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Microfibrous entrapment of small catalyst or sorbent particulates for high contacting-efficiency removal of trace contaminants including CO and H_2S from practical reformates for PEM H_2–O_2 fuel cells

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Abstract

The four catalyst systems, Pt-Co/Al_2O_3, Pt/Al_2O_3, Au/α-Fe_2O_3, and CuO-CeO_2, which demonstrated promising catalytic activity among more than 150 catalysts investigated for the preferential oxidation (PROX) of CO from practical reformate in our previous studies [B. Chang, L. Chen, B.J. Tatarchuk, unpublished work], were further examined in differential reactor in the absence of heat and mass transfer limitations in order to compare their specific activities. Differential reactor studies reveal that the cobalt promoted Pt/Al_2O_3 (Pt-Co/Al_2O_3) is the best candidate among those four catalyst systems for the preferential oxidation (PROX) of CO from practical reformate for PEM fuel cells.

A high void and tailorable sintered microfibrous carrier consisting of 5 vol% 4 and 8 μm diameter Ni fibers was used to entrap 15 vol% 150–250 μm Al_2O_3 particulates. SEM images showed the microstructures of the thin microfibrous entrapped alumina support particles. The alumina support particulates were uniformly entrapped into a well sinter-locked three-dimensional network of 4 and 8 μm Ni fibers. Cobalt and platinum were then dispersed onto the microfibrous entrapped alumina support particles by impregnation method so as to prepare microfibrous entrapped Pt-Co/Al_2O_3 catalysts. The composite catalysts possessed 80 vol% voidage. The microfibrous entrapped Pt-Co/Al_2O_3 catalysts showed stable long-term activity for the preferential CO oxidation in wide temperature range. A microfibrous entrapped H_2S sorbent layer was then placed upstream of a microfibrous entrapped PROX catalyst layer to remove both H_2S and CO from a sulfur-contaminated practical reformate stream. Operating in this fashion, an outermost H_2S sorbent layer promotes the activity maintenance of a secondary non-poison tolerant PROX CO catalyst, which ultimately serves to provide activity maintenance to CO-intolerant precious metal-based MEA assemblies in PEM fuel cells.

Keywords: Microfibrous materials; Ni fibers; Pt-Co/Al_2O_3; Preferential oxidation (PROX) of CO; H_2S removal; Fuel processing; PEM fuel cells

1. Introduction

1.1. Preferential oxidation (PROX) of CO from practical reformate for PEM fuel cells

Recently, fuel cells have received a great deal of attention since they offer a clean and efficient alternative for conventional automotive combustion engines [2]. A polymer electrolyte membrane fuel cell (PEMFC) is believed to be the most suitable one for mobile application.

Due to both kinetic and thermodynamic constrains of hydrocarbons reforming, however, significant concentration of CO is produced from catalytic reformers producing hydrogen. And there is a limit, unfortunately, regarding the thermodynamic conversion of the water-gas shift reaction (WGSR), so that a CO concentration which is sufficiently low to be acceptable by the PEMFC system cannot be achieved using WGSR only. The reformate coming from the fuel processing section contains 50–65 vol% H_2, 25–40 vol% CO_2, 2–5 vol% H_2O, and 1 vol% CO. The PEM fuel cell performance significantly deteriorates if the feed stream contains even trace amount of CO (more than 10 ppm) since the Pt or Pt-Ru anodes are poisoned by CO, which strongly chemisorbs on the active sites thus blocking the sites where the dissociation/oxidation of H_2 takes place.

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There are several approaches to remove CO in the H_2-rich gas feed to a few ppm levels that are required for PEM fuel cell applications. Recent significant attention has been paid to preferential oxidation (PROX) of CO using catalyst and air. This seems to be the most promising and lowest cost approach:

$$\text{Desired oxidation reaction}: CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad (1)$$

$$\text{Undesired oxidation reaction}: H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad (2)$$

Since the preferential oxidation (PROX) unit is placed between the low-temperature water-gas shift reactor (200 °C) and the PEMFC (80–100 °C), it should operate between these temperatures [3]. PROX system operating at low temperature (room temperature) is also very important for start-up of fuel cells used in transportation applications. Therefore, the PROX system must operate over a wide temperature range to be practical.

Our previous study showed that Pt-Co/Al_2O_3, Pt/Al_2O_3, Au/α-Fe_2O_3, and CuO-CeO_2 demonstrated promising catalytic activity and selectivity among more than 150 catalysts prepared and investigated for the preferential CO oxidation (PROX) from practical reformate for PEM fuel cells [1]. In this preliminary screening study, conventional Pt/Al_2O_3 was promoted by cobalt (Pt-Co/Al_2O_3) and the promoted catalysts demonstrated enhanced activity and selectivity compared to the unpromoted catalysts. In particular, CO conversion takes place at significantly lower temperature over Pt-Co/Al_2O_3 catalysts and the active reaction temperature window is enlarged to 25–200 °C compared with a narrow window around 200 °C over conventional Pt/Al_2O_3. Comparing overall catalytic performance of Au/α-Fe_2O_3, CuO-CeO_2, Pt/γ-Al_2O_3, and Pt-Co/Al_2O_3 catalyst in integral reactor systems, Pt-Co/Al_2O_3 was found to be a superior candidate for preferential CO oxidation considering its widely applicable temperature range (25–200 °C) and high CO conversion activity (90–100%) while keeping relatively moderate O_2 selectivity (50–60%).

In the present study, these four catalyst systems were further investigated and compared in differential reactor conditions in the absence of heat and mass transfer limitations.

1.2. Wet lay paper-making/sintering process

Microstructured materials have potential for enhanced mass and heat transfer compared to typical catalyst particulates used in industrial processes. A new-patented class of composite materials made by a wet lay paper-making/sintering process can incorporate particles as small as 10 μm into a micrometal fiber matrix [4]. Sintered microfibrous composites using a 16% Ni/alumina catalyst for toluene hydrogenation in a trickle bed reactor have demonstrated two to six times higher specific activities than conventional packed bed catalysts on a gravimetric basis, while volumetric activities of 40 vol% composite catalysts were 80% higher than conventional extrudates [5].

The high thermal conductivity of the micrometal fiber matrix produces radial heat transfer coefficients that are about twice those in packed beds. Enhanced heat transfer due to the larger surface to volume ratio of small particles and the micrometal matrix results in more nearly isothermal conditions in fixed bed reactors minimizing hot spots, resulting in higher selectivity, and allowing processing to be done with smaller safety factors [4].

The wet lay paper-making/sintering process also allows continuous adjustment of void volume from upwards of 98% down to values similar to packed beds of particles [6]. This allows the composite catalyst/adsorbent material to be optimized to the appropriate void volume for different types of applications.

1.3. Microfibrous entrapment of small particles of catalysts

In this study, a generic approach that utilizes a high void volume and tailorable microfibrous carrier was used to entrap, with high contacting-efficiency, a catalyst or supported catalyst material. The microfibrous material can be made into thin sheets of large area and/or pleated to control pressure drop and contacting-efficiency in a beneficial manner different than other traditionally employed contacting schemes including packed beds, fluidized beds, trickle beds, monoliths, gauzes, or wovens. These materials provide advantages over conventional large particulate systems typically used in industrial processes. These advantages include enhanced heat and mass transfer, significantly reduced pressure-drop, ultra-high contacting-efficiency, etc.

The Pt-Co/Al_2O_3 catalyst has shown extremely superior catalytic activity for the preferential oxidation of CO from practical reformats at low temperature compared to the unpromoted conventional Pt/Al_2O_3 catalyst [1]. In the present study, the cobalt promoted Pt/Al_2O_3 (Pt-Co/Al_2O_3) was prepared by incipient wetness impregnation of the appropriate metal salts into a 150–250 μm diameter gamma alumina support entrapped within a sintered matrix of 4 and 8 μm diameter Ni fibers. The high activity of this catalyst, combined with a favorable selectivity and high contacting-efficiency provided superior catalytic performance in practical reformate streams at 25–200 °C. Microfibrous entrapped catalysts are well suited for applications to PROX at the PEM fuel cell stack temperature in the absence of complicated process controls. The structure and physical attributes of microfibrous media are amenable to facile packaging, manufacture, and system miniaturization for chemical processing needs.

High contacting-efficiency microfibrous media can also be used to entrap various reactive materials including: heterogeneous catalysts, electrocatalysts, sorbents, and various solid reactants. These media are then layered so as to permit multiple staged chemical reactions to be achieved within the space of a few millimeters of thickness. Layered media may be used alone or in combination with more traditional contacting schemes (i.e., packed beds, monoliths, etc.) so as to be employed as polishing sorbents, polishing catalysts, or both. As a demonstrated example of this generic approach, a microfibrous entrapped polishing H_2S sorbent was placed upstream of a microfibrous entrapped polishing PROX catalyst to remove both H_2S and CO from a sulfur-contaminated model reformate stream. It is required to ensure downstream stability of a membrane electrode assembly for the anode compartment of a PEM H_2-air fuel cell stack. Operating in this fashion, an outermost H_2S sorbent layer promotes activity maintenance of a secondary non-poison tolerant PROX CO catalyst which ultimately serves to provide activity maintenance to CO-intolerant precious metal-based MEA assemblies in PEM fuel cells.

2. Experimental

2.1. Differential reactor studies: comparison of specific activity of catalysts

For the differential reactor studies, 0.01 g of catalysts were diluted with 0.1 g of inert support material (α-Al_2O_3) to make the reactor isothermal. The particle size was 150–250 μm (60–100 mesh). Practical reformate consisted of 1% CO, 1% O_2, 20% CO_2, 40% H_2, and balance N_2. The total feed flow rate was changed from 50 to 250 ml/min. The temperature range investigated was from 25 to 150 °C.

2.2. Preparation of microfibrous entrapped catalysts

Traditional high speed and low cost paper-making equipment and technique were used in this study to prepare microfibrous composite materials. In this process, 4 and 8 μm diameter metal (Ni) fibers in a variety of compositions and alloys were slurried in an aqueous suspension with cellulose fibers and other selected particulates, such as alumina support particles. The particle size of alumina support was 150–250 μm (60–100 mesh). The resulting mixture was then cast into a preform sheet using a wetlay process and dried to create a sheet of preform material. Subsequent pre-oxidation in O_2 flow at 500 °C for 1 h and sintering of the preform in H_2 flow at elevated temperature (900 °C) for 30 min removed the cellulosic binder/pore former and entrapped the selected support particulates within a sinter-locked network of conductive metal fibers. The resulting preform generally consisted of 10–15 vol% support particles, 5 vol% metal (Ni) fibers, and 80–85 vol% voidage. Finally, the microfibrous entrapped support particles, such as alumina were impregnated with the metal salt precursor solutions as in the preparation of powder catalysts. Then, microfibrous entrapped catalysts were dried and calcined at desired temperatures.

2.3. Activity and selectivity measurements of the microfibrous entrapped catalysts

The reaction conditions used in the investigation of the microfibrous entrapped catalysts are as follows:

(a) Practical reformate consisted of 1% CO, 20% CO_2, 40% H_2, and balance N_2.
(b) Gas flow rates were controlled by gas mass flow controllers.
(c) Face velocity was approximately 2.12 cm/s.
(d) Bed depth of the microfibrous entrapped catalyst was approximately 2–6 mm.
(e) Particle sizes of the catalysts entrapped into the microfibrous materials were 60–100 mesh (150–250 μm).
(f) CO:O_2 ratio in the feed stream was 1:1 for all tests.
(g) Temperature range investigated was 25–150 °C.
(h) Pressure of the system was 1 atm.
(i) Microfibrous entrapped catalysts were reduced in H_2 flow at 250 °C for 2 h before the reaction gas mixture was passed over.

2.4. Scanning electron microscopy (SEM)

The samples were coated with carbon using SPI module carbon coater to avoid charge building inside the sample while performing SEM. The SEM images of microfibrous materials were obtained using a JEOL JSM 840 (20 kV) SEM. The SEM images were recorded at magnification levels of 37 and 200 using an in-built digital camera.

2.5. Pressure drop measurement across the microfiborus entrapped catalyst bed

Pressure drop through the microfibrous material was measured using a sample cell consisting of 0.75 in. Swagelock® Ultratorr fitting with 0.75 in. SS tubing inserted into the ends of the fitting. The cell was equipped fitted with spacers inside the fitting to hold the sample of microfibrous material properly. The cell was connected to the outlet of a mass flow controller (Cole-Parmer, 0–1000 cm^3/min). Pressure drop was measured by a DP cell (Omega, PX 154-010DI) and the readings were indicated by a four-digit process meter (Omega DP24E). The pressure drop was measured at various values of the inlet flow rate.

2.6. Combined H_2S and PROX CO removal by layering microfibrous entrapped sorbent and catalyst layers

A microfibrous entrapped proprietary ZnO/SiO_2 sorbent layer for H_2S removal was placed upstream of a microfibrous entrapped proprietary Pt-Co/Al_2O_3 catalyst for PROX CO removal. To prepare a microfibrous entrapped ZnO/SiO_2 sorbent layer, a sintered microfibrous carrier consisting of 5 vol% 4 and 8 μm diameter Ni fibers was used to entrap 25 vol% 150–250 μm diameter SiO_2 support particulates. ZnO was impregnated into the support by incipient wetness so as to produce 18 wt% loading. Approximately, 50 ppmv H_2S was added in the feed stream. Total flow rate of the feed stream was 100 ml/min and cross-sectional area of the microfibrous bed was 0.7854 cm^2 making the face velocity 2.12 cm/s.

3. Results and discussion

3.1. Differential reactor studies

Figs. 1 and 2 show the comparisons of Pt-Co/Al_2O_3, Pt/Al_2O_3, Au/α-Fe_2O_3, and CuO-CeO_2 catalysts in differential reactor conditions at 100 and 150 °C, respectively. As it can be clearly seen in those figures, the reaction rate (slope) increases as reaction temperature increases in differential reactor for all four-catalyst systems. In integral reactor studies, on the other hand, Au/α-Fe_2O_3 shows its highest CO conversion

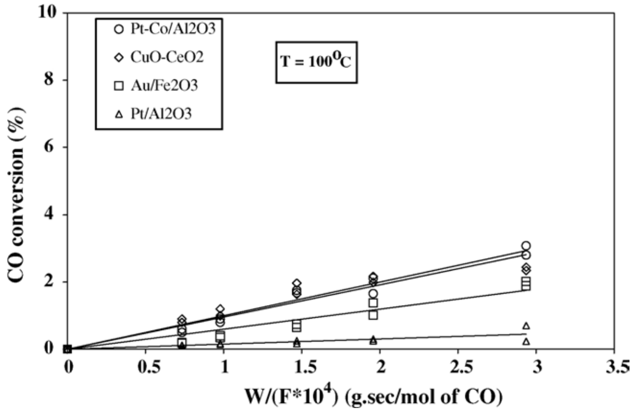

Fig. 1. Comparison of the four catalyst systems in differential reactor at 100 °C.

activity at relatively low temperature below 100 °C and CO conversion decreases as temperature further increases above 100 °C. These different behaviors of CO conversion activities in terms of reaction temperature in integral and differential reactor studies can be explained by the competitive H_2 oxidation, taking place with the desired CO oxidation reaction and also by the competitive CO/H_2 adsorption mechanism. It has been known that the reactants, CO and H_2, compete for the same active sites when they are adsorbed for the reaction. That is, in integral reactor in which the catalyst systems demonstrate complete CO conversion activities (100% CO conversion) at its active temperature, as temperature further increases competitive H_2 oxidation reaction begins taking place, and therefore CO conversion may drop at temperatures above the catalyst's active temperature. On the other hand, in differential reactor in which the CO conversion usually does not exceed 15%, there is always CO remaining in the system to be adsorbed on the active site, which therefore keeps the other reactant, H_2, from being adsorbed and it causes the CO conversion to increase further as reaction temperature increases.

Specific activities occur in the absence of H_2O in the following order:

$$\mathrm{Pt\text{-}Co/Al_2O_3} \approx \mathrm{CuO\text{-}CeO_2} > \mathrm{Au/Fe_2O_3} > \mathrm{Pt/Al_2O_3}\,(T = 100\,^{\circ}\mathrm{C})$$

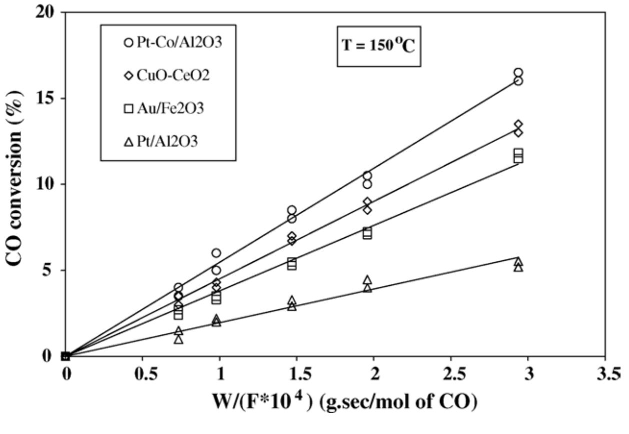

Fig. 2. Comparison of the four catalyst systems in differential reactor at 150 °C.

$$\mathrm{Pt\text{-}Co/Al_2O_3} > \mathrm{CuO\text{-}CeO_2} > \mathrm{Au/Fe_2O_3} > \mathrm{Pt/Al_2O_3}\,(T = 150\,^{\circ}\mathrm{C})$$

Comparison of the specific activities in differential reactor over the temperature range from 100 to 150 °C reveals that promoted Pt-Co/Al_2O_3 is the best candidate for operation in the absence of H_2O for preferential CO oxidation for PEM H_2–O_2 fuel cells.

Transport processes, i.e., heat and mass transfer between the fluid and the solid or inside the porous solid, may influence the overall rate so that the conditions over the local reaction site do not correspond to those in the bulk fluid around the catalyst particle. Therefore, in order to measure intrinsic reaction rates, heat and mass transfer limitations have to be eliminated.

The most conventional way to verify that there are no heat transfer resistances during the differential reactor studies is by Mears' criterion [7]. Mears' criterion says that interparticle heat transfer resistance is negligible if the following criterion is met;

$$\frac{|\Delta H| \cdot R_{\mathrm{b}} \cdot R_{\mathrm{o}}^2}{K_{\mathrm{e}} \cdot T_{\mathrm{w}}} < \frac{0.4R \cdot T_{\mathrm{w}}}{2E} \tag{3}$$

where ΔH is the heat of reaction; R_{b} the average reaction rate per unit bed volume; R_{o} the radius of reactor; R the gas constant; T_{w} the reactor wall temperature; K_{e} the effective thermal conductivity; and E is the reaction activation energy.

Mears' criterion was tested using the differential reactor data obtained over the four catalyst systems, Pt-Co/Al_2O_3, Pt/Al_2O_3, Au/α-Fe_2O_3, and CuO-CeO_2 catalysts, and it was satisfied, indicating that there was no heat transfer limitation across the reactor bed of Pt-Co/Al_2O_3, Pt/Al_2O_3, Au/α-Fe_2O_3, and CuO-CeO_2 in the differential reactor studies.

Thiele moduli (ϕ_{S}) were also calculated [8–10] using the differential reactor data and the calculated Thiele moduli yielded effectiveness factors (η) close to 1 for all four catalyst systems, indicating the absence of intraparticle mass transfer limitations in the differential reactor studies.

Turnover Frequency (TOF) values determined in the present study shows 0.005–0.01 (mol CO/s mol Pt) at 100 °C and 0.02–0.05 (mol CO/s mol Pt) at 150 °C for the unpromoted Pt/Al_2O_3 and 0.03–0.04 (mol CO/s mol Pt) at 100 °C and 0.2–0.3 (mol CO/s mol Pt) at 150 °C for the promoted Pt-Co/Al_2O_3. It was found that the turnover frequencies were greatly increased at both temperatures when the conventional Pt/Al_2O_3 catalysts were modified by Co.

Table 1 shows the activation energies over the four catalyst systems calculated using the differential reactor data. Table 1 also compares the activation energy values calculated in this study with those found in the literature. The activation energies for Pt-Co/Al_2O_3 and CuO-CeO_2 are not available in the literature. The activation energies over Pt/Al_2O_3 and Au/Fe_2O_3 calculated in this study show excellent agreement with the values found in the literature for the two-catalyst systems indicating that the differential reactor system designed in this study produced reliable data. It is important to note that the activation energy over Pt/Al_2O_3 dramatically decreases in the presence of Co-promoter implying that the

Table 1
Comparison of activation energies obtained in the differential reactor studies with the values found in the literature

Catalyst	Activation energy (kJ/mol)		
	This work	Literature	Note
Pt-Co/Al_2O_3	54	N/A	
Pt/Al_2O_3	80	78	[11]
		72–76	[12]
Au/Fe_2O_3	30	31	[13]
CuO-CeO_2	56	N/A	

activity of Pt/Al_2O_3 is greatly enhanced when it is promoted by Co-promoter.

3.2. Microfibrous entrapped Pt-Co/Al_2O_3

Fig. 3 shows a SEM image of the microstructures of the thin microfibrous entrapped Al_2O_3 support particulates, i.e., alumina support particles entrapped in the microfibrous metal (Ni) mesh after sintering at magnification level of 200. As shown in figure, the alumina support particles were uniformly entrapped into a well sinter-locked three-dimensional network of 4 and 8 μm diameter Ni fibers. Approximately, 80–85, 5, and 10–15 vol% of the microfibrous materials were voidage, nickel fibers, and alumina support particles entrapped, respectively.

In the preparation of microfibrous entrapped catalysts, it is very important to verify that there are no negative effects of sintering of microfibrous materials at high temperature (900–950 °C) on the alumina support particles entrapped in them and that the properties of the fresh gamma-phase alumina support particles entrapped during the preparation of microfibrous preform do not change in the process of sintering at 900–950 °C. XRD patterns were collected (not shown) from both fresh alumina support particles and alumina particles that went through heat treatment at 900 °C to observe the effect of sintering process during the preparation of microfibrous entrapped catalysts on the phase of alumina support particles. The peak positions from those two XRD patterns were exactly matched with each other indicating that the phase change of the alumina particles does not occur during the sintering process at 900 °C since the peak positions of alumina particles of different phases should be different from each other. BET study also revealed that the total surface area of alumina support particles did not change significantly before (220 m^2/g) and after the sintering process (208 m^2/g).

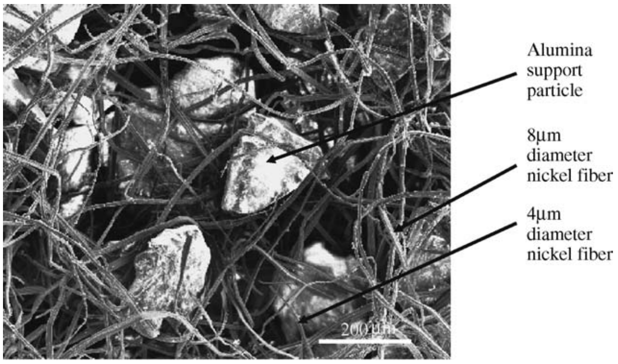

Fig. 3. SEM image of 150–250 μm γ-Al_2O_3 support particles entrapped in a mirometal fiber matrix of 4 and 8 μm nickel fibers at magnification level of 200.

The cobalt-promoted Pt/Al_2O_3 catalyst (Pt-Co/Al_2O_3) which was identified in our previous study [1] as a superior candidate for PROX reaction from practical reformate stream was entrapped into the 4 and 8 μm Ni fibers and the stability of the microfibrous entrapped Pt-Co/Al_2O_3 catalysts and effect of H_2O on the microfibrous entrapped catalysts were investigated. As a basis of comparison, microfibrous entrapped alumina support particles before metal components impregnation were tested for the PROX reaction to check the reactivity of Ni fibers and blank alumina support particles entrapped in the microfibrous materials. The microfibrous entrapped blank alumina support particles showed no reactivity for the PROX. Pt content in the microfibrous entrapped Pt-Co/Al_2O_3 catalyst was 4.7 wt% and Co:Al ratio was 0.04:1. Total feed flow rate was 100 ml/min and face velocity was 2.12 cm/s.

Stability at room temperature is very important for effective start-up in transportation application fuel cells. Three percent of H_2O in the feed stream is the maximum amount of water which can be maintained in the vapor phase at room temperature, 25 °C. Above this amount, water will condense in the reactor causing negative water flooding effect. The lines were covered with heat-tape in order to prevent water added in the feed stream from being condensed in the lines. As a basis of comparison, complete CO conversion activity is maintained for approximately a week in the absence of H_2O in the feed stream at 25 °C. Complete CO conversion means that no CO is detected from the outlet stream by the TCD used in this study and it indicates that CO conversion is 99.5–100% since CO sensitivity of the TCD used in this study is 50 ppm. At 25 °C, 3 and 10% H_2O which are added in dry practical reformates – which also correspond to 100 and 333% of the saturated amount at 25 °C, respectively – do not cause any negative effects on the stability of the microfibrous entrapped Pt-Co/Al_2O_3 catalysts. In other words, complete CO conversion activity over the microfibrous entrapped Pt-Co/Al_2O_3 catalysts is maintained for approximately a week in the presence of 3 and 10% H_2O added in the dry feed stream at 25 °C even if 10% H_2O added in the dry feed stream is much higher than the amount of H_2O which the dry feed stream can hold in the vapor phase at 25 °C. The stability of the microfibrous entrapped Pt-Co/Al_2O_3 catalysts at 25 °C, however, is dramatically reduced in the presence of 20 and 30% H_2O mainly due to the water flooding effect which is a negative effect on catalysis since the condensed water fills pores of the catalysts and blocks active sites present on the surface of the catalysts. Complete CO conversion activity is maintained for about 150 and 40 min in the presence of 20 and 30% H_2O, respectively, and dramatically decreased. Therefore, considering the stability of the microfibrous entrapped Pt-Co/Al_2O_3 catalysts at 25 °C, 10% H_2O is the maximum amount of H_2O found in this study which can be added in dry practical reformate stream without any negative effects on the catalysts.

Stability of PROX unit at PEM fuel cell stack temperature (70 °C) is important considering that PROX unit would be integrated into PEMFC stack if it is stable at stack temperature. Thirty percent of H_2O in the feed stream is the maximum amount of water which can be maintained in the vapor phase at 70 °C which is the PEMFC stack temperature. At 70 °C, 0 (no H_2O added), 10, 20, and 30% H_2O which are added in the dry practical reformates – which also correspond to 0, 33, 67, and 100% of the saturation amount at 70 °C, respectively – do not cause any negative effects on the stability of the microfibrous entrapped Pt-Co/Al_2O_3 catalysts mainly since none of the water vapor added in the feed stream does condense at 70 °C. In other words, complete CO conversion activity over the microfibrous entrapped Pt-Co/Al_2O_3 catalysts is maintained for approximately a week in the presence of 0, 10, 20, and 30% H_2O added in the dry feed stream at 70 °C.

At 150 °C, complete CO conversion activity over the microfibrous entrapped Pt-Co/Al_2O_3 catalyst is maintained for about 30 h even in the presence of 30% excess H_2O. The high catalytic activity and long-term stability of the microfibrous entrapped Pt-Co/Al_2O_3 catalyst at 150 °C even in the presence of 30% excess H_2O make it superior candidate for PROX CO reaction in steady state operating conditions.

3.3. Layering of microfibrous entrapped reactive media to achieve multiple staged chemical reactions/processes in flow through geometries of millimeter thickness

As mentioned earlier, high contacting-efficiency microfibrous media can be used to entrap various reactive materials including heterogeneous catalysts, electrocatalysts, sorbents, and various solid reactants. These media are then layered so as to permit multiple staged chemical reactions to be achieved within the space of a few millimeters of thickness. Layered media may be used alone or in combination with more traditional contacting schemes (i.e., packed beds, monoliths, etc.) so as to be employed as polishing sorbents, polishing catalysts, or both. As a demonstrated example of this generic approach, a microfibrous entrapped polishing H_2S sorbent was placed upstream of a microfibrous entrapped polishing PROX CO catalyst to remove both H_2S and CO from a sulfur-contaminated practical reformate stream. Operating in this fashion, an outermost H_2S sorbent layer promotes the activity maintenance of a secondary non-poison tolerant PROX CO catalyst, which ultimately serves to provide activity maintenance to CO-intolerant precious metal-based MEA assemblies.

The benefits and attributes of the above approach may be extended to a variety of entrapped materials and chemical processes. The enabling attribute is the high contacting-efficiency afforded by microfibrous entrapment, and the thin layer design of these materials that permit facile and effective layering, packaging, and sealing.

Fig. 4 shows performance of the integrated bed of microfibrous entrapped ZnO/SiO_2 H_2S sorbent layer and Pt-Co/Al_2O_3 PROX CO catalyst layer at 25 °C in the presence of 50 ppmv H_2S in the feed. Total flow rate of the feed stream was 100 ml/min and cross-sectional area of the microfibrous bed was 0.7854 cm^2 making the face velocity 2.12 cm/s. Complete CO conversion activity is maintained at least 35 h without any catalytic deactivation over the microfibrous entrapped Pt-Co/Al_2O_3 PROX CO catalyst when H_2S does not present in the feed stream. CO conversion activity, however, starts dropping dramatically around

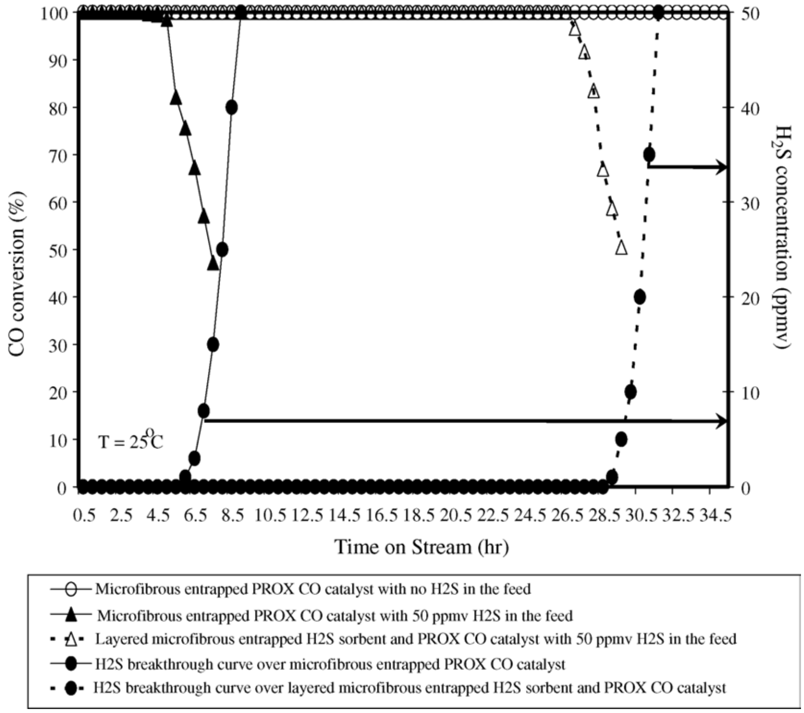

Fig. 4. Performance of integrated bed of microfibrous entrapped ZnO/SiO_2 H_2S sorbent and Pt-Co/Al_2O_3 PROX CO catalyst at 25 °C in the presence of 50 ppmv H_2S in the feed stream.

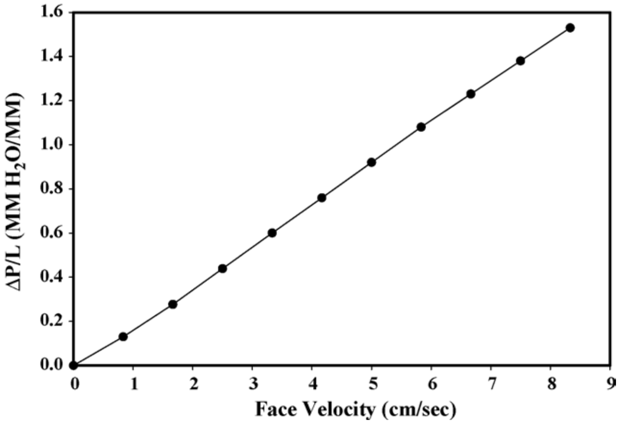

Fig. 5. Pressure drop per unit length of microfibrous bed ($\Delta P/L$) measured as a function of face velocity (cm/s).

4 h after 50 ppmv H_2S is introduced in the feed stream together with CO mainly due to irreversible and permanent H_2S poisoning on the entrapped PROX catalysts. Finally, a microfibrous entrapped H_2S sorbent layer was placed upstream of a microfibrous entrapped PROX CO catalyst layer and the integrated H_2S and PROX CO removal units was investigated at 25 °C in the presence of both 1% CO and 50 ppmv H_2S in the feed stream. Thickness of the microfibrous entrapped H_2S sorbent layer and the microfibrous entrapped PROX catalyst layer was approximately 2 mm each making the total bed thickness 4 mm. As it can be seen clearly in Fig. 4, complete CO conversion activity is recovered for approximately 27 h before CO is detected in the outlet. H_2S is detected approximately 29 h after introduction of 50 ppmv H_2S in the feed stream, and it is the breakthrough time for the H_2S over the integrated system.

3.4. Pressure drop measurements

Sintered microfibrous materials with alumina support particles entrapped were used to measure pressure drop across the microfibrous bed. The thickness of the microfibrous bed was 1.1 mm and the cross-sectional area of the microfibrous bed was 2 cm^2. Flow rate (ml/min) was increased from 50 to 1000, and then decreased from 1000 to 50 in order to verify that the pressure drop measurements in both cases were identical. Flow rates then were converted to face velocity (cm/s) using the cross-sectional area of the microfibrous bed, which is 2 cm^2. Fig. 5 shows the pressure drop measured using O_2 across the microfibrous bed at face velocities from 0.42 to 8.33 cm/s. These pressure drops across the microfibrous bed are significantly less than those observed across a conventional packed bed of particles of the same size (not shown) as those entrapped in the microfibrous mesh demonstrating an additional advantage of the microfibrous entrapped small particles over conventionally used large particulates in packed bed.

4. Conclusions

The four catalyst systems, Au/α-Fe_2O_3, CuO-CeO_2, Pt/γ-Al_2O_3, and Pt-Co/Al_2O_3, which showed promising catalytic activity for the preferential CO oxidation in our previous study [1] were further investigated in differential reactor. By plotting inverse space velocity versus CO conversion the actual rankings of catalytic activity for the four catalyst systems could be observed. It was found that the newly developed Pt-Co/Al_2O_3 catalyst was a superior catalyst for the preferential CO oxidation in the differential reactor conditions in which the reaction conversions are below 10–15%. Additionally turnover frequencies were calculated by incorporating the dispersions obtained by hydrogen and oxygen chemisorption/titration technique in order to compare specific activity of the promoted Pt-Co/Al_2O_3 with the unpromoted conventional Pt/Al_2O_3. It was found that turnover frequencies were significantly increased when the conventional catalyst was modified by the promoter cobalt.

High contacting-efficiency microfibrous media can be used to entrap various reactive materials including heterogeneous catalysts, sorbents, and various solid reactants. Small particles of Pt-Co/Al_2O_3 catalysts (150–250 μm) were entrapped into the microfiber composite materials and investigated for preferential CO oxidation (PROX) reaction for PEM fuel cells. The microfibrous entrapped PROX catalysts demonstrated a long-term stability and high activity in temperature range of 25 (room temperature) to 150 °C (PROX unit operating temperature). These microfibrous media then could be layered so as to permit multiple staged chemical reactions to be achieved within the space of a few millimeters of thickness. As a demonstrated example of this generic approach, a microfibrous entrapped polishing ZnO/SiO_2 H_2S sorbent was placed upstream of a microfibrous entrapped polishing Pt-Co/Al_2O_3 PROX catalyst to remove both H_2S and CO from a sulfur-contaminated practical reformate stream. Operating in this fashion, an outermost H_2S sorbent layer promoted the activity maintenance of a secondary non-poison tolerant PROX catalyst, which ultimately served to provide activity maintenance to CO-intolerant precious metal-based MEA assemblies.

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