

# Structural Changes of a Ni/Mg/K/Al<sub>2</sub>O<sub>3</sub> Catalyst Used for Multiple Cycles of Steam Reforming Gasified Biomass

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## Introduction

Environmental, economic, and sustainability concerns make it desirable to decrease the world's dependence on fossil fuels for its energy demands. There is currently interest in displacing petroleum-based transportation fuels with renewable, liquid fuels. The utilization of cellulosic biomass to create fuels such as ethanol or Fischer-Tropsch liquids is receiving significant research attention. The conversion of biomass to liquid fuels may employ gasification as the first step, which produces a crude syngas that must undergo further conditioning before it is suitable for liquid fuel synthesis [1]. Steam reforming of biomass-derived syngas helps to utilize the carbon and hydrogen content of hydrocarbons and tars, as well as protect downstream equipment and catalysts [2]. These steam reforming catalysts generally have limited lifetimes due to deactivation by coking and sulfur poisoning [3]. In this study, a series of catalysts was collected and characterized over the course of ten reaction cycles for steam reforming of gasified biomass to identify processes leading to deactivation and aid in the design of improved catalysts and processing conditions.

## Materials and Methods

A catalyst was prepared by aqueous impregnation of 6.1wt% Ni, 2.4wt% Mg, and 3.9wt% K to an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> based fluidizable support using nitrate salts, followed by calcination in air at 650 °C. The catalyst was then used in a pilot plant study for steam reforming of gasified biomass. Oak pellets (15 kg/h) and steam (15 kg/h) were fed to a gasifier (700 °C) containing olivine and the resulting gas then went to a thermal cracker (850 °C). This gas stream was sent to a fluidized bed reactor at 850 °C containing 60 kg of the Ni/Mg/K/Al<sub>2</sub>O<sub>3</sub> catalyst with a GHSV ~5000 h<sup>-1</sup>. During the pilot plant operation of this catalyst, ten (10) reaction cycles were conducted. During each reaction cycle a catalyst was denoted as oxidized, reduced, or post-reaction. Oxidized samples were reduced in H<sub>2</sub> at 850 °C to produce the reduced samples. The reduced samples were exposed to process gas until the CH<sub>4</sub> conversion dropped below 50% to produce the post-reaction samples. The post-reaction samples were regenerated offline by exposure to steam at 850 °C to produce the next oxidized samples in the series. At each step in the process, 5-10 g of catalyst was collected, providing a series of nearly 30 samples over the stages of the catalyst's life. The catalysts collected from the pilot plant were examined using characterization techniques that including X-ray diffraction (XRD), H<sub>2</sub> temperature-programmed reduction (TPR), X-ray photoelectron spectroscopy (XPS), and thermal cycling experiments on fresh catalyst samples.

## Results and Discussion

During the pilot plant reforming study, loss of activity was observed during each reaction cycle, which was mainly attributed to deactivation by H<sub>2</sub>S which was present at 40 ppm in the feed gas. When the catalyst was regenerated through steaming, the activity was only partially recovered. Figure 1 shows the maximum CH<sub>4</sub> conversion for each reaction

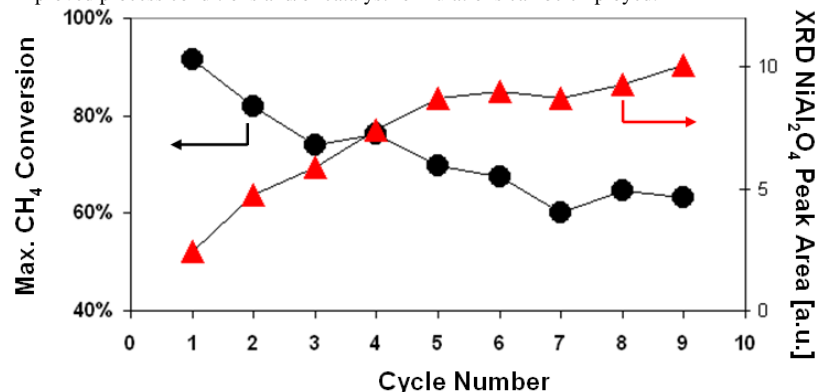
cycle, which occurred in the first few minutes. The trend shows the general decrease in catalyst activity, as denoted by the maximum CH<sub>4</sub> conversion, with subsequent catalyst regenerations.

Analysis of the bulk catalyst structures by XRD indicates that NiO and Ni<sup>0</sup> were fully reduced and oxidized, respectively, by the reduction and oxidation/regeneration processes. As the sample aged, an increase in intensity of a NiAl<sub>2</sub>O<sub>4</sub> diffraction peak was observed, and the NiAl<sub>2</sub>O<sub>4</sub> phase was present in all of the catalyst samples (oxidized, reduced, and post-reaction). Figure 1 shows the integrated area of the NiAl<sub>2</sub>O<sub>4</sub> peak near 65.5° 2 $\theta$  on the reduced catalyst samples. The NiAl<sub>2</sub>O<sub>4</sub> content of the reduced samples increased and started to reach a plateau. Analysis of the oxidized catalyst by H<sub>2</sub> TPR showed a decrease in H<sub>2</sub> consumption as the catalyst aged.

The increase in NiAl<sub>2</sub>O<sub>4</sub> as shown by XRD correlated with the loss of initial activity in the pilot plant reforming study and the amount of reducible metal species as determined by TPR. During the treatments to which the catalyst is exposed, the formation and inability to reduce NiAl<sub>2</sub>O<sub>4</sub> may be attributed to the loss in initial activity for subsequent reaction cycles.

## Significance

Effective tar reforming catalysts are needed for the synthesis of liquid fuels from biomass. By understanding the deactivation routes that are leading to loss of catalyst activity, improved process conditions and/or catalyst formulations can be employed.



**Figure 1.** Maximum methane conversion (●) and NiAl<sub>2</sub>O<sub>4</sub> peak area at 65.5° 2 $\theta$  from XRD (▲) as a function of catalyst cycle number.

## References

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