

## Development of Novel Sulfur Tolerant Catalysts for Heavy Fuel Reforming

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### Introduction

Development of highly active and sulfur tolerant catalysts are required for the reforming of logistic fuels to produce hydrogen for solid oxide fuel cell auxiliary power systems (SOFC-APUs) in trucks. A typical SOFC operates at nearly the same temperature as conventional fuel reformers, providing good opportunities for heat integration. For example, it is reported that a 33% increase in engine idling efficiency can be achieved using an SOFC-APU unit compared to an existing diesel APU unit [1]. Steam reforming remains an attractive processes for the conversion of diesel and logistics fuel because of the high yield and concentration of hydrogen in the effluent gas [2, 3, 4]. However, catalyst deactivation from sulfur poisoning and coke formation remains as challenges to successful implementation. In the present study, we have evaluated a number of catalyst formulations that combine high reforming activity with improved sulfur tolerance, to provide a stable catalyst for reforming of sulfur-containing fuels.

### Materials and Methods

Catalysts were prepared from a commercially available support with active metals added through wet impregnation. The catalyst was calcined in air for 5 hrs at 800°C. Catalysts NCAT1 and NCAT3 were unmodified noble metal catalysts, while catalysts NCAT2=NCAT1+modifier, NCAT4=NCAT3+modifier and NM4 is an alternate version of NCAT4 where we modified the metal impregnation procedure. The catalyst was reduced prior to reaction for 2 hrs using 5% H<sub>2</sub> in nitrogen mixture. All reactions were carried out at 800°C at a steam to carbon ratio of 5 and 25-250 ppm sulfur content of the fuel. Thiophene doped n-hexadecane was used as a surrogate for diesel fuel. The effluent from the reactor was separated into liquid and non condensable gas products and analyzed using Shimadzu 2010 gas chromatograph equipped with pulsed discharge ionization detector.

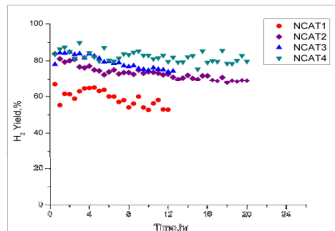


Figure 1: Performance of trial catalyst at S/C=5, T=800°C, S=25ppm

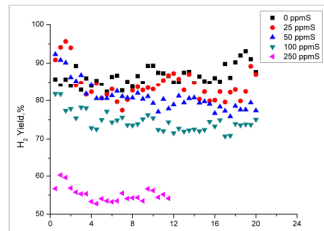


Figure 2: Performance of NM4 with increasing sulfur loading in fuel

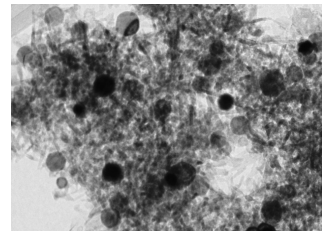


Figure 3: TEM image of used NM4 after reaction at 50 ppm S.

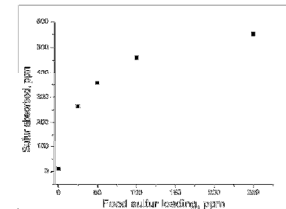


Figure 4: ICP analysis of used catalyst for adsorbed sulfur after reaction.

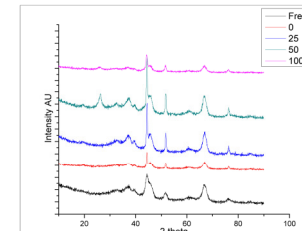


Figure 5: XRD of fresh and used NM4

### Results and Discussion:

Figure 1 indicates that catalyst NCAT4 was the most stable of those catalysts evaluated at 25 ppm sulfur. Further analysis at higher sulfur loadings (Figure 2) indicated an initial 5 hrs of deactivation, followed by roughly stable performance for an additional 15 hrs. Increasing the sulfur concentration in the fuel gave increasingly poor performance, but even at 250 ppm sulfur, NM4 gave greater than 50% hydrogen yield for 12 hrs. These results are consistent with the studies done on the steam reforming of trimethylpentane [5] that show a similar decrease in the hydrogen yield with increasing sulfur loading.

Increase in the catalyst particle diameter, coke formation, and sulfur accumulation were some of the mechanisms considered to describe the catalyst deactivation. TEM images (Figure 3) of used catalyst showed an average increase in the catalyst particle diameter from 5 nm to 25 nm following reaction at all sulfur concentrations tested, suggesting that sintering is likely a result of high temperature operation and occurs independent of the presence of sulfur in the fuel. The ICP analysis (Figure 4) of used catalyst showed the increased accumulation of sulfur in the catalyst matrix with increasing sulfur loadings in the feed. XRD (Figure 5) analysis showed the formation of coke on catalyst surface at both 50 and 100 ppm sulfur loading. This implies that higher sulfur loadings (>25ppm) promote coke formation during steam reforming. This might be due to increase in the surface acidity of the catalyst in the presence of higher concentration of sulfur in the feed leading to coke formation [5].

### Significance

Fuel cell technology has good potential for addressing many energy needs, but requires a catalyst capable of operating on high sulfur logistics fuels. The current work describes the analysis of a selected sulfur-tolerant catalyst, and characterizes the mechanisms of deactivation underway during reforming of sulfur-containing fuels.

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