

Transformation of Sulfur Species on Regenerated Nickel Catalysts used for Biomass-syngas Conditioning

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Introduction

For the syngas conditioning catalysts used for hydrocarbon/tar steam reforming, short lifetimes are an obstacle that leads to high cost of the finished fuel product [1]. While there are many components of syngas that can contribute to catalyst deactivation, hydrogen sulfide (H₂S) is generally considered to be one of the most severe poisons. In order to overcome this deactivation challenge, it would be beneficial to have a catalyst that is either i) resistant to deactivation, ii) can be readily regenerated, or iii) both. In the present work, we report the first direct evidence of sulfur surface chemistry during catalyst regeneration cycles on a Ni tar reforming catalysts used in real biomass-derived syngas with ~ 50 ppm H₂S. These groundbreaking results, in the context of previous results for these samples, demonstrate the importance of the regeneration protocols, which we are in the process of developing.

Materials and Methods

A commercial, attrition resistant support (AD90) composed of 90% α -Al₂O₃ with surface area of 1 m²/g was used to prepare a 6.1%Ni/2.4%Mg/3.9%K/AD90 support was prepared via aqueous impregnation and air calcination at 900°C. This catalyst was used for conditioning of biomass-derived syngas at 900°C and regenerated at 850°C using H₂O/O₂ followed by H₂ reduction [2]. XRD, H₂ TPR, and Ni K-edge EXAFS were conducted on the samples [2,3]. Sulfur K-edge XANES was performed at the Stanford Synchrotron Radiation Lightsource on fresh and spent catalyst samples. The energy range collected was from 2440-2600 eV, with 0.1 eV steps from 2460-2483, using a fluorescence detector.

Results and Discussion

Previous work has been done on a Ni-Mg-K/Al₂O₃ catalyst for conditioning of syngas created from gasification of oak pellets [2]. This catalyst was used for several cycles of syngas reforming, followed by steam/air regeneration. Table 1 shows maximum methane conversion and % reducibility of these catalysts samples for each reaction cycle. From these results, it is apparent that regeneration partially restored activity with respect to maximum methane conversion. This decrease in activity was attributed to the formation of nickel phases that were not reduced in the regeneration protocol (e.g. NiAl₂O₄), as monitored via TPR and XRD [2]. Further investigation by Ni K-edge EXAFS indicated that the formation of oxide and/or sulfur phases occurred on the spent catalyst [3]. While XRD results showed the presence an oxidized nickel phase [2], there was no evidence of a sulfur phase.

In order to understand how/if sulfur interacted with the catalyst during reaction and regeneration schemes, sulfur K-edge XANES was performed on spent catalysts from both lab-scale and pilot plant reactions. Figure 1 shows sulfur K-edge XANES spectra for several catalyst samples, along with the dashed lines for reference sulfide (NiS) and sulfate (CaSO₄).

The fresh sample shows no sulfur species and, following reaction, the formation of a clear sulfide phase was found, along with some sulfate species. Regeneration with steam removed sulfides and led to the formation of sulfates. A regeneration mechanism for nickel sulfides with steam is: NiS + H₂O → NiO + H₂S. While H₂S was observed in the reactor effluent during regeneration, it is evident that this treatment also led to transformation of some of the sulfides into sulfate species. Following steam regeneration, this catalyst was reduced in H₂, which was shown to partially reduce the sulfates back to sulfide. When exposed to another cycle of reaction testing, sulfides were the most prominent of the sulfur species. This work will be presented in the context of activity measurements and additional characterization.

Table 1. Maximum methane conversion during each reaction cycle and % reducibility of the catalysts based on H₂ consumption during TPR.

Reaction Cycle #	1	2	3	4	5	6	7	8	9	10
X _{CH₄,max} (%)	91	82	74	76	70	68	60	65	63	58
Reducibility (%)	94	88	85	68	59	62	-	53	53	47

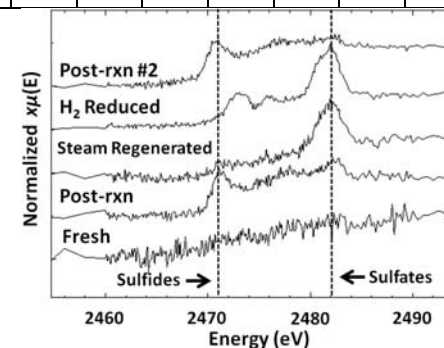


Figure 1. Sulfur K-edge XANES on a Ni-Mg-K catalyst used for conditioning biomass-derived syngas, following various regeneration protocols. Energies for reference sulfide and sulfate materials shown with dashed lines.

Significance

Short lifetimes are a concern for catalysts used for conditioning biomass-derived syngas prior to the synthesis of liquid fuels. Understanding how regeneration affects sulfur species found on the catalyst will lead to improved processes and conditions to more completely regenerate catalysts and thus, decrease production prices for syngas-derived biofuels.

References

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