Sulfur Tolerant Fuel Processor Catalysts

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Introduction

Hydrogen is generated from hydrocarbon fuels such as natural gas, LPG, gasoline and diesel by steam reforming (SR), auto-thermal reforming (ATR) or by catalytic partial oxidation (CPO). Further CO reduction is required for low temperature PEM fuel cells and is accomplished by water gas shift (WGS) and selective CO methanation or oxidation to achieve <50 ppm CO. These fuels contain significant amounts of sulfur compounds and must be removed to protect the fuel processing catalysts from being poisoned. Conventional catalysts used for reforming and water gas shift process such as nickel (for reforming) and Cu-Zn (for WGS) are poisoned by ppm quantities of sulfur.

There are significant development efforts to demonstrate sulfur tolerant fuel cells. High temperature PBI membranes have been demonstrated to be somewhat sulfur tolerant and SOFC-EFS has demonstrated a SOFC operating on un-sulfurized diesel fuel.[1] However, sulfur tolerant fuel processing catalysts are required to take advantage of new fuel cell technologies. The concept of a sulfur tolerant fuel cell can impact the commercialization of fuel cells by greatly simplifying the fuel processor. First the desulfurization system can be eliminated reducing a significant operating cost. CO purification by selective methanation or oxidation can be eliminated as well with high temperature membranes, further reducing the fuel processor cost. Only sulfur tolerant reforming or partial oxidation catalysts and water gas shift catalysts would be required reducing the fuel processing steps from 4 to 2 catalytic steps.

The present paper describes our studies in the development of sulfur tolerant steam reforming, autothermal reforming and water gas shift catalysts and the impact on reducing the fuel processor costs. Sulfur compounds react with base metal forming metal sulfides which are less active than the metal in steam reforming. For example the reactions of Ni with H_2S forming NiS or with Cu forming CuS significantly deactivate conventional catalysts. Our efforts in developing sulfur tolerant catalysts comprised of 1) replacing the base metals by noble metals; 2) replacing the conventional insulator oxide supports by oxides such as ceria, zirconia and titania and 3) identifying optimal operating conditions using sulfurized fuels.

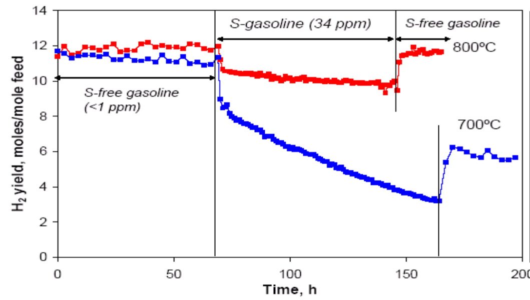
Results

Auto-thermal catalysts containing Pt, Rh supported on a reducible oxide were tested using low sulfur gasoline[2]. Figure 1 demonstrates the ability of the catalyst to tolerate sulfurized gasoline. By raising the temperature from 700 to 800 °C, the hydrogen yield is equal to un-sulfurized gasoline. Similar results were demonstrated using sulfurized diesel and natural gas.

HydrogenSource LLC demonstrated the sulfur tolerance of a Pt based WGS catalyst over thousands of hours of operation.[3] Figure 2 shows the stability of the WGS catalyst when exposed to sub-ppm levels of H_2S. While operating for up to 2000 hours the CO conversion was quite stable.

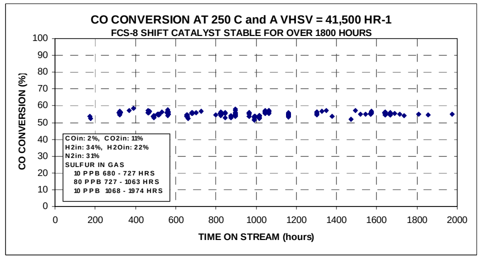
The combination of sulfur tolerant fuel processing and fuel cell electro-catalysts can significantly simplify the fuel processor therefore reducing the economic barriers needed for fuel cell commercialization.

Figure 1



Conditions: O_2:C=0.45, H_2O:C=2.0. GHSV= 50 000 h^{-1}.

Figure 2



References

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