Morphology dynamics of precious metal catalysts for use in steam reforming of oxygenated fuels

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Introduction

The advancement in liquid fuel production from biological sources will result in oxygenated fuel compositions. The presence of oxygen within the chemical makeup of the fuel is detrimental to the fuel's energy density. We have been exploring ethanol reforming as a test case to remove the oxygen functional groups. Initial results show for the first time that the oxidation state of catalytic Rh nanoparticles changes dynamically under reaction conditions with ethanol and appears to control catalyst activity and deactivation. Catalyst deactivation is one of the major challenges faced in fuel reforming and there exists a need not only to determine the primary causes, but model them in order to take preventative measures.

Through the use of common analytical techniques the surface morphology of the catalysts has been examined. Each formulation was calcined at various temperatures and characterized for their conformation. The extent of sintering of the precious metal catalysts as well as any changes in oxidation state are suspected to result in lower catalytic activity. This presentation will correlate and explain the active metal distribution and catalytic activity.

Materials and Methods

The rhodium-platinum catalysts were prepared via an incipient wetness impregnation technique. Highly porous silica-zirconia, used as the carrier, along with precious metal salt solutions were provided by BASF. Total metal loading of the carrier was held constant at 4 wt%. The ratio of rhodium to platinum was varied stepwise by 1 wt%, including catalysts composed of pure rhodium and pure platinum on the silica-zirconia carrier. 200-proof ethanol from EMD was used as the model fuel. Dispersion of the precious metals was quantified through CO chemisorption. XRD was used to determine any change to the crystal structure of the precious metals. SEM images were taken of catalysts exposed to various calcination temperatures for a visual representation of any morphological changes. Ethanol reforming experiments were performed in a packed bed continuous-flow reactor. The following conditions were used during each fuel reforming experiment: S/C = 1.5, GHSV = $44,000 \text{ h}^{-1}, 650^{\circ}\text{C}$, and 1 atm. Reaction products were quantified using an Agilent 3000A micro GC.

Results and Discussion

The measured dispersion of precious metal catalysts calcined at temperatures ranging from 550-950°C is shown in **Figure 1**. It was determined that the catalysts with a higher rhodium loading exhibited a greater dispersion of the precious metals. It should also be noted that the pure platinum on silica-zirconia maintained its measured dispersion at higher calcination temperatures.



Calcination Temperature (°C)

Figure 1. Dispersion of precious metals on silica-zirconia as a function of calcination temperature determined through CO chemisorption.

Initial activity data was taken for the reforming of ethanol on a 3 wt% Rh/1 wt% Pt on silicazirconia as shown in **Figure 2**.



Figure 2. Product distribution for the reforming of ethanol over 3 wt% Rh/1 wt% Pt on silicazirconia as a function of time on stream.

Significance

Near-equilibrium values of 4.05 mole% for the production of hydrogen were achieved for upwards of 85 hours on stream using this catalyst formulation. The presence of platinum in a primarily rhodium-containing catalyst enables us to achieve the maximum level of hydrogen production in the shortest amount of time.