

INFLUENCE OF SULFUR AND THERMAL AGING ON MECHANISMS OF REFORMING CATALYST DEACTIVATION

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Introduction

Fuel reforming is currently employed for engine-out emissions reductions and SOFC fuel cell power units. In this process a fuel-oxidant mixture is catalytically converted into a gaseous reformate containing significant amounts of H₂ and CO. Unlike automotive 3-way catalysts, fuel reforming catalysts can be subjected to continuous operating temperatures in excess of 1000 °C. These high temperatures lead to a variety of degradation mechanisms and represent a significant challenge in meeting durability requirements. Additionally, the fuels can contain variable levels of sulfur, which can lead to increased rates of degradation. Mitigation of these degradation mechanisms is important if durability requirements are to be met. We are currently involved in understanding how thermal and chemical degradation, brought on by exposure to sulfur and/or high reforming temperatures, influence the global kinetic behavior of rhodium-based fuel reforming catalysts, and in turn, catalyst performance.

Materials and Methods

Rhodium/alpha-alumina was washcoated onto ceramic foams and monoliths, or planar metallic substrates. Tubular or planar reactors were used in partial oxidation (POx) or autothermal (ATR) modes. Fuels employed were methane or low-sulfur diesel. Oxygen to Carbon (O/C) ratio for POx reforming tests varied between 1.07 or 1.30; POx space velocity varied from 84,000 - 97,000/hr. ATR was operated with a feed composition of 39.9 % N₂, 4.5 % CO, 5.9 % CO₂, 9.5 % H₂, 21.8 % CH₄, 7.2 % O₂, and 11.2 % H₂O, at space velocities from 62,800 – 125,000/hr. The feed composition for the ATR reforming tests were representative of a blend of SOFC anode exhaust products and fresh air under a representative operating condition. Gaseous reactant products were analyzed by TCD and FID detectors fitted onto gas chromatographs, or by low- or medium-energy chemical ionization mass spectroscopy (CMIS). In some cases, prior to gas analysis, product water was collected and measured. Typical mass balances were closed to within 1%, with no evidence of accumulation of material in the catalyst or reactor system. Catalysts were tested in their fresh state, after reactor aging for 2000 hours in POx mode, after thermal aging at 1200 °C for six hours in air, or in the fresh state with added Sulfur. Sulfur addition comprised 100 ppm S, as SO₂, for diesel fuel POx, or 23 ppm S, added as H₂S, for CH₄ ATR. For each operating mode, reactant product concentrations were measured over a range of operating temperatures, controlled by a furnace.

Results and Discussion

The planar reactor operates in the absence of transport limitations – conversion were limited by either chemical equilibrium or reaction rate; data from this configuration was used to determine global reaction kinetics for both POx and ATR modes. Compared to a fresh catalyst, the

reactor aged catalyst was found to deactivate through loss of active sites, as both the fresh and used catalysts have the same activation energy in the reaction rate limiting operating regime, at O/C 1.30, (i.e., parallel slope on a ln k vs. 1/T plot) Figure 1a. When tested at O/C 1.07, both the fresh and aged catalysts transitioned into a transport rate limiting regime at higher temperatures, as shown by the change to a lesser slope at higher temperatures in Figure 1b.

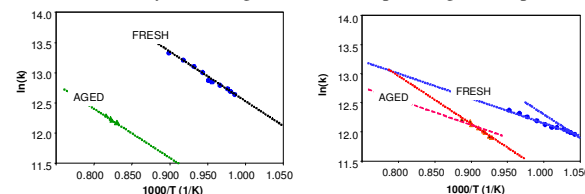


Figure 1 Methane partial oxidation kinetics for fresh and reactor aged catalysts at O/C 1.30 (left), purely reaction rate limited, and 1.07 (right), transitioning from rate to transport limited.

The presence of sulfur, whether in the POx or ATR mode, was found to reduce the number of active sites, and consequently conversions to H₂ and CO, but without changing the rate limiting mechanism. Measurements of reformate product compositions by medium-energy mass spectrometry show that the major and minor reaction products have the same relative concentrations, regardless if the catalyst was fresh, tested in the presence of sulfur, or aged, Figure 2. Additional work has shown that the effects of sulfur on fuel reforming conversion are reversible provided that no thermal aging has occurred on the catalyst.

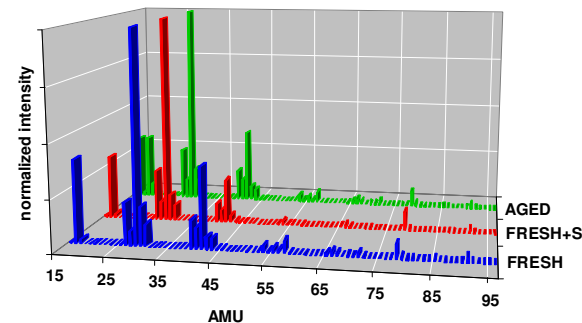


Figure 2. Medium-energy CMIS analysis of reformate product from POx of diesel fuel over fresh and aged catalysts with or without added sulfur to the fuel.

Significance

Taken together, these results suggest that sulfur and thermal aging inhibit fuel reforming reactions in a similar manner - by reducing the active sites. Given that the effects of sulfur are similar regardless of fuel or operating mode may indicate that sulfur is most impacting those active sites responsible for CH₄ activation or H₂ formation – however, more detailed kinetic characterization would be needed to support this argument.