Effect of Fuel Type and Sulfur Compound Variation on the Performance of Partial Oxidation Reforming Catalysts

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Introduction

Fuel reforming is important for the generation of hydrogen and CO for a range of applications, including solid oxide fuel cells (SOFCs), proton exchange membrane (PEM) fuel cells, and for vehicle emission control systems. The heavy hydrocarbon fuels used in mobile applications contain a range of sulfur compounds. It is important to know the impact of these compounds on reforming performance and how that performance depends on the fuel used. We have measured reformate (H_2+CO) generation by catalytic partial oxidation (CPO) over a Rh-based catalyst for a range of fuels from methane to low S diesel fuel. We have determined the performance impact by sulfur species, sulfur content, and their variation with fuel type. We have shown the reversibility of sulfur addition/removal and have speciated the exiting species.

Materials and Methods

The Rh-based catalysts used in this study were washcoated onto zirconia toughened alumina (ZTA) foams or ceramic monolith supports. Catalysts, typically 1" long, were placed in a 1" OD cylindrical quartz reactor within a furnace. The fuels were methane, propane, isooctane (IO), California Phase II gasoline, dodecane, and Swedish city diesel fuel. For isooctane and several other fuels we have added sulfur compounds up to 2000 wppmS, including SO_2, and several aromatic compounds found in logistic fuels (thiophene [C_4H_5S], benzothiophene [C_8H_6S], and dibenzothiophene (DBT) [$C_{12}H_8S$]). To see the effect of aromaticity alone the structural analog of DBT, fluorene [$C_{13}H_{10}$], was also added. Bench analyzers, a GC, and both an electron-excited and a chemical ionization mass spectrometer measured products. Mass balances were obtained within 1%. The O/C ratio was held at 1.07 for all fuels; typical space velocities were 50,000 h^{-1}, although this was varied in other studies. Catalysts were tested in a de-greened "fresh" state or after baking six hours in air at 1200 ºC.

Results and Discussion

For tests with several sulfur compounds, S and hydrocarbon species exiting the reactor were determined. In all cases from SO_2 to dibenzothiophene, the predominant sulfur species was H_2S, in agreement with equilibrium modeling. Fig.1 shows the drop in H_2 concentration from 0 to 500 wppmS of each compound. In these experiments, each data point was collected 10 minutes after a step change in sulfur content. The curve is non-linear with the initial sulfur quantities having the largest effect and saturation occurring after 300 wppm S for all compounds. The impact scales with sulfur content, not with sulfur compound or aromatic concentration. The DBT analog compound, three-ringed fluorene, had no negative effect. When sulfur was removed from the feed, the effect of sulfur was found to be highly reversible. All of the data were consistent with the S concentration being in adsorption-desorption

equilibrium at the surface, where it blocks active sites. The exit temperature of the catalyst rose with increasing sulfur content, consistent with its poisoning endothermic steam reforming, one of the main pathways to H_2 formation, after the initial formation of CO_2 and H_2O. These results imply that the S compounds are completely dissociated by the catalyst at these 700-1000 ºC operating temperatures and that aromatic compounds, or their cracking products, compete with sulfur for adsorption sites on the catalyst surface. Additionally, aromatic compounds do not inhibit hydrogen-forming reactions, as demonstrated by the results with fluorene addition.
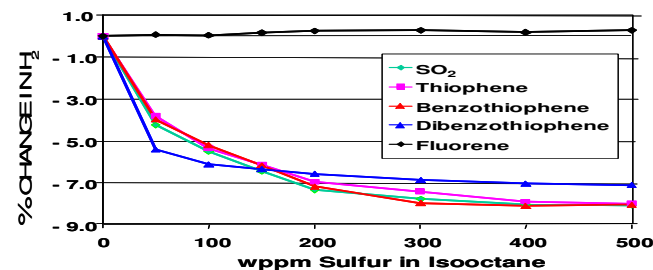

Figure 1. Effect of four S compounds on the CPO of isooctane, showing the absolute % drop from the 27% H_2 level for zero S to ~19% for 500 wppmS, a 30% drop. Flourene, a carbon-only structural analog of dibenzothiophene, has no impact.

To examine the effect of fuel variation, Fig. 2 shows the effect of adding 0 to 100 ppm of SO_2 in the five fuels shown, CH_4, C_3H_8, IO, IO with added aromatics to achieve the C/H ratio of gasoline, and CA Ph II gasoline. What is clear from this plot is that increasing both the molecular weight and the aromaticity make the fuel more sulfur tolerant for H_2 generation.
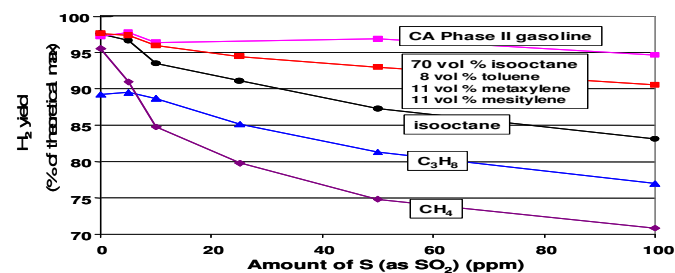

Figure 2. Effect of S on H_2 yield (% of theoretical maximum) compared for five fuels. The impact is largest for CH_4 & smallest for fuels with aromatic content, such as CA Ph II gasoline.

Significance

The effects of fuel sulfur on Rh-based reformer operation are highly reversible, limited at high levels of S, and very manageable at current sulfur levels (≤ 30 ppm) in transportation fuels.