A new generation of water gas shift catalysts for fuel cell applications

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Abstract

The generation of high-purity hydrogen from hydrocarbon fuels for fuel cell applications is essential for efficient operation of the solid polymer electrolyte (PEM) fuel cell. In general, most feasible strategies to generate hydrogen from hydrocarbon fuels consist of a reforming step to generate a mixture of H_2, CO, CO_2 and H_2O (steam) followed by water gas shift (WGS) and CO clean-up steps.

The WGS reaction is industrially carried out using two particulate catalysts—FeCr and CuZn—at temperatures between 350–500 and 180–250 °C, respectively. Both catalysts are pyrophoric: they spontaneously generate heat to dangerously high temperatures when exposed to air after activation. In addition, CuZn needs to be carefully activated before use. We have developed a base metal non-pyrophoric alternative to commercial CuZn. The catalyst, referred to as Selectra Shift, activates in process gas, has stable activity under a wide variety of process conditions and is safer if accidentally exposed to air. It therefore represents a safer alternative to the commercial CuZn for fuel cell applications. In addition, Engelhard has developed base metal and precious metal monolith WGS catalysts for applications where the catalyst must be optimized for small reactor volumes, lower pressure drop and mechanical integrity. Inhibitors are added to the precious metal catalyst to suppress the undesirable methanation side reaction.
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1. Introduction

Fuel cells promise to be an efficient and clean alternative to fuel combustion for primary power generation for stationary and mobile source applications in the near future. They are about twice as fuel efficient as the internal combustion engine and produce virtually no CO, HC or NO_x and a reduced level of CO_2. They operate on the basic principle of direct conversion of chemical energy into electrical energy, avoiding the mechanical steps and thermodynamic limitations of traditional combustion energy generation cycles. Hydrogen gas is electrochemically oxidized to hydrogen ions at the anode which pass through a proton conductive membrane to the cathode where they combine with electrochemically reduced O_2 (from the air) producing H_2O. The electrons flow through the external circuit providing power.

The hydrogen may be provided to the fuel cell in pure form (compressed gas, etc.) or one may generate hydrogen from hydrocarbons in a fuel processor. Fuel processing is the most convenient method of supplying hydrogen in the absence of a suitable infrastructure for hydrogen. Fuel processors generate hydrogen from hydrocarbons (i.e. natural gas) by either steam reforming [1] or autothermal reforming [2,3]. This reforming step generates a gas which contains 8–12% CO besides hydrogen and CO_2. This CO must be converted with the help of steam to CO_2 and hydrogen via the water gas shift (WGS) reaction before a final clean-up step can reduce the CO content to <10–50 ppm for the fuel cell. Such low CO levels are needed at the fuel cell anode to efficiently carry out the electrochemcial oxidation of hydrogen.

The water gas shift reaction is catalyzed industrially by two catalysts: A high-temperature shift catalyst, FeCr, and a low-temperature shift catalyst, CuZn [4]. Even though these catalysts have been optimized for many years, they are not suitable for use in residential or automotive fuel processors. For residential applications, where vibration resistance and small volume is not critical, pelletized catalysts can be used. However, the lengthy and difficult reduction procedure associated with commercial CuZn catalyst as well as the pyrophoricity of the active catalyst are not acceptable [5]. For mobile applications monolith catalysts are needed.

This paper describes catalysts developed at Engelhard Corp. to overcome those problems.

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2. Experimental

Catalytic activity was measured in a 1 in. diameter quartz microreactor equipped with inlet and outlet thermocouples. Monoliths were mounted using ceramic paper which was previously heated to 500 °C to burn out all organic impurities. Particulate catalysts were supported on a quartz frit. The feed gas was mixed using mass-flow controllers. Water was dosed to the dry feed gas using an HPLC pump. Gas analysis was conducted on-line using a CO analyzer from Fuji Electric and a total hydrocarbon analyzer from Rosemount Scientific.

Pyrophoricity studies were done by purging the reactor with nitrogen after the catalyst has been activated and measured in simulated reformate, followed by a purge with air. The increase in outlet temperature was registered. For calculations, the weight percent of the reducible oxide in the catalyst was used to calculate heat capacity and enthalpy of oxidation. The adiabatic temperature rise was then calculated using the HSC chemistry software package. The software was also used to calculate equilibrium compositions.

3. Particulate catalysts

The water gas shift reaction generally has to reduce the CO content of reformate to 0.5% or less and deliver it to a PROX catalyst for further reduction to <10 ppm to protect the fuel cell anode.

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (\Delta H = -40.6\,kJ/mol)$$
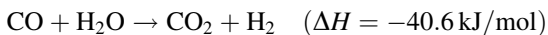
The equilibrium amount of CO in the reformate increases with the temperature, as shown in Fig. 1.

The catalyst has to be sufficiently active to achieve equilibrium conversion at temperatures below 270 °C to achieve CO outlet concentrations below 0.5% CO. This stands in contrast to catalytic activity, which increases with the temperature. The activity of commercial FeCr catalyst is poor, gaining catalytic activity only above 300 °C. It is, therefore, not active enough to achieve the necessary conversion.
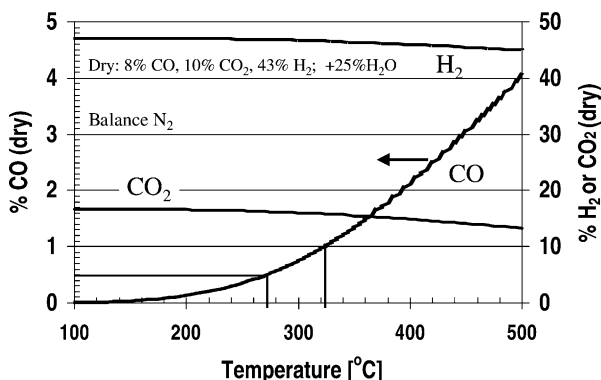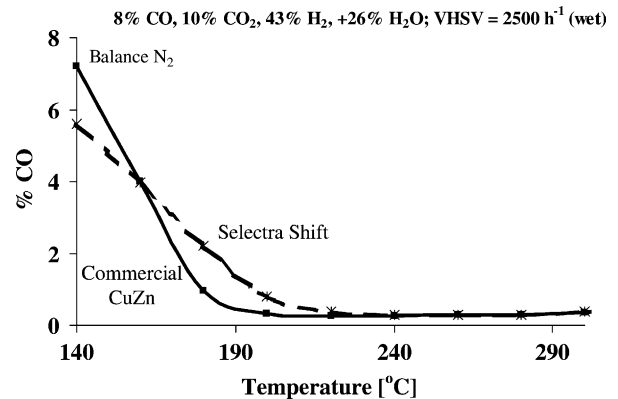

Fig. 2. Activity of Selectra Shift vs. commercial CuZn.

Commercial CuZn on the other hand is a very active catalyst, having activity above 160 °C. Fig. 2 shows a comparison of catalytic activity between commercial CuZn and a non-pyrophoric base metal catalyst, Selectra Shift. The initial slope of the curve is slightly lower for Selectra Shift. Equilibrium conversion is achieved at about 220 °C versus about 200 °C for CuZn.

The pyrophoricity of a catalyst (temperature rise when exposed to air) poses a significant risk to the consumer. Not only must accidental exposure to air be completely avoided, but the reduction of such a material is complicated and hazardous [4] with the necessity of careful temperature control. In our laboratory, temperatures as high as 700 °C were measured during air exposure of commercial CuZn catalyst. Fig. 3 shows the temperature rise during oxidation that was measured for commercial CuZn and two generations of our non-pyrophoric base metal catalyst. The temperature rise for Selectra Shift (gen. 3) was as low as 40 °C. This makes this catalyst safer for use in a consumer application. Even during accidental exposure to air, the temperature rise is low enough to be safe. The temperature rise during reduction is similarly low, and no special precautions to control the temperature have to be taken.

Another advantage of the low temperature rise is the stability of the catalyst when exposed to air. Commercial

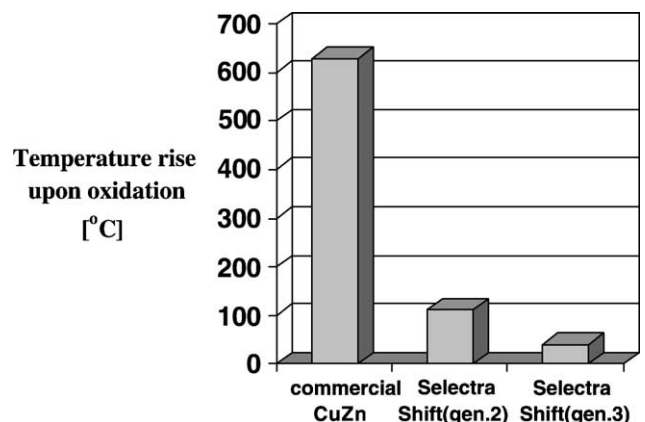Fig. 1. Equilibrium CO content of simulated reformate.

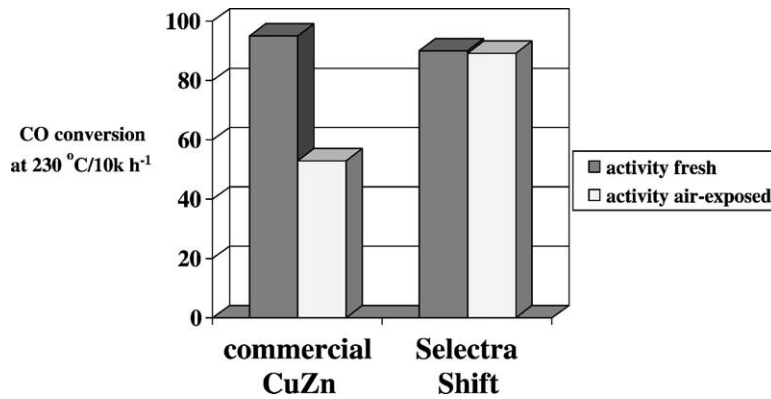Fig. 3. Pyrophoricity of WGS catalysts.

Fig. 4. Activity before and after air exposure.

CuZn catalyst loses activity when exposed to temperatures above 280–300 °C due to sintering of the Cu crystallites. Our catalyst can be fully reactivated after exposure to air. To confirm this aspect of the catalyst, we tried exposing the catalyst repeatedly to air at 150 °C and reactivated it after each exposure. Whereas Selectra Shift kept the activity during this treatment, commercial CuZn lost as much as 40% of its initial activity. This is shown in Fig. 4. There has been one report of a base metal catalyst, which keeps its activity after exposure to air [6], however no pyrophoricity data was reported.

Another important aspect in fuel processors is the resistance of the catalyst to exposure to liquid water or low-temperature steam during shutdown of the reformer. Commercial CuZn catalysts deactivate after repeated exposure to liquid water. Precious metal catalysts are often resistant to water exposure, but their high cost is often prohibitive. We improved our base metal catalyst to have a greatly enhanced

stability towards this operating environment. Fig. 5 shows the results of an accelerated aging test. In this test the catalyst is repeatedly cooled to 60 °C (below the dew point of the gas mixture) to condense a limited amount of water on the catalyst. After each low temperature exposure, the catalyst is heated to 200 and 250 °C to test its activity. During such treatment the catalyst loses very little activity.

We have further improved this catalyst and a comparative graph is shown in Fig. 6. Another advantage of this catalyst is that the lost activity due to liquid water exposure can be regenerated in situ and full activity restored.

Table 1 shows a list of comparative features and benefits of Selectra Shift versus commercial CuZn WGS catalyst. The main benefit of this base metal catalyst is its non-pyrophoric nature while maintaining high catalytic activity and stability. This feature enables one to activate the catalyst 'in situ' while commercial CuZn catalyst needs a lengthy and carefully controlled reduction step. Also, exposure to
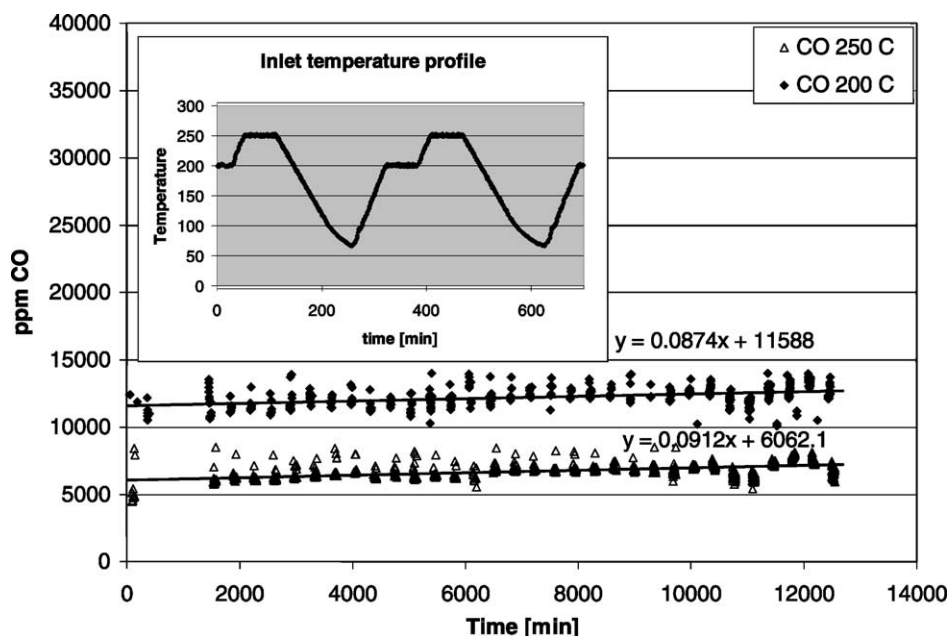

Fig. 5. Stability of Selectra Shift towards condensing water.

Table 1

| Commercial CuZn WGS catalyst	Engelhard Selectra Shift particulate WGS catalyst
Needs controlled activation; long start-up time	No-control activation; fast start-up
Pyrophoric; unsafe handling and maintenance	Non-pyrophoric; safer handling and maintenance
Irreversible loss of activity upon exposure to liquid water during start-up and shut-down; cannot be regenerated	Small activity loss due to liquid water exposure; fully regenerable
Low thermal stability	Thermally stable to 350 °C
Density: ∼1.5 g/cm^3	Density: 0.85 g/cm^3
High catalytic activity	High catalytic activity
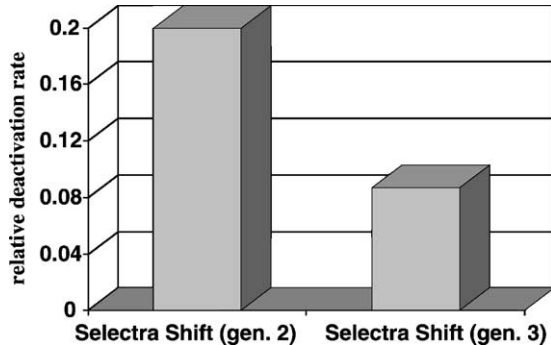
Fig. 6. Comparative aging characteristics and Selectra Shift (gen. 2 and gen. 3).

air, accidental or intentional (e.g. during maintenance) does not lead to a dangerous exotherm or loss of activity.

4. Monolithic catalysts

Catalysts for mobile applications need to withstand the road vibration and fast heat-up and cool-down cycles that are typical when operating a car. Furthermore, much more active catalysts are sought to make the fuel processor as compact as possible. The challenge is formidable to achieve such high catalytic activity at low temperature. Progress has been made towards that goal [7–10]. Carbon monoxide concentrations as high as 1% are tolerated by PROX catalysts, which are used in mobile fuel processors, without sacrificing too much efficiency. This enables one to run monolithic WGS catalysts at temperature as high as 300–350 °C. Also for stationary applications this concept is appealing because of the immense space savings and the ruggedness of the catalysts. A comparison of a fuel processor having particulate (extrudate) and monolithic catalysts is shown in Fig. 7. The efficiency of the monolith system shown on the right side is approximately 3% lower. However, the unit is also about 90% smaller than a comparable system with a particulate catalyst. A two-stage PROX catalyst is necessary to reduce the CO content of the reformate to <10 ppm.

Engelhard Corp. has developed precious metal containing catalysts for this purpose. Precious metal catalysts, which were made as described in the literature, however, lost activity rapidly. A new catalyst formulation was developed which shows stable performance. Fig. 8 shows a comparison of both WGS and methanation activity of four of these catalysts with different precious metal loading and different support materials.

The support plays a major role with respect to catalyst activity. Switching from the "old support" to a new
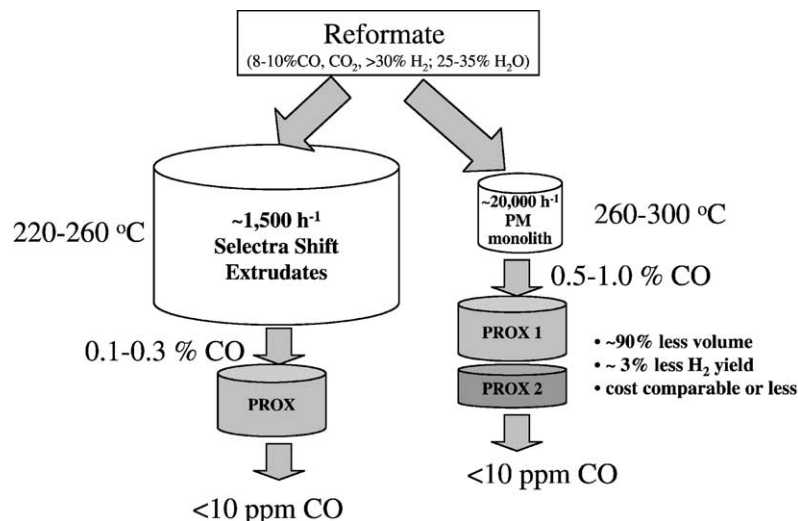

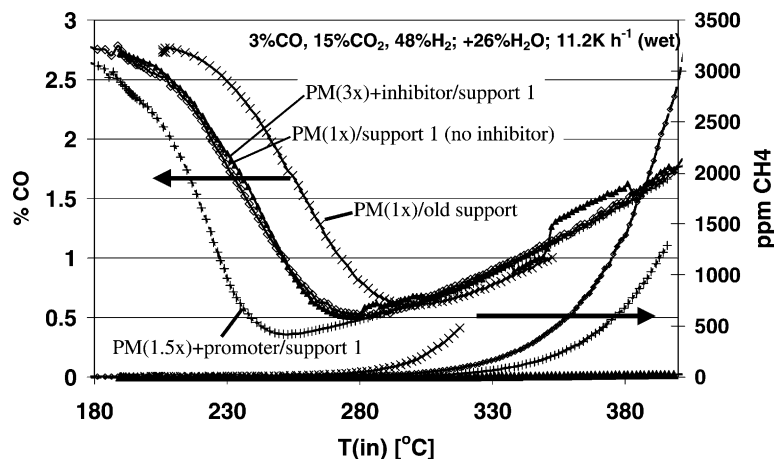Fig. 7. Comparison between particulate (extrudate) and monolith system.

Fig. 8. Monolith catalyst performance.

improved material (support 1), boosts the activity while suppressing methanation. An additional methanation inhibitor is added to the catalyst to control this undesired side reaction. However, there is a penalty in activity when the inhibitor is added to the catalyst and the same level of activity is achieved only when three times more precious metal is used.

When adding more precious metal and an additional promoter, the activity can be greatly enhanced. This is shown for catalyst 4, which contains $1.5\times$ more precious metal than catalyst 2. This catalyst can operate at space velocities in excess of $30,000\,h^{-1}$ and still achieve the 1% CO required for the PROX system.

5. Conclusions

Engelhard Corp. has developed a range of catalysts for fuel processing. Among those are a base metal water gas shift catalyst extrudate for stationary application and a precious metal monolithic catalyst. The base metal catalyst is not pyrophoric and compares well in terms of activity with commercial low temperature shift catalyst. It possesses enhanced stability towards conditions which are common in fuel processors, especially water condensation as it occurs during start-up and shut-down. It has a wider operating temperature than commercial CuZn catalyst, being stable up to 350 °C. Its non-pyrophoric nature renders it safer

during accidental exposure to air, without losing any activity. Lost activity due to liquid water exposure can be regenerated in situ or ex situ.

Precious metal monolith catalysts have also been developed for use in automotive and residential fuel processors. The catalysts are stable up to high temperatures (>450 °C). An optional methanation inhibitor for high-temperature catalysts, inhibits the methanation side reaction effectively.

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