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Selective catalytic oxidation of CO in H_2: fuel cell applications

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Abstract

An essential requirement for the proton exchange membrane (PEM) fuel cell is to deliver clean H_2 to the anode electrode, the kinetics of which are greatly hindered by traces of CO present from the upstream hydrocarbon steam reforming and water-gas shift processes. A technology receiving much attention is the selective oxidation of CO to CO_2. Ideally the catalyst must selectively oxidize about 1% (10 000 ppm) CO to less than 5 ppm without oxidizing any of the 30–70% H_2 present. This paper describes performance results of a Pt promoted catalyst deposited on a monolith for selective oxidation of CO under simulated fuel processing conditions for PEM fuel cell applications. The effect of space velocity, gas composition and temperature on activity and selectivity is presented. Preliminary mechanism ideas are also presented. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Selective oxidation of CO; Fuel processing; PEM fuel cells; Monolith; Pt catalyst

1. Introduction

Development of the proton exchange membrane (PEM) fuel cell has been accelerating during the last 5 years advancing the commercial possibilities for generating clean and efficient power for stationary and mobile source applications [1,2]. It promises to deliver electricity with virtually no emission of harmful pollutants with increased efficiency because it directly converts chemical energy to electricity avoiding the thermodynamic mechanical cycle losses associated with combustion in conventional power generation. The electrochemical system operates at about 70–80°C using H_2 (essentially free of CO which poisons the Pt anode reaction) as the anode fuel and O_2 (air) at the cathode. The net reaction generates H_2O and electricity. In the absence of large capacity hydrogen storage systems, the H_2 will likely be generated on site. Given the extensive infrastructure existing for natural gas (stationary source applications) and gasoline (mobile source), these are the preferred sources of H_2. The production of clean H_2 for the chemical industry from hydrocarbon feeds [3] is well known and is accomplished by a series of catalytic steps including desulfurization, steam reforming, water-gas shift and CO removal by pressure swing absorption or methanation. All of these technologies are now being reviewed for possible use in the fuel cell, however CO removal by pressure swing absorption requires expensive compressors and methanation is complicated by hydrogenation of the CO_2 present. For this reason selective oxidation is now the primary technology of choice.

In the early 1960s Engelhard developed and commercialized the Selectoxo^{TM} catalyst and process for H_2 plants to remove CO to levels acceptable for the Fe ammonia synthesis catalyst [4–6]. The heart of this technology is a highly selective Pt containing catalyst which oxidizes up to 10 000 ppm CO without significantly oxidizing the 70% H_2 (dry) present in the reformate.

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

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

CO levels are reduced to less than 5 ppm under steady state conditions (50°C, 10 000 h^{-1} and 200–400 psig). The Selectoxo^{TM} system was located downstream from the CO_2 and H_2O scrubber. For fuel cell applications the catalyst must operate at much higher space velocities at temperatures above about 90°C at ambient pressure in the presence of large amounts of CO_2 and H_2O. Furthermore, it must be designed for transient operation since power demands will vary considerably depending on the application. A large consumption of H_2 is undesirable since it decreases power generation and complicates heat management. Therefore, having a catalyst with high selectivity is critical.

2. Experimental

The family of Selectoxo^{TM} catalysts contains 0.3–0.5% Pt supported on γ-alumina $\frac{1}{8}$ in. (3 mm) tablets promoted with a base metal oxide. The composition of the new catalyst is 5% Pt promoted by a base metal oxide impregnated onto γ-alumina, dried and calcined. The material is milled to form a powder suitable for deposition onto a monolith structure. The cordierite monolith is 400 cells per square inch (62 cells/cm^2) and was dipped into an aqueous slurry of the catalyst followed by drying and calcination using proprietary conditions. Typically a washcoat loading of about 1.5 g/$in.^3$ (∼0.1 g/cm^3) is obtained. We refer to this material as the Pt promoted monolith catalyst.

Testing of powdered catalysts was accomplished by pressing particles 40–60 microns in size and diluting in a 1:2 ratio of catalyst to quartz in order to maintain the bed isothermal. Monoliths were wrapped with insulation and fitted into a 1-inch (2.54 cm) ID quartz reactor. A control thermocouple was positioned in the inlet section of the catalyst bed.

Selectivity is defined as the moles of CO converted to CO_2 divided by the total moles of O_2 reacted multiplied by 100:

$$\%\,\text{Selectivity} = \frac{\frac{1}{2}[\text{moles of CO converted to } CO_2]}{[\text{total moles of } O_2 \text{ reacted}]} \times 100$$

The test gas contained typically 1000 ppm CO, 20 vol.% H_2, 10 vol.% H_2O and varying O_2 to CO ratios with the balance N_2. Variations are indicated in the text. The model test gas did not contain CO_2 due to interference with the O_2 measurement, but some experiments containing 20 vol.% CO_2 were conducted. Total flow rate of gas was 4 l/min and space velocity studies were conducted by varying the amount of catalyst. Water was supplied to the reactor by peristaltic or syringe pumps through a preheated evaporator to generate steam.

The VHSV is calculated by dividing the volumetric flow rate under the normal conditions by the volume of the monolith as a cylinder. This is the conventional method for designing monolithic reactors for environmental applications.

The consumption of CO and generation of CO_2 was measured with a California Analytical Instruments infrared gas analyzer. O_2 consumed was measured with a Rosemount electrochemical analyzer. The generation of hydrocarbons was monitored with a Rosemount Analytical flame ionization analyzer, but under the conditions of these experiments none was detected. Reproducibility of analytical measurements was ±1–2%. The excess O_2 reacted above the stoichiometric amount of CO consumed determined the amount of H_2 oxidized. This is possible since the only other consumption path for O_2 is by oxidation of H_2.

3. Results and discussion

3.1. Studies with catalyst particles

3.1.1. Effect of H_2O, H_2 concentration and O_2/CO mole ratio

The conversion of CO and O_2 over the promoted Pt catalyst is about 75% at the stoichiometric condition ($O_2/CO = 0.5$) at 90°C. The initial CO concentration is 1000 ppm at a VHSV = 120 000 h^{-1}. The addition of 3 vol.% H_2O decreases CO conversion to about 68%. Increasing H_2O to 10% does not change catalyst activity or selectivity. With 20 vol.% H_2 in the gas mixture, the conversion of CO remains essentially constant with selectivity about 80%.

Increasing the O_2/CO ratio from 0.5 to 0.75 (O_2 from 500 to 750 ppm) at a CO concentration of

1000 ppm increases conversion from 65 to more than 90% with about 65% selectivity.

3.2. Effect of CO_2

The effect of CO_2 on catalyst activity was conducted at 90°C by first exposing the catalyst for 17 h in a gas stream composed of 1000 ppm CO, $O_2/CO = 0.5$, 20 vol.% H_2, 10 vol.% H_2O and 20 vol.% CO_2. The CO_2 was then removed and the conversion measured again. The CO conversion remained essentially constant throughout the experiment; 78.7% before CO_2 exposure and 79.9% after CO_2 exposure. It was then exposed for another 18 h under the same conditions and the conversion once again remained constant at 80.6%. In each case the selectivity remained unchanged.

3.3. Comparison of promoted Pt catalyst with Pt/γ-Al_2O_3

To further understand the unique performance of this catalyst, a study comparing it to a Pt/γ-Al_2O_3 prepared identically with the same Pt loading (5%) but without the promoter oxide was conducted. This comparison is shown in Table 1. The CO conversion is clearly enhanced for the promoted catalyst, 68 versus 13.2% at 90°C and $O_2/CO = 0.5$. The selectivities are very similar at 78 and 82%, respectively, indicating that the promoter metal oxide enhances both CO and H_2 oxidation. We believe that the promoter metal oxide provides sufficient dissociated oxygen to enhance both oxidation rates.

When the O_2/CO is increased to 0.75 at 150°C, conversion with the Pt catalyst is increased, but is still one half the conversion of the promoted Pt catalyst. The data in the last line of Table 1 compare the Pt promoted metal oxide monolith catalyst to Pt/Al_2O_3 powder. Although not a direct comparison, the results do clearly show the increased CO conversion for the promoted catalyst even at a considerably higher weight hourly space velocities (WHSV; 923 000 vs. 150 000 l/g-h). The WHSV for the monolith is based on the actual weight of catalyst on the walls of the monolith.

4. Monoliths

4.1. Effect of CO concentration

The effect of CO concentration at 90 and 150°C is shown in Table 2. At 90°C and $O_2/CO = 0.5$, the conversion of CO was virtually independent of concentration at 2000 ppm (68.9%) and 5000 ppm (69%). Similarly, the selectivity showed only a small sensitivity for CO concentration varying from 66.1% for 2000 ppm to 77.6% for 5000 ppm. At $O_2/CO = 0.75$, increases in the CO concentration had little effect on the conversion of CO or catalyst selectivity. At 150°C neither the conversion of CO nor the selectivity showed much sensitivity for CO concentration of 2000 and 5000 ppm. At $O_2/CO = 1$, essentially all of the CO was converted at a selectivity of about 50%. So, clearly the conversion of CO increases with O_2/CO.

The conversion of CO over Pt is well known to obey a single site Langmuir–Hinshelwood kinetic model [7], where O_2 and CO compete for the same sites. There is a decrease in reaction rate as the CO concentration is increased especially near the stoichiometric O_2/CO ratio of 0.5. For the Pt promoted

Table 1
Comparison of the promoted Pt/Al_2O_3 with Pt/Al_2O_3 (particles 40–60 μm, 1000 ppm CO, 20 vol.% H_2, 10 vol.% H_2O, VHSV = 120 000 h^{-1}, WHSV = 150 000 l/g-h)

#	Test conditions	Promoted Pt catalyst		Pt/Al_2O_3	
		X_{CO} (%)	Selectivity (%)	X_{CO} (%)	Selectivity (%)
1	Fresh, at 90°C, $O_2/CO = 0.5$	68	78	13.2	82
2	At 90°C, $O_2/CO = 0.75$	90	65	12.7	66.2
3	At 150°C, $O_2/CO = 0.5$	62[a]	60[a]	26.8	56.7

[a] Data were obtained with the monolith catalyst at VHSV = 80 000 h^{-1}, WHSV = 923 000 l/g-h.

Table 2
Effect of CO concentration on the monolith promoted Pt catalyst performance (VHSV = 20 000 h^{-1}, WHSV = 214 000 l/g-h)

#	Test conditions		2000 ppm CO		5000 ppm CO	
	Temperature (°C)	O_2/CO mole ratio	X_{CO}(%)	Selectivity (%)	X_{CO} (%)	Selectivity (%)
1	90	0.5	68.9	66.1	69.0	77.6
2	90	0.75	96.8	64.4	100	68.1
3	90	1.0	100	50.7	–	–
4	150	0.5	61.2	57.7	65.6	64.6
5	150	0.75	90.6	57.8	97.5	64.6
6	150	1.0	100	50.6	100	50.9

catalyst increasing concentrations of CO do not inhibit the reaction. This result is consistent with a dual site non-competitive mechanism in which CO adsorbs onto the Pt sites and the O_2 dissociatively adsorbs onto the metal oxide site. Surface reaction occurs between CO and O on adjacent but different sites. The exact nature of the interaction between the Pt and the metal oxide will be the subject of a future paper.

4.2. *Effect of temperature*

The activity and selectivity data points between 90 and 150°C are shown in Fig. 1 with the model gas composition. The monolith catalyst space velocity (VHSV) is 80 000 h^{-1} and O_2/CO = 0.5. Increasing the temperature from 90 to 150°C shows a small increase in CO conversion (43–51%), but the total O_2 conversion increases more dramatically approaching 100%. The increased O_2 conversion is primarily due to an increase in H_2 oxidation as evident by the selectivity decreasing from 80 to 60%. For this reason, we recommend operating at lower temperatures whenever possible.

4.3. *Effect of space velocity*

The CO and O_2 conversion and selectivity are plotted in Fig. 2 as a function of space velocity. The monolith VHSVs studied were 20 000, 38 000 and 80 000 h^{-1} accordingly. The corresponding WHSV are 214 000, 429 000 and 923 000 l/g-h, respectively. The WHSV is calculated by dividing the volumetric flow rate by the weight of catalyst washcoat. The latter is shown on the top of the *x*-axis, while the VHSV is shown on the bottom. The gas composition was 1000 ppm CO, 20 vol.% H_2, 10 vol.% H_2O. The

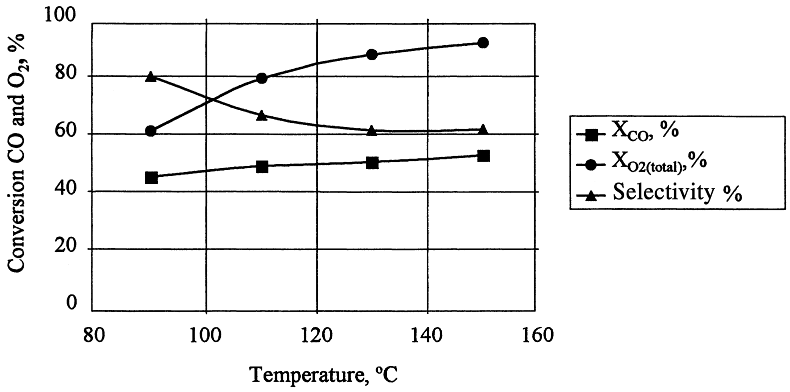

Fig. 1. Monolith promoted Pt catalyst activity and selectivity dependence on temperature (O_2/CO = 0.5, 1000 ppm CO, 20 vol.% H_2, 10 vol.% H_2O, VHSV = 80 000 h^{-1}). Selectivity : X_{O_2} for CO.

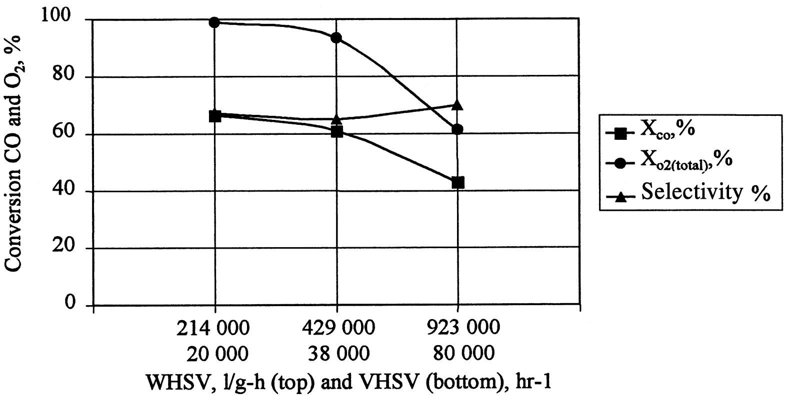

Fig. 2. Monolith promoted Pt catalyst activity and selectivity dependence on space velocity ($O_2/CO = 0.5$, 90°C, 1000 ppm CO, 20 vol.% H_2, 10 vol.% H_2O). Selectivity : X_{O_2} for CO.

O_2/CO mole ratio was 0.5 and the temperature was 90°C. The conversion of O_2 is essentially 100%, while both the CO conversion and selectivity are about 65% at a VHSV = 20 000 h^{-1}. The conversion of CO decreases to 60% at 38 000 h^{-1} and 43% at 80 000 h^{-1}. In parallel the O_2 conversion also decreases; however, the catalyst selectivity remains essentially constant.

4.4. Optimum design conditions

Figs. 3 and 4 demonstrate the trade-off between temperature, space velocity and O_2/CO for achieving optimum reduction of CO for the Pt promoted monolith catalyst. At 90°C (Fig. 3) and a volumetric space velocity (VHSV) of 20 000 h^{-1} increasing O_2/CO to 1.0 yields 100% conversion of CO and O_2, but with a decrease in the selectivity from 65 to about 51%. At 150°C (Fig. 4) the process can operate at a space velocity of 80 000 h^{-1}, but $O_2/CO = 1.5$ is necessary for the CO and O_2 conversions to approach 100%. However, the selectivity decreases from 61% at stoichiometric O_2/CO (0.5) to 33% at $O_2/CO = 1.5$.

It should be noted that as the temperature exceeds 180°C, the reverse water-gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) may occur limiting the amount of CO conversion obtainable with the promoted catalyst.

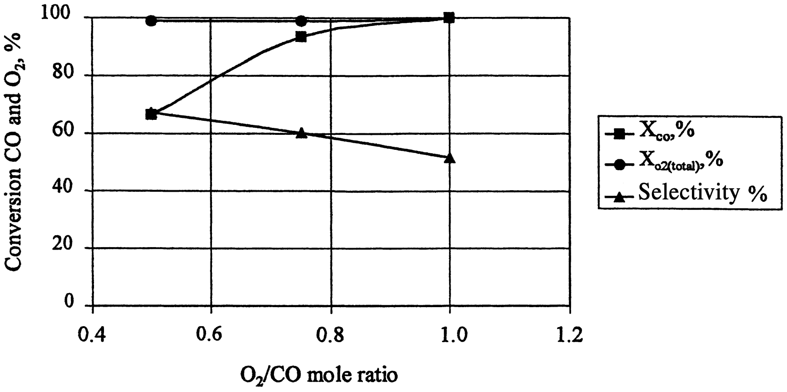

Fig. 3. Monolith promoted Pt catalyst activity and selectivity dependence on O_2/CO mole ratio (90°C, 1000 ppm CO, 20 vol.% H_2, 10 vol.% H_2O, VHSV = 20 000 h^{-1}). Selectivity : X_{O_2} for CO.

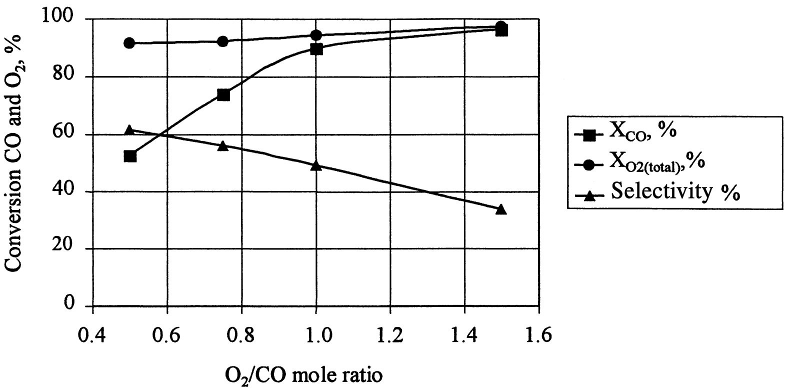

Fig. 4. Monolith promoted Pt catalyst activity and selectivity dependence on O_2/CO mole ratio (150°C, 1000 ppm CO, 20 vol.% H_2, 10 vol.% H_2O, VHSV = 80 000 h^{-1}). Selectivity : X_{O_2} for CO.

Consequently, it is recommended that the temperature within the catalyst bed be controlled to below about 180°C. It should be added that even at temperatures in excess of 250°C, no hydrocarbon production (i.e. methanation) was observed.

5. Conclusions

A Pt catalyst promoted with a metal oxide is shown to have good activity and selectivity for reducing the CO in fuel processing applications. Its enhanced activity is due to the presence of a metal oxide promoter, which provides the site for O_2 adsorption and dissociation and therefore eliminates the normal inhibition observed in the oxidation of CO on Pt catalysts. The catalyst has been deposited on a ceramic monolith and its performance can be optimized by controlling the reactor inlet and bed temperature, space velocity and O_2/CO ratio.

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