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Microfibrous Entrapment of Small Catalyst Particulates for High Contacting Efficiency Removal of Trace CO From Practical Reformates for PEM H_2-O_2 Fuel Cells

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Preferential oxidation (PROX) of CO in H_2 is the most efficient way to remove CO from a practical reformate stream for PEM H_2-O_2 fuel cells. Pt/Al_2O_3 has long been known as a suitable catalyst for this purpose. Over the conventional Pt/Al_2O_3 catalyst, however, PROX of CO in H_2 has been known to occur at temperatures above 150 °C, and the maximum CO conversion usually takes place at about 200 °C. In this study, the promotion of Pt/Al_2O_3 with a transition metal results in significantly enhanced catalytic performance in the temperature range of 25 to 150 °C. The active reaction temperature window is enlarged to 25 to 200 °C compared with a narrow window at about 200 °C over the conventional Pt/Al_2O_3. A high void and a tailorable sintered microfibrous carrier consisting of 5 vol.% of 4 and 8 μm diameter Ni fibers is used to entrap 15 vol.% 150 to 250 μm diameter Al_2O_3 particulates. The alumina support particulates are uniformly entrapped into a sinter-locked, three-dimensional network of 4 and 8 μm Ni fibers. Promoter and Pt are then dispersed onto the microfibrous entrapped alumina support particles by the incipient-wetness impregnation method. The composite catalysts possess 80 vol.% voidage. At equivalent bed volumes, microfibrous entrapped catalysts achieve complete CO reduction (GC detection limit ~40 ppm CO) at five times the higher gas hourly space velocity value compared with packed beds of 1 to 2 mm catalyst particles demonstrating ultrahigh contacting efficiency provided by the microfibrous entrapped catalysts.

Keywords fuel processing, microfibrous materials, preferential oxidation of CO, PEM fuel cells

1. Introduction

Preferential oxidation (PROX) of CO in H_2 is believed to be the most efficient way to remove CO from practical reformate for polymer electrolyte membrane (PEM) fuel cells (PEMFCs) (Ref 1). Pt/Al_2O_3 has long been known as a suitable catalyst for this purpose. However, preferential oxidation of CO in H_2 over Pt/Al_2O_3 occurs at temperatures above 150 °C, and the maximum CO conversion takes place at ~200 °C. The overall objective of this study was to develop a novel catalyst material for effective removal, particularly at low temperatures, of small amounts (1-2%) of CO present in H_2-rich gases, such as practical reformate produced by partial oxidation or steam reforming of hydrocarbons for PEMFCs.

Conventional Pt/Al_2O_3 was promoted by transition metal (Pt-M/Al_2O_3) in this study, and the promoted catalysts demonstrated enhanced activity and selectivity compared with the unpromoted catalysts. In particular, CO conversion takes place at significantly lower temperatures than Pt-M/Al_2O_3 catalysts, and the active reaction temperature window is enlarged to 25 to 200 °C compared with the narrow window, about 200 °C over conventional Pt/Al_2O_3.

A high void and tailorable sintered microfibrous carrier consisting of 5 vol.% of 4 and 8 μm diameter Ni fibers is used to entrap 15 vol.% of 150 to 250 μm Al_2O_3 particulates. The scanning electron microscopy (SEM) images show the microstructures of the thin microfibrous entrapped alumina support particles. The alumina support particulates are uniformly entrapped into a sinter-locked, three-dimensional network of 4 and 8 μm Ni fibers. Promoter and Pt are then dispersed onto the microfibrous entrapped alumina support particles by an impregnation method so as to prepare microfibrous entrapped Pt-M/Al_2O_3 catalysts. The composite catalysts possess 80 vol.% of voidage. A thin bed of microfibrous entrapped small catalyst (150-250 μm) was investigated for PROX of CO from practical reformate for PEMFCs. At equivalent bed volumes, microfibrous entrapped catalysts demonstrate superior catalytic activity compared with conventional packed beds of same and larger particles demonstrating ultrahigh contacting efficiency provided by the microfibrous entrapped catalysts. 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 S-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 PEMFCs.

2. Experimental

2.1 Preparation of Microfibrous Entrapped Catalyst

Traditional high-speed and low-cost papermaking equipment was used in this study to prepare microfibrous composite

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materials. In this process, 4 and 8 μm diameter metal (Ni) fibers in a variety of compositions and alloys are slurried in an aqueous suspension with cellulose fibers and other selected particulates such as alumina support particles. The particle size of the alumina support was 150 to 250 μm (60-100-mesh). The resulting mixture is then cast into a preformed sheet using a wet-lay process and dried to create a sheet of preformed material. Subsequent preoxidation in O_2 flow at 500 °C for 1 h and preform sintering in flowing H_2 900 °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 consists of 10 to 15 vol.% support particles, 5 vol.% of metal (Ni) fibers, and 80 to 85 vol.% voidage. Finally, the microfibrous entrapped support particles such as alumina are impregnated with the metal salt precursor solutions as in the preparation of powder catalysts. The microfibrous entrapped catalysts are then dried and calcined at the desired temperatures.

2.2 Catalytic Activity and Selectivity Investigation

A practical reformate consists of 1% CO, 20% CO_2, 40% H_2, and balance N_2. Reaction products were analyzed using an HP6890 gas chromatograph equipped with a thermal conductivity detector (TCD) detector. Water condenser was used to prevent water vapor from entering the gas chromatograph. An empty reactor without catalyst showed no CO conversion.

2.3 Catalyst Characterization Methods

For SEM, the samples were coated with carbon using an 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) scanning electron microscope. The SEM images were recorded at magnification levels of 37 and 200 using a built-in digital camera. For x-ray diffraction (XRD) analysis, structural phases were determined for catalysts in an x-ray diffractometer using Cu-Kα radiation. A continuous scan mode was used to collect 2θ data from 10 to 80° with a 0.02 sampling pitch and a 4°/min scan speed. The x-ray tube voltage and current were set at 40 kV and 40 mA, respectively. For energy-dispersive x-ray (EDX) spectroscopy analysis, the catalyst sample was coated with carbon using an SPI module carbon coater to avoid the charge building inside the sample while doing EDX. The EDX data for the catalyst was obtained using a JEOL JSM 840 (20 kV) scanning electron microscope/EDX spectrometer.

3. Results and Discussion

3.1 Microfibrous Entrapped Preferential Oxidation Catalyst

Figure 1 shows an SEM image of the microstructures of the thin microfibrous entrapped Al_2O_3 support particulates, that is, alumina support particles entrapped in the microfibrous metal (Ni) mesh after sintering (magnification level 200). As shown in Fig. 1, the alumina support particles are uniformly entrapped into the sinter-locked three-dimensional network of 4 and 8 μm diameter Ni fibers. Approximately 80 to 85, 5, and 10 to 15 vol.%, respectively, of the microfibrous materials are voidage, nickel fibers, and alumina support particles are entrapped.

Figure 2 shows the stability of microfibrous entrapped Pt-M/Al_2O_3 catalysts at 70 °C (the PEMFC stack temperature) with the effect of H_2O on the stability. The stability of the PROX unit at the PEMFC stack temperature is important considering that PROX unit would be integrated into the PEMFC stack if it is stable at the stack temperature. The 30% H_2O in the feed stream is the maximum amount of water that can be maintained in the vapor phase at 70 °C, which is the PEMFC stack temperature. As shown in Fig. 2, at 70 °C, 0% (no H_2O added), 10, 20, and 30% H_2O, which are added in the dry practical reformates and 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-M/Al_2O_3 catalysts, mainly because none of the water vapor added in the feed stream condenses at 70 °C. In other words, complete CO conversion activity over the microfibrous entrapped Pt-M/Al_2O_3 catalysts is maintained for approximately a week without any catalytic deactivation in the presence of 0, 10, 20, and 30% H_2O added in the dry feed stream at 70 °C.

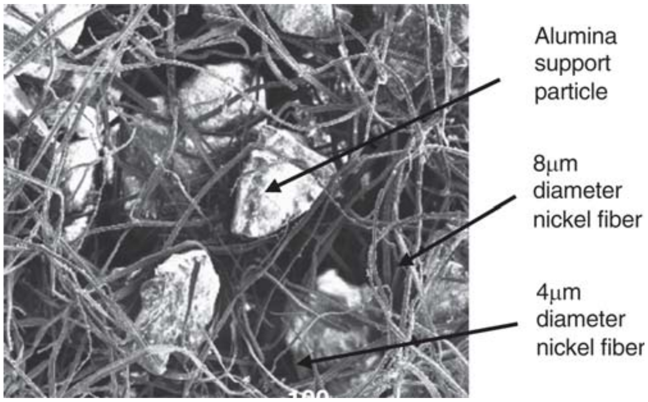

Fig. 1 An SEM image of 150 to 250 μm γ-Al_2O_3 support particles entrapped in a micrometal fiber matrix of 4 and 8 μm nickel fibers at a magnification level of 200

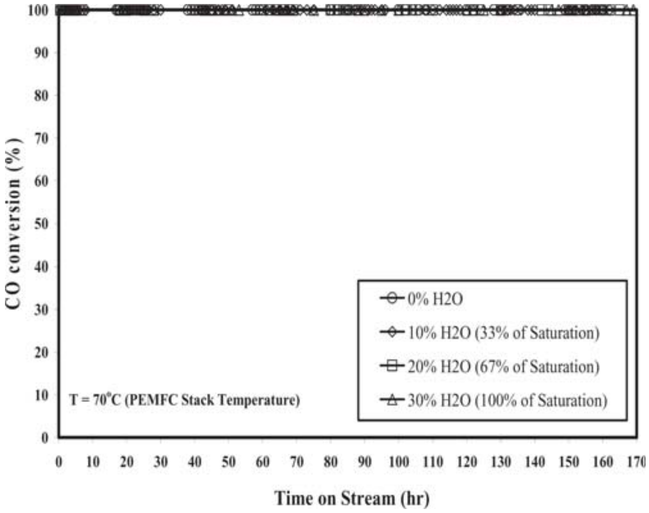

Fig. 2 Stability of microfibrous entrapped Pt-M/Al_2O_3 catalysts at 70 °C (PEMFC stack temperature): effect of H_2O

3.2 Layering of Microfibrous Entrapped Reactive Media to Achieve Multiple Staged Chemical Reactions/Processes in Flow-Through Geometries of Millimeter Thickness

High-contacting-efficiency microfibrous media are used to entrap various reactive materials, including heterogeneous

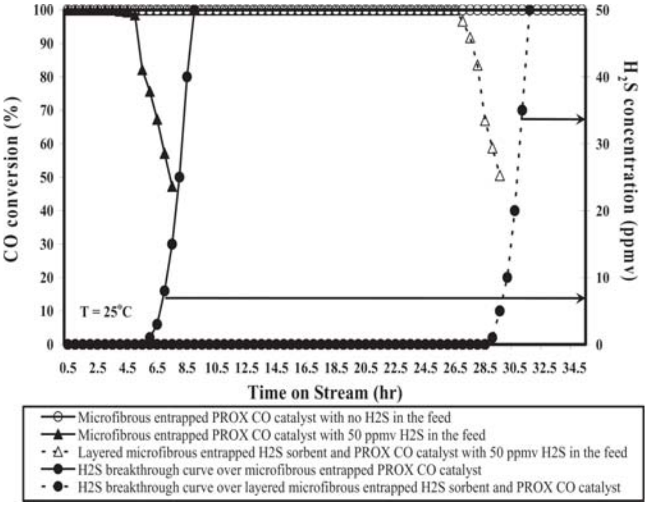

Fig. 3 Performance of an integrated bed of microfibrous entrapped ZnO/SiO_2 H_2S sorbent and Pt-M/Al_2O_3 PROX CO catalyst at 25 ℃ in the presence of 50 ppmv H_2S in the feed stream

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 (e.g., packed beds and monoliths) so as to be used 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 an S-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.

Figure 3 shows the performance of the integrated bed of the microfibrous entrapped ZnO/SiO_2 H_2S sorbent layer and the Pt-M/Al_2O_3 PROX CO catalyst layer at 25 ℃ in the presence of 50 parts per million in volume (ppmv) H_2S in the feed. The total flow rate of the feed stream was 100 mL/min, and the 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 for at least 35 h without any catalytic deactivation over the microfibrous entrapped Pt-M/Al_2O_3 PROX CO catalyst when H_2S does not present in the feed stream. The CO conversion activity, however, starts dropping dramatically at about 4 h after 50 ppmv H_2S is introduced into 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 were investigated at 25 ℃ in the presence of both 1% CO and 50 ppmv H_2S in the feed stream. The 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 can be seen clearly in Fig. 3, 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 the introduction of 50 ppmv H_2S in the feed stream, and it is the breakthrough time for the H_2S over the integrated system.

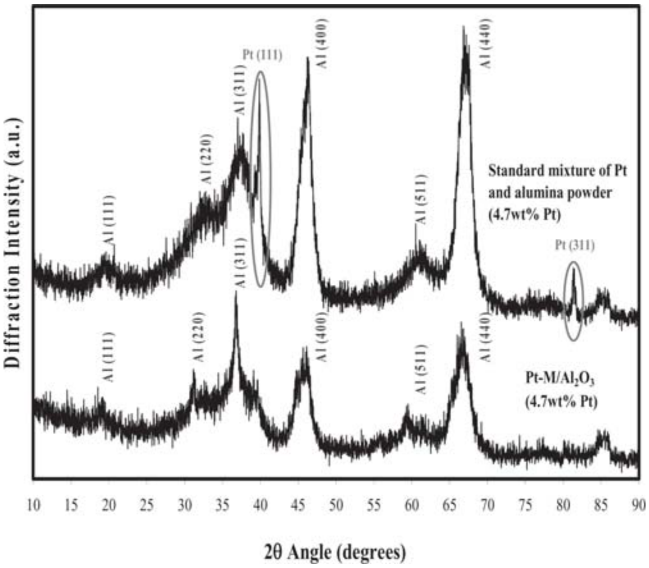

Fig. 4 Comparison of XRD patterns of Pt catalyst supported on alumina (Pt-M/Al_2O_3) with those of a mixture of Pt and alumina powder (4.7 wt.% Pt)

3.3 Catalyst Characterization

Figure 4 shows the XRD patterns of Pt catalyst supported on alumina (4.7 wt.% Pt-M/Al_2O_3) compared with those of mixtures of Pt (4.7 wt.%) and alumina powder. The strongest peak of Pt (111), which is not detected from the catalyst samples, is detected at a 2θ angle of 39.76° in a standard sample of 4.7 wt.% Pt mixed with alumina powder. The Pt (311) peak is also detected at a 2θ angle of 81.29° in standard samples. The XRD analysis indicates that nanosized Pt and promoter particles are highly dispersed on the alumina support.

4. Summary and Conclusions

Promoted Pt/Al_2O_3 (Pt-M/Al_2O_3) catalyst is significantly superior to unpromoted catalyst for a PROX of CO in excess H_2. The XRD patterns for Pt-M/Al_2O_3 catalysts with different Pt and promoter content verify the fact that nanosized Pt and promoter particles are highly dispersed on the surface of the alumina support. All of the peaks observed in XRD experiments are from alumina supports. With the attachment of EDX, however, the presence of Pt and promoter particles is repeatedly verified, the precise elemental composition of catalysts can be obtained with high spatial resolution by SEM, and the values obtained by EDX show good agreement with the calculated values during the catalyst preparation.

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-M/Al_2O_3 catalysts (150-250 μm) were entrapped in this study into the microfiber composite materials and investigated for a preferential CO oxidation (i.e., PROX) reaction for PEMFCs. The microfibrous entrapped PROX catalysts demonstrate long-term stability and high activity in a temperature range of 25 to 150 °C (PROX unit operating temperature). The nanodispersed nature of Pt and promoter particles combined with the packaging of metal fibers and small support particles promote high contacting efficiency in the microfibrous entrapped catalysts compared with the conventional packaging of catalysts in a packed bed of particles of the same size.

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-M/Al_2O_3 PROX catalyst to remove both H_2S and CO from an S-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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