

MICROFIBROUS ENTRAPMENT OF SMALL CATALYST PARTICULATES FOR HIGH CONTACTING EFFICIENCY REMOVAL OF TRACE CO FROM REFORMATES AT LOW TEMPERATURES FOR PEM FUEL CELLS

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Abstract

Preferential oxidation (PROX) of CO is the most efficient way to remove CO from reformat streams for PEM fuel cells. Pt/Al₂O₃ has long been used for this purpose. Pt/Al₂O₃ catalysts are effective for preferential oxidation of CO only at temperatures above 150°C, and the maximum CO conversion usually takes place at around 200°C. In this study, promotion of Pt/Al₂O₃ with transition metals results in enhanced catalytic activity and selectivity in the temperature range from 25 to 150°C.

A high void and tailorable sintered microfibrous carrier consisting of 5vol% 4 and 8µm diameter Ni fibers is used to entrap 15vol% of 150-250µm diameter Al₂O₃ particulates. SEM images show that the alumina support particulates are uniformly entrapped within the matrix. Promoter and platinum are then dispersed onto the microfibrous entrapped alumina support particles by incipient-wetness. *In-situ* FTIR investigations have been employed to reveal the reaction mechanism / pathway of PROX using the promoted Pt/Al₂O₃ at low temperatures. The transition metal oxide promoters provide active oxygen for selective CO oxidation. The transition metal promoter appears to provide a separate non-competitive site for O₂ activation. On the other hand, data collected over un-promoted Pt/Al₂O₃ indicates both oxygen and CO competition for surface Pt sites resulting in strong CO inhibition at lower temperatures.

1. Introduction

1.1. Preferential oxidation (PROX) of CO from practical reformat 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 (Dudfield *et al.*, 2001). A polymer electrolyte membrane fuel cell (PEMFC) is believed to be the most suitable one for mobile application.

Due to both kinetic and thermodynamic constraints of hydrocarbons (e.g.: methanol) 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 reformat coming from the fuel processing section contains 50-65vol% H₂, 25-40vol% CO₂, 2-5vol% H₂O, and 1vol% CO. The PEM fuel cell performance significantly deteriorates if the feed stream contains even trace amount of CO (more than 10ppm) 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 H₂ takes place.

There are several approaches to remove CO in the H₂-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;

Desired oxidation reaction: $\text{CO} + 1/2\text{O}_2 \rightarrow \text{CO}_2$ (1)

Undesired oxidation reaction: $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$ (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 (Son *et al.*, 2002). 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 integral reactor studies (Chang *et al.*) showed that promoted Pt/Al₂O₃, Au/ α -Fe₂O₃, and CuO-CeO₂ demonstrated promising catalytic activity and selectivity among more than 150 catalysts prepared and investigated for the preferential CO oxidation (PROX) reaction from practical reformat for PEM fuel cells. In particular, CO conversion takes place at significantly lower temperatures over the promoted Pt/Al₂O₃ catalysts and the active reaction temperature window is enlarged to 25-200°C over the promoted catalyst compared with a narrow window around 200°C over the conventional Pt/Al₂O₃.

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 10µm into a micrometal fiber matrix [4]. Sintered microfibrinous composites using a 16%Ni/alumina catalyst for toluene hydrogenation in a trickle bed reactor have demonstrated 2-6 times higher specific activities than conventional packed bed catalysts on a gravimetric basis, while volumetric activities of 40vol.% composite catalysts were 80% higher than conventional extrudates (Meffert, 1998).

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 (Cahela and Tatarchuk, 2001).

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 (Marrion *et al.*,

1994). 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 promoted Pt/Al₂O₃ catalyst has shown extremely superior catalytic activity for the preferential oxidation of CO from practical reformates compared with the un-promoted conventional Pt/Al₂O₃ catalyst (Chang *et al.*). In this study, the promoted Pt/Al₂O₃ is prepared by incipient wetness impregnation of the appropriate metal salts into a 150-250µm diameter gamma alumina support entrapped within a sintered matrix of 4 and 8µm diameter Ni fibers. The high activity of this catalyst, combined with a favorable selectivity and high contacting efficiency provide superior catalytic performance in practical reformat streams at 25 to 200°C with 0 to 30vol% H₂O. 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 H₂S sorbent was placed upstream of a microfibrous entrapped polishing PROX catalyst to remove both H₂S and CO from a sulfur-contaminated model reformat stream. It is required to ensure downstream stability of a membrane electrode assembly for the anode compartment of a PEM H₂-air fuel cell stack. Operating in this fashion, an outermost H₂S 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. Preparation of Microfibrous Entrapped Catalyst

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 are 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 is 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 $^\circ\text{C}$ for 1hr and sintering of the preform in H_2 flow at elevated temperature (900 $^\circ\text{C}$) for 30mins remove the cellulosic binder/pore former and entraps the selected support particulates within a sinter-locked network of conductive metal fibers. The resulting preform generally consists of 10-15vol% support particles, 5vol% metal (Ni) fibers, and 80-85vol% 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. Then, microfibrous entrapped catalysts are dried and calcined at desired temperatures.

2.2. Catalytic Activity and Selectivity Investigation

Practical reformat consists of 1% CO , 20% CO_2 , 40% H_2 , and balance N_2 . Reaction products were analyzed using a HP6890 gas chromatograph equipped with a TCD detector. Water condenser was used to prevent water vapor from entering the gas chromatograph. Empty reactor without catalyst showed no CO conversion.

2.3. Catalyst Characterization Methods.

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

3. Results and Discussion

3.1. Microfibrous Entrapped PROX Catalyst.

Figure 1 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, respectively. As shown in the Figure 1, the alumina support particles are uniformly entrapped into a well sinter-locked three-dimensional network of 4 and 8 μm diameter Ni fibers. Approximately 80-85vol%, 5vol%, and 10-15vol% of the microfibrous materials are voidage, nickel fibers, and alumina support particles entrapped, respectively.

Figure 2 shows stability of microfibrous entrapped promoted Pt/Al₂O₃ catalysts at 70°C (PEMFC stack temperature) with effect of H₂O on the stability. Stability of PROX unit at PEM fuel cell stack temperature is important considering that PROX unit would be integrated into PEMFC stack if it is stable at stack temperature. 30% H₂O 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. As shown in Figure 2, at 70°C, 0% (no H₂O added), 10%, 20%, and 30% H₂O 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 promoted Pt/Al₂O₃ 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 promoted Pt/Al₂O₃ catalysts is maintained for approximately a week without any catalytic deactivation in the presence of 0%, 10%, 20%, and 30% H₂O added in the dry feed stream at 70°C.

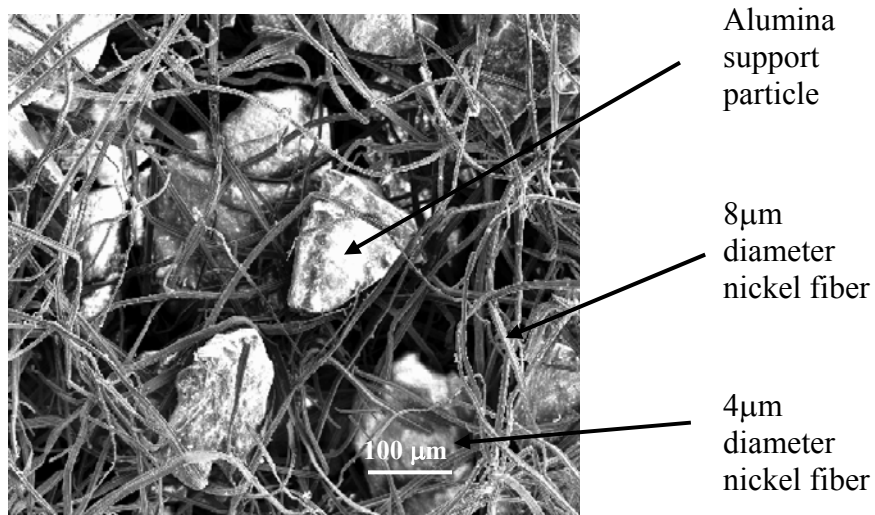


Figure 1. SEM image of 150-250 μm γ -Al₂O₃ support particles entrapped in a microfibrous matrix of 4 and 8 μm nickel fibers at magnification level of 200.

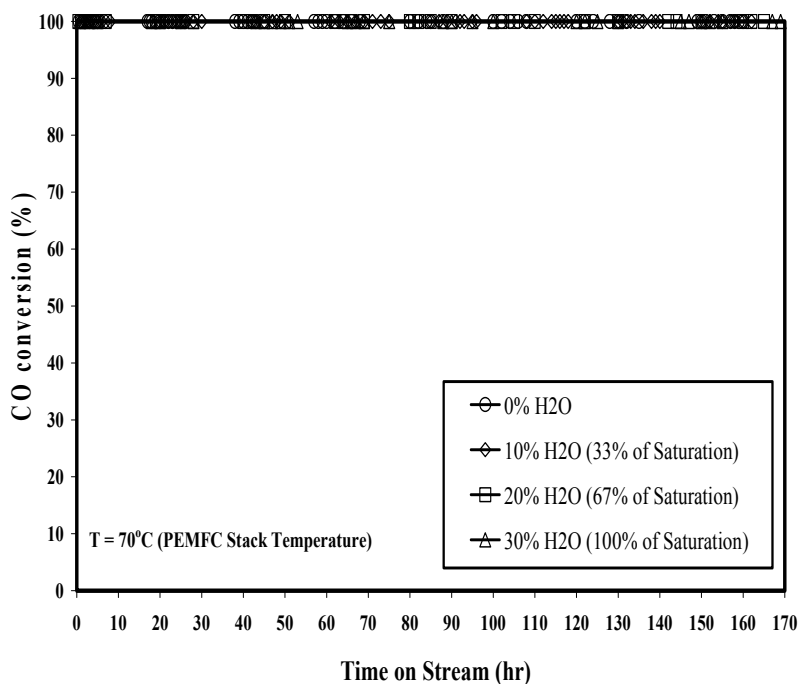


Figure 2. Stability of microfibrus entrapped promoted Pt/Al₂O₃ catalysts at 70°C (PEM fuel cell stack temperature) – Effect of H₂O.

3.2. Catalyst Characterization

Figure 3 shows the XRD patterns of Pt catalyst supported on alumina (promoted Pt/Al₂O₃, 4.7wt%) compared with those of mixtures of Pt (4.7wt%) and alumina powder. The strongest peak of Pt (111) which is not detected from the catalyst samples is detected at 2θ angle of 39.763° in standard sample of 4.7wt% Pt mixed with alumina powder. Pt (311) peak is also detected at 2θ angle of 81.286° in standard samples. XRD analysis indicates that nano-sized Pt and promoter particles are highly dispersed on the alumina support.

Figure 4 shows the EDX spectrum of promoted Pt/Al₂O₃ (4.7wt% Pt) catalyst. As seen in the figure, there are two peaks corresponding to Pt, two peaks to promoter, one peak to Al, and one peak to O in the alumina support. The weight % of Pt obtained by EDS (4.1wt% Pt) is in good agreement with the calculated value (4.7wt% Pt) during the incipient-wetness impregnation process. The atomic ratio of M (promoter):Al measured by EDX (0.034:1) is also in good agreement with the calculated atomic ratio (0.04:1).

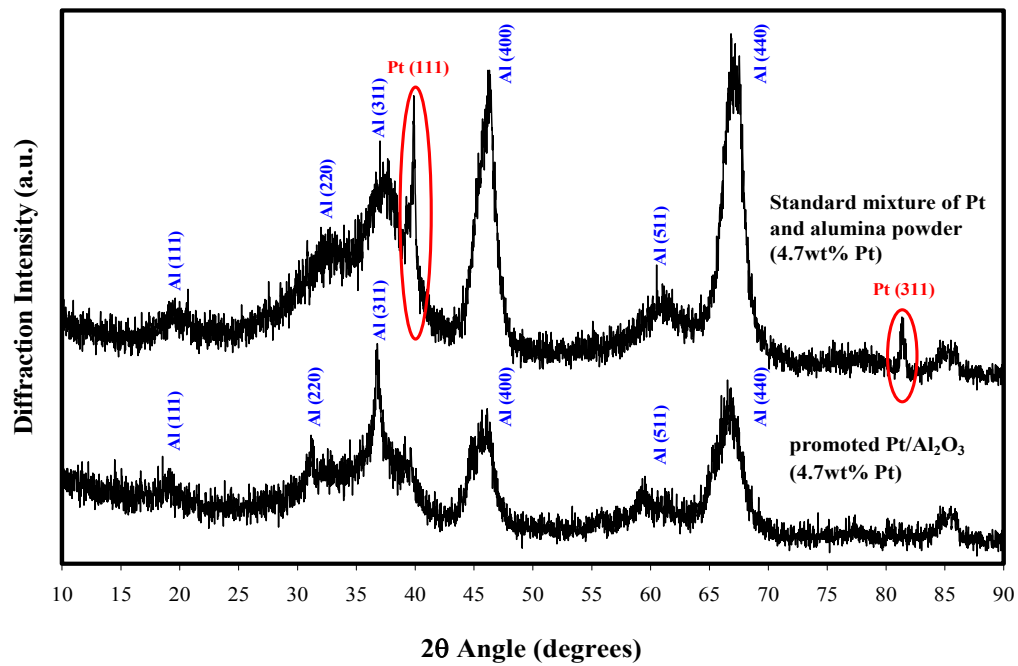


Figure 3. Comparison of XRD patterns of Pt catalyst supported on alumina (promoted Pt/Al₂O₃) with those of mixture of Pt and alumina powder: 4.7wt% Pt.

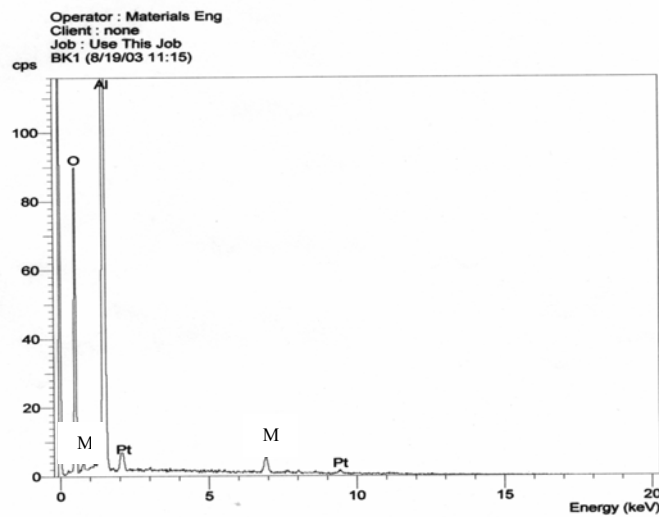


Figure 4. EDX spectrum of promoted Pt/Al₂O₃ catalyst (M: promoter).

4. Conclusions

Promoted Pt/Al₂O₃ catalyst is significantly superior to un-promoted catalyst for preferential oxidation of CO in excess H₂. XRD patterns for the promoted Pt/Al₂O₃ catalysts with different Pt and promoter content verify the fact that nano-sized small Pt and promoter particles are highly dispersed on the surface of alumina support. All the peaks observed in XRD experiments are from alumina supports. With the attachment of the energy dispersive X-ray spectrometer (EDX), however, the presence of Pt and promoter particles is repeatedly verified and the precise elemental composition of catalysts can be obtained with high spatial resolution by scanning electron microscopy (SEM) and the values obtained by EDX show good agreement with the calculated values during the catalyst preparation.

High contacting efficiency microfibrillar media can be used to entrap various reactive materials including heterogeneous catalysts, sorbents, and various solid reactants. Small particles of the promoted Pt/Al₂O₃ catalysts (150-250 μm) were entrapped in this study into the microfibrillar composite materials and investigated for preferential CO oxidation (PROX) reaction for PEM fuel cells. The microfibrillar entrapped PROX catalysts demonstrate a long-term stability and high activity at temperature range of 25 (room temperature) to 150°C (PROX unit operating temperature). The nano-dispersed nature of Pt and promoter particles combined with packaging of metal fibers and small support particles promotes high contacting efficiency in the microfibrillar entrapped catalysts compared with conventional packaging of catalysts in packed bed of even same particle size.

These microfibrillar 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 microfibrillar entrapped polishing ZnO/SiO₂ H₂S sorbent was placed upstream of a microfibrillar entrapped polishing PROX catalyst to remove both H₂S and CO from a sulfur-contaminated practical reformat stream. Operating in this fashion, an outermost H₂S 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.

5. References

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