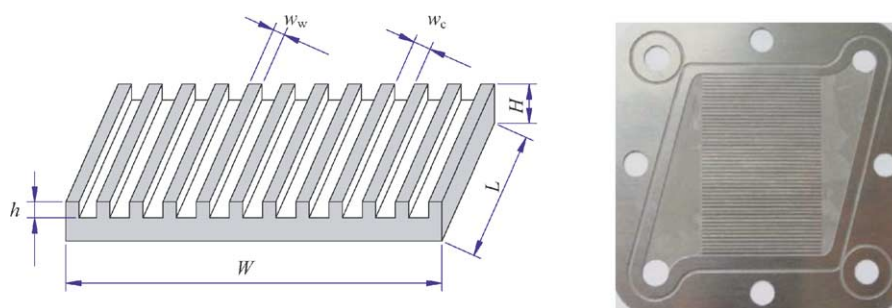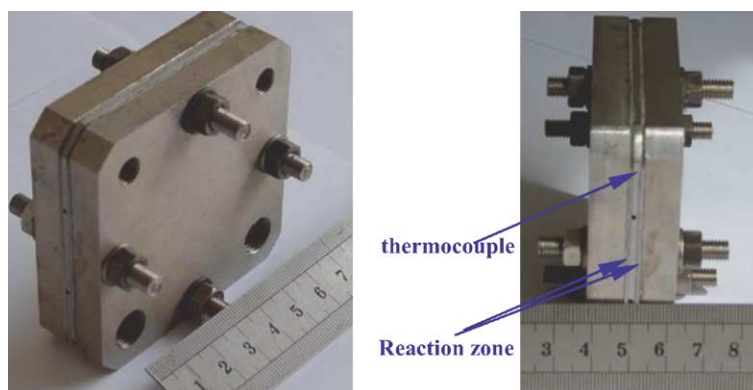

Fig. 1. Chip of microchannel reactor.

Fig. 2. Microchannel reactor.

alyst at atmospheric pressure. The dry feed stream contained 40 vol.% H_2, 20 vol.% CO_2, 0.2–1.0 vol.% CO and 0.2–1.5 vol.% O_2 (N_2 balance). The mole ratio of water to dry gas is 1:10.

The effluent of the reactor was consisted of H_2, CO_2, CO, N_2 and CH_4 as well as H_2O. H_2O was removed from the exit gas by passing the stream through a cold trap and a dryer, while the dry gas entered an on-line gas chromatograph (GC, 4000A) equipped with TCD and FID detectors for analyzing the composition. Detection limit of CO, CO_2 and CH_4 is about 1.0 ppm using a carbon molecular sieve column with carrier gas Ar and FID detector at oven temperature of $100\,^\circ$C, while O_2 and N_2 was separated using 5 Å zeolite with carrier gas H_2 and TCD detector at oven temperature of $70\,^\circ$C.

Space velocity GHSV $= F/V$, F is a volumetric flow rate of dry feed stream under the normal conditions, V is defined as the effective volume ($0.88\,\text{cm}^3$) of microchannel reactor including microchannel and triangular inlet and outlet zone as well, or catalyst volume ($4.5\,\text{cm}^3$) for ceramic monolith reactor. The load of Rh on Rh/Al_2O_3 and $Rh\text{-}K/Al_2O_3$ catalyst is based on the ratio of weight of Rh metal to volume of catalyst or reactor. The catalyst activity is defined as the ratio of the reactant CO or O_2 reacted divided by its input:

$$X_{CO} = \frac{\text{moles of CO reacted}}{\text{moles of CO in feed}},$$

$$X_{O_2} = \frac{\text{moles of } O_2 \text{ reacted}}{\text{moles of } O_2 \text{ in feed}}$$

In order to enhance system efficiency, hydrogen oxidation should be minimized. The catalyst selectivity towards CO in the H_2-rich stream is defined as the ratio of the O_2 consumed for CO oxidation over total O_2 consumed for both H_2 and CO oxidation

$$S_{CO} = 0.5 \times \frac{\text{moles of CO converted to } CO_2}{\text{total } O_2 \text{ consumed}}$$

3. Results and discussion

3.1. Monolith reactor

The activity of CO oxidation in H_2-rich gas on the K-promoted and unpromoted Rh catalysts ($\sim$4.5 g/l Rh) versus reaction temperature was shown in Fig. 3. It is obvious that addition of potassium promotes activity of catalyst remarkably comparing with that of Rh/Al_2O_3 catalyst (see Fig. 3(a) and (b)). On Rh/Al_2O_3 catalyst, the CO conversion increased from 77 to 93.6% at reaction temperature from
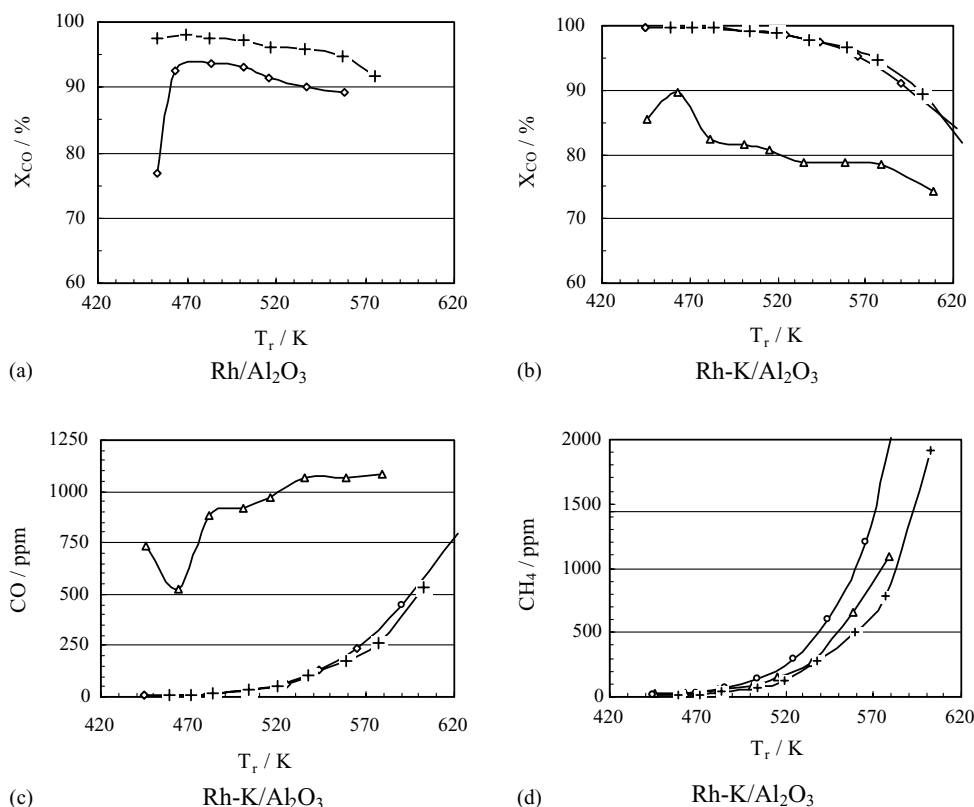

Fig. 3. CO conversion in CO selective oxidation in H_2-rich stream vs. reaction temperature over Rh/Al_2O_3 and $Rh\text{-}K/Al_2O_3$ ($\sim$4.5 g/l Rh) catalysts in ceramic monolith reactor. CO = 5000 ppm, GHSV = 20 000 h^{-1}. O_2/CO: ($\triangle$) 0.5, ($\bigcirc$) 1.0, (+) 1.5.

Table 2
Effect of O_2/CO on performance of catalyst ($Rh-K/Al_2O_3$, 2.25 g/l Rh, CO = 1%)

O_2/CO	CO (ppm)	O_2 (ppm)	X_{CO} (%)	S_{CO} (%)	X_{O_2} (%)	T_c (°C)	T_r (°C)
0.2	7200	129	28.00	74.83	93.55	190.2	206.8
0.3	5700	180	43.00	76.24	94.00	187.3	218.8
0.4	4300	74	57.00	72.59	98.15	165.7	210.7
0.5	3000	87	70.00	71.23	98.26	150.6	205.3
0.6	1500	96	85.00	71.97	98.40	142.5	213.6
0.7	600	93	94.00	68.02	98.67	131.5	219.4
0.8	219	95	97.81	61.83	98.81	119.8	218.5
0.9	76	134	99.24	55.93	98.51	105.2	212.2
1.0	52	74	99.48	50.08	99.26	100.0	222.5

Note: T_c is the control temperature of reactor, T_r is the reaction temperature.

453 to 473 K, then decreased slowly from 473 to 563 K at CO = 5000 ppm, GHSV = 20 000 h^{-1} and O_2/CO = 1.0; while on the $Rh-K/Al_2O_3$, the CO conversion was higher than 99% from 443 to 523 K, the highest conversion was 99.82% and CO concentration outlet was below 10 ppm. When O_2/CO = 0.5, the selectivity of CO oxidation was higher than 80% from 443 to 513 K, the highest selectivity is 89.5% at 463 K, which showed that $Rh-K/Al_2O_3$ possesses excellent activity and selectivity to remove CO in H_2-rich reforming gas for PEMFC.

But from Fig. 3(c) and (d), the result indicated that CH_4 in product increased remarkably with increasing reaction temperature, especially when reaction temperature was higher than 523 K. CH_4 was about 300 and 1200 ppm at 523 and 573 K, respectively. The reactions of CO and H_2 oxidation were highly exothermic reactions. From Table 2, it is clear that O_2 was nearly completely consumed, therefore, difference between control temperature T_c and reaction temperature T_r was more notable when O_2 concentration was higher than 1%. Therefore, how to control reaction temperature is an important issue to enhance the activity and selectivity of the catalyst for CO PROX. In the practical use of this process, several series of reactors must be adopted to control reaction temperature to enhance the activity and selectivity of CO oxidation and to inhibit the methanation. The microchannel reactor with uniform temperature distribution along the reaction bed is suitable to be used in this process.

3.2. Microreactor

3.2.1. Effect of CO concentration

The effect of CO concentration was shown in Fig. 4. At 500 K, O_2/CO = 1.0 and GHSV = 500 000 h^{-1}, the conversion of CO was virtually independent of the concentration at 2000 ppm (94.5%), 5000 ppm (96.9%) and 10 000 ppm (96.8%). Similarly, the selectivity showed very little sensitive for CO concentration varying from 2000 to 10 000 ppm.

3.2.2. Effect of reaction temperature

The activity and selectivity under temperature from 423 to 523 K were shown in Fig. 5 with the simulating gas composition. The microchannel reactor space velocity (GHSV)
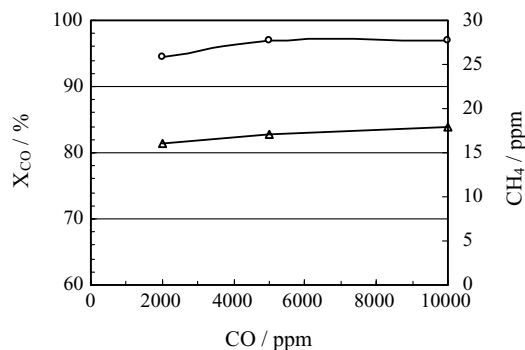

Fig. 4. CO conversion vs. inlet CO concentration in microchannel reactor. T = 500 K, O_2/CO = 1.0, CO = 5000 ppm, GHSV = 500 000 h^{-1}. (○) CO conversion, (△) outlet CH_4 concentration.

is 500 000 h^{-1}, O_2/CO = 1.0 and 1.25. Increasing the temperature from 430 to 523 K showed a large increase in CO conversion (27–93.8% for O_2/CO = 1.0, 34.7–98.1% for O_2/CO = 1.25). The CH_4 concentration in the effluent gas was less than 30 ppm when temperature was lower than 523 K. From Fig. 5, it was obvious that the suitable reaction temperature was between 463 and 523 K.

3.2.3. Effect of space velocity

The CO conversions were plotted in Fig. 6 as a function of space velocity both in microchannel reactor and ceramic
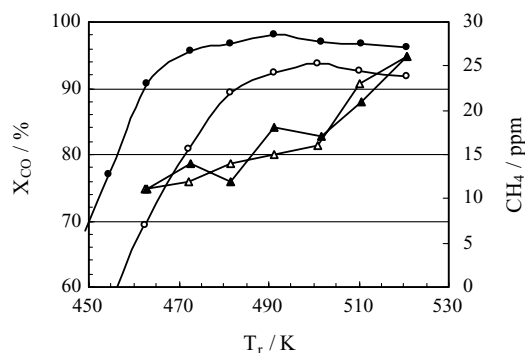

Fig. 5. CO Conversion vs. reaction temperature in microchannel reactor. CO = 5000 ppm, GHSV = 500 000 h^{-1}. O_2/CO: (○, △) 1.0; (●, ▲) 1.25. (○, ●) CO conversion; (△, ▲) outlet CH_4 concentration.
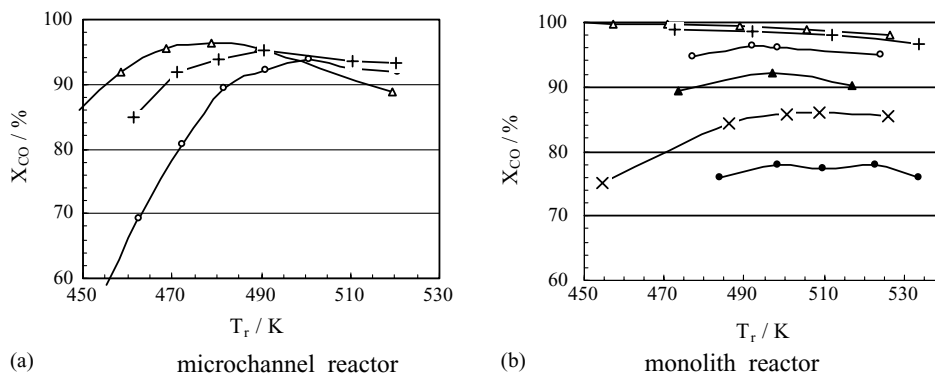
Fig. 6. CO conversion vs. reaction temperature in microchannel and monolith reactor. CO = 5000 ppm, O_2/CO = 1.0. GHSV: (a) microchannel ($\triangle$) 100 000 h^{-1}, (+) 300 000 h^{-1}, ($\bigcirc$) 500 000 h^{-1}; (b) monolith ($\triangle$) 20 000 h^{-1}, (+) 50 000 h^{-1}, ($\bigcirc$) 100 000 h^{-1}, ($\blacktriangle$) 200 000 h^{-1}, ($\times$) 300 000 h^{-1}, ($\bullet$) 400 000 h^{-1}.

monolith reactor. The GHSVs in microreactor Fig. 6(a)) were kept at 100 000, 300 000 and 500 000 h^{-1}, respectively. The CO inlet concentration was 5000 ppm and O_2/CO mole ratio was 1.0. The CO conversion was decreased as GHSV increasing from 100 000 to 500 000 h^{-1} when reaction temperature below 490 K, while catalyst activity kept nearly constant at the temperature from 490 to 523 K. From Fig. 6(b), CO conversion in monolith reactor decreased rapidly when GHSV was greater than 100 000 h^{-1} during the reaction temperature from 453 to 533 K.

Comparing with ceramic monolith reactor, it was clear that the CO conversion was as high as 93.8% in microchannel reactor even at GHSV of 500 000 h^{-1}, which was about five times higher than that in the monolith reactor. The reason lies in that the intrinsic rate of CO oxidation was very high, so the apparent reaction rate was heavily limited by mass and heat transport rate in monolith reactor. Due to its rapid heat and mass transfer effects with its inherent small dimensions, the reaction rate was increased remarkably and conversion was still high even at high GHSV in microchannel reactor. At GHSV of 500 000 h^{-1}, the flow rate of product in dry gas was about 440 l/h, hydrogen was about 176 l/h
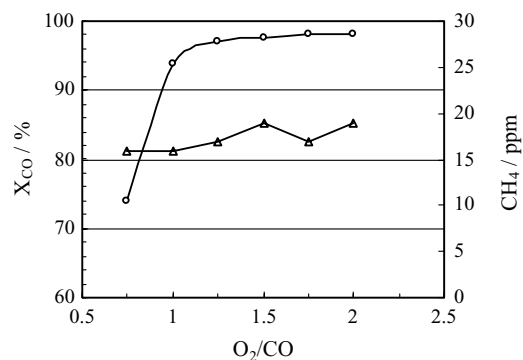

Fig. 7. CO conversion vs. ratio of O_2 to CO in microchannel reactor. CO = 5000 ppm, GHSV = 500 000 h^{-1}, T = 500 K. ($\bigcirc$) CO conversion, ($\triangle$) outlet CH_4 concentration.

at the concentration of 40%, which means that this stainless steel microchannel reactor with four chips has the potential ability to remove the CO to the low level concentration in H_2-rich gas of hydrogen generation system for the need of PEMFC in the level of 0.25 kW.
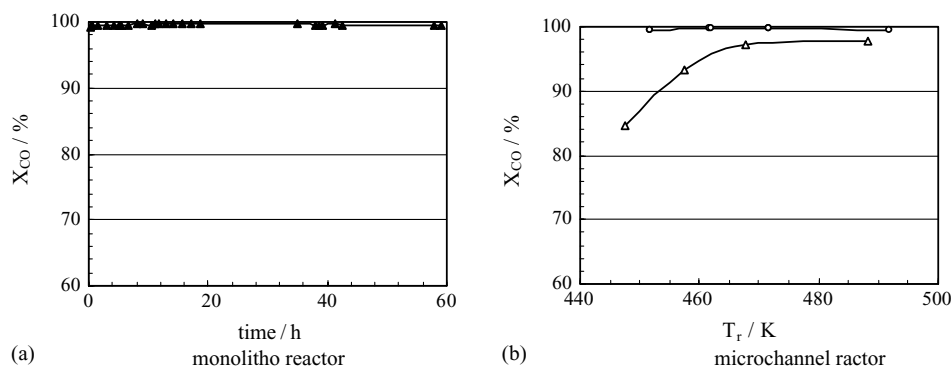

Fig. 8. Catalyst stability test in ceramic monolith and microchannel reactors. (a) monolith reactor: GHSV = 20 000 h^{-1}, CO = 5000 ppm, O_2/CO = 1.5, T = 460 K; (b) microchannel reactor: GHSV = 100 000 h^{-1}, CO = 10 000 ppm, O_2/CO = 1.0, in (b) ($\bigcirc$) fresh catalyst, ($\triangle$) catalyst used for 100 h.

3.2.4. Effect of mole ratio of O_2 to CO

The effect of mole ratio of O_2 to CO was shown in Fig. 7. The CO conversion increased from 74 to 98.3% when increasing the O_2/CO ratio from 0.75 to 2.0 at CO concentration of 5000 ppm and reaction temperature of 500 K. The CO conversion kept nearly constant as O_2/CO ratio was higher than 1.0. So in order to enhance the reaction system efficiency, low O_2/CO ratio should be adopted as possible.

3.2.5. Stability of catalyst

Stability of catalysts was investigated both in ceramic monolith reactor and microchannel reactor. It is clear in Fig. 8(a) that CO conversion over monolith catalyst (Rh-K/Al$_2$O$_3$, 2.25 g/l Rh) was as high as 99.6% and CO concentration in the effluent gas was as low as 20 ppm during the 60 h at GHSV $= 20\,000\,h^{-1}$, $CO = 5000$ ppm, O_2/CO $= 1.5$ and reaction temperature of 460 K, showing both good activity and stability of monolith catalyst used to the removal of CO in H$_2$-rich gas. The catalyst coated in microchannel reactor also showed high activity as 99.5% during its fresh phase at the condition of GHSV $= 100\,000\,h^{-1}$, CO $= 10\,000$ ppm, O_2/CO $= 1.0$ and reaction temperature from 450 to 493 K, while the activity of catalyst decreased to 85% at 448 K and 97.8% at temperature from 470 to 483 K after 100 h experiment (see Fig. 8(b)). Therefore, catalyst coated in microchannel reactor with high activity and stability should be further improved.

4. Conclusion

In conclusion, it is obvious that addition of potassium promoted catalyst Rh-K/Al$_2$O$_3$ had higher activity (99.82%) and selectivity and stability comparing with that of unpromoted catalyst. The activity of fresh catalyst coated in microchannel reactor was higher than 99.5% at the conditions of CO $= 10\,000$ ppm, GHSV $= 100\,000\,h^{-1}$, O_2/CO $= 1.0$ and temperature from 450 to 493 K.

Due to the small characteristics dimension of the microchannel reactor, the effect of heat and mass transport is increased remarkably, so that the reaction rate increases and the reaction conversion keeps in high level as well at very high GHSV of $500\,000\,h^{-1}$ and short contact time in the order of 4–6 ms. The miniaturization of CO selective catalytic oxidation in H$_2$-rich gas of hydrogen generation system can be achieved with microchannel reactor.

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