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Transformation of Sulfur Species during Steam/Air Regeneration on a Ni Biomass Conditioning Catalyst

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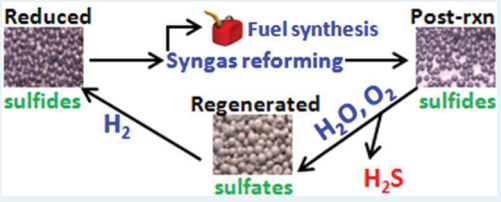
ABSTRACT: Sulfur K-edge XANES identified transformation of sulfides to sulfates during combined steam and air regeneration on a Ni/Mg/K/Al_2O_3 catalyst used to condition biomass-derived syngas. This catalyst was tested over multiple reaction/regeneration/reduction cycles. Postreaction catalysts showed the presence of sulfides on H_2S-poisoned sites. Although H_2S was observed to leave the catalyst bed during regeneration, sulfur remained on the catalyst, and a transformation from sulfides to sulfates was observed. Following the oxidative regeneration, the subsequent H_2 reduction led to a partial reduction of sulfates back to sulfides, indicating the difficulty and sensitivity in achieving complete sulfur removal during regeneration for biomass-conditioning catalysts.



KEYWORDS: *XANES, nickel, biomass, sulfates, sulfides, regeneration*

1. INTRODUCTION

Catalyst deactivation and regeneration must be addressed during development of an industrially viable catalyst. These issues are especially relevant in the development of syngas conditioning catalysts used for hydrocarbon and tar reforming, which removes problematic tars and improves carbon efficiency. Although base metal catalysts, such as nickel, are desirable due to their low cost relative to precious metal catalysts, they are susceptible to deactivation during conditioning of biomass-derived syngas by impurities in the feedstocks.[1] Sulfur-containing species, particularly H_2S, are common catalyst deactivating agents due to the strong chemisorption of sulfur to nickel.[2,3] Biomass-derived syngas may contain 20−600 ppmv H_2S,[4−6] which results in the deactivation of Ni sites in conditioning catalysts. Therefore, the development of efficient regeneration protocols is necessary for reforming of hydrocarbons in biomass-derived syngas.

Regeneration protocols for sulfur-poisoned nickel, involving steaming to remove sulfur as H_2S and subsequent reduction in H_2 to reduce NiO to metallic Ni, have been developed and used for reforming catalysts.[7] These techniques have had some success[7] and refinement of the regeneration protocol to decrease the cycle time (i.e., to reduce process downtime), although these may come at the expense of using high operating temperatures that are detrimental to process economics and have other potentially negative impacts on catalyst properties, such as active metal dispersion.[8] A recent study by Li et al. examines various regeneration protocols used for sulfur-poisoned nickel catalysts and shows that there is a great deal of sensitivity to molar ratios of gas components and even flow rates/space velocities.[8] In addition, Li et al. reported a regeneration scheme to remove sulfur from poisoned-Ni catalysts involving a four-step process consisting of (i) controlled oxidation, (ii) thermal decomposition in inert gas, (iii) H_2-reduction, and (iv) reaction in H_2S-free syngas.[8] Although there have been previous studies on regeneration of sulfur-poisoned catalysts, the chemical transformations happening between sulfur and nickel have not been fully observed using the available analytical techniques. Being able to identify these chemical transformations during regeneration can aid in the improvement of regeneration protocols.

The observation of sulfur and nickel species is possible through spectroscopic techniques, including laser Raman spectroscopy,[9−12] X-ray photoelectron spectroscopy (XPS),[10] and X-ray absorption near edge spectroscopy (XANES).[13,14] Each technique has its strengths and weaknesses. For example, depending on the system configuration, Raman spectroscopy is largely a bulk technique and also may not be sensitive enough to detect trace levels of sulfur on a catalyst surface. XPS is surface-sensitive, but requires high surface compositions for detection and is not the preferred method for trace element analysis. The challenge of routinely using XANES is that it requires access to specific equipment at a synchrotron facility. Despite this, XANES is a robust technique capable of unraveling complex material systems, including the one currently under investigation, and is able to differentiate among different species and oxidation states. Chen et al. successfully used XANES to monitor and describe sulfur poisoning mechanisms on Ni and Rh catalysts and were able to identify sulfide, sulfite, and sulfate species.[13] After attempting several techniques[1] (XRD, Raman spectroscopy, energy dispersive spectroscopy, and XPS) to look at sulfur species on postreaction catalysts, we were only able to successfully identify sulfur using XANES. Building on the work by Chen et

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al.[13] and to gain insight into improving regeneration protocols, we aimed to identify if sulfur remained on the biomass-conditioning catalysts following regeneration and determine how the regeneration procedures involving H_2O and $H_2O + O_2$ treatments affected the sulfur species.

2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis and Characterization. A commercial, attrition-resistant support (AD90) composed of 90% α-Al_2O_3 was used to prepare a 6.1% Ni/2.4% Mg/3.9% K/AD90 catalyst via aqueous impregnation and air calcination at 900 °C as previously described.[1] This catalyst was used for conditioning of biomass-derived syngas at 900 °C and regenerated at 850 °C using H_2O/O_2, followed by H_2 reduction.[1] Several other characterization methods, including XRD, H_2 TPR, and Ni K-edge EXAFS were conducted on the samples, and the results have been reported.[1,15] TPR experiments were conducted on 100 mg of catalyst, using 35 sccm of 10% H_2/Ar and heating at 10 K/min from 50 to 850 °C, with a 30 min hold.

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 to 2600 eV, with 0.1 eV steps from 2460 to 2483 and 2 eV steps outside that range, using a four-element Si drift detector. Merging of individual scans and data reduction were performed with the Athena software package.[16,17] Reference materials of nickel sulfide (NiS), nickel sulfide (Ni_3S_2), sodium sulfite (Na_2SO_3), and calcium sulfate ($CaSO_4$) were analyzed using S K-edge XANES. The XANES spectra of the reference materials showed clear white lines for sulfides (2472 eV), sulfites (2478 eV), and sulfates (2483 eV). These spectra were used for assignments of sulfur species on the catalyst samples along with literature values,[18] but they were not used as quantitative calibration standards.

2.2. Reaction Testing and Regeneration. A more detailed description of the pilot-scale reaction experiments, apparatus, and procedures has been previously reported.[1] The raw syngas stream used in the experiments was generated by indirect steam gasification of white oak. Crushed white oak pellets (which contain 125 ppm sulfur in dry basis) were fed at a rate of 15 kg/h along with 15 kg/h of vaporized H_2O into an 8-in. i.d. fluidized bed reactor filled with olivine at 700 °C. The vapors leaving the gasifier were then sent through a thermal cracker operating at 850 °C to crack the primary pyrolysis products into less complex secondary products and raw syngas. This resulted in a steam-to-total-carbon ratio of ∼2 or, neglecting the contribution of CO and CO_2, a steam-to-reactive-carbon ratio of ∼7,[1] with reactive carbon being defined as hydrocarbons and tars. Following the thermal cracker, cyclones were used to remove solids (e.g., char, ash), and the gas phase products were sent to a 14-in. i.d. fluidized bed reactor loaded with 60 kg of the reforming catalyst, where tars and hydrocarbons could undergo steam reforming to produce additional syngas. Ar and He were added to the gas stream as inert tracer gases. A molecular beam mass spectrometer was used to sample this stream and measure tar compositions both before and after the reactor. The gas stream was then sent to a scrubbing unit, where cooled dodecane condensed steam and any remaining tar vapors. Following the scrubber, the composition of the gas stream was measured using Varian gas chromatographs (GCs) and nondispersive infrared (NDIR) detectors before being sent to a thermal oxidizer/vent. The total gas flow was calculated using helium as an internal standard from its measured concentration and its known molar flow. During the start-up of each reaction cycle, the catalyst reactor was flushed with 1 kg/h N_2 while the process gas leaving the gasifier was diverted and allowed to reach a steady gas composition. The catalyst was kept online until the conversion levels for CH_4, benzene, or both fell below the technical targets for the experiment, which were conversion of $CH_4 \geq 50\%$, $C_6H_6 \geq 90\%$, and heavy tars ≥ 97%.

Steam/air regeneration and H_2 reduction steps were conducted following raw syngas reforming. Steam (15 kg/h) and nitrogen (3 kg/h) were sent to the reactor at 850 °C, and air was slowly introduced to the stream over the course of ∼2 h to obtain the final air flow (0.39 kg/h). The oxidant combination of H_2O and O_2 was used to regenerate the catalysts by the removal of sulfur poisoned metal sites ($M-S + H_2O \leftrightarrow M-O + H_2S$) and oxidization of residual carbon/coke ($C + O_2 \rightarrow CO_2$). The gas phase products leaving the reactor were monitored, and the regeneration procedure continued for 1−1.5 h beyond the time at which H_2S was no longer detected at the reactor outlet (7−10 h). Measurement of H_2S concentrations could be reliably performed down to a concentration of 2 ppm. After $H_2O + O_2$ regeneration, the catalyst was reduced at 850 °C by exposure to H_2 (0.11 kg/h) and N_2 (11 kg/h) until no further H_2 uptake was measured with the GC and NDIR detectors (∼8 h). Catalyst samples (∼8−10 g) were taken after each of the reactions, $H_2O + O_2$ regeneration, and reduction processes (except for the one following the seventh regeneration), which resulted in <0.5 wt % total catalyst loss via sampling from the original catalyst bed (60 kg). The change in catalyst mass in the reactor was assumed to be negligible during the course of the experiment. Because the catalyst was operated in a fluidized-bed reactor, it was assumed that, on average, the catalyst in the reactor was well-mixed, and it all experienced the same reaction conditions, such that the 10 g catalyst samples were representative of the catalyst within the entire reactor. A summary of the conditions used for the pilot-scale reforming reactions are shown in Table 1.

Table 1. Process Conditions during Reaction, $H_2O + O_2$ Regeneration, and H_2 Reduction

process	T (°C)	feed conditions
syngas reforming[a]	900	15 kg/h H_2O, 15 kg/h oak pellets,[a] 1 kg/h N_2
$H_2O + O_2$ regeneration	850	15 kg/h H_2O, 3 kg/h N_2, ramp from 0 to 5 SLM air
H_2 reduction	850	11 kg/h N_2, 20 SLM H_2

[a]Syngas composition of main constituents (dry, N_2-free, vol %): 33% H_2, 24% CO, 22% CO_2, 13% CH_4, 3.2% C_2H_4, 43 ppm H_2S, 14 000 mg/Nm^3 total tar (MW > 78), and 1% He (tracer).

Bench-scale catalyst reforming experiments were conducted on a microactivity test system using model syngas with H_2S to create a series of catalysts that underwent various regeneration treatments. The reforming cycles were conducted at 900 °C, GHSV of 119 000 h^{-1}, and steam-to-carbon (S/C) of 7, which corresponded to 62% H_2O in the gas phase over the catalyst bed for 60 min. The simulated syngas (dry basis) had a composition of 30% H_2, 30% CO, 18.5% CO_2, 15% CH_4, 6.4% C_2H_4, 600 ppm C_6H_6, and 53 ppm H_2S. Regeneration was conducted with the same H_2O content as during the reforming

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reaction for 60 min at 850 °C and total GHSV of 114 000 h^{-1}. Bench-scale regeneration was with H_2O, without the addition of O_2. Following H_2O regeneration, H_2 reduction was performed at 850 °C in 28% H_2/N_2 for 60 min to reactivate the catalyst. This approach simulated pilot scale reforming via sequential reforming and regeneration cycles with H_2S-containing, oak-derived syngas.

3. RESULTS AND DISCUSSION

3.1. Syngas Conditioning Reactions. The CH_4 conversion during the first two reforming cycles is shown in Figure 1. Conversion of other species, such as benzene and tars, has

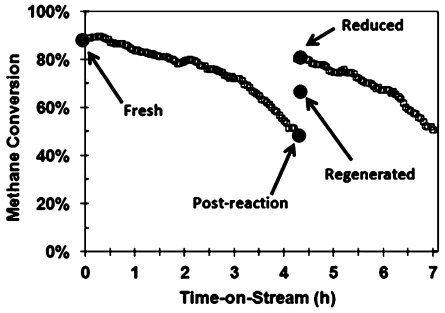

Figure 1. Methane conversion during the first cycle of pilot-scale conditioning of biomass-derived syngas at 900 °C and locations where catalyst samples were obtained for XANES analysis.

been reported elsewhere and is not shown here because it is not a good indicator of activity due to high initial conversion levels that were observed.[1] Figure 1 also indicates where catalyst samples were obtained for sulfur XANES analysis (fresh, postreaction, regenerated, and reduced).

During the first 4 h of reaction, the CH_4 conversion decreased from 91% to 50%, which is mainly caused by H_2S poisoning, as determined by bench-scale control CH_4 steam reforming experiments with and without the presence of H_2S. When the catalyst had deactivated and a postreaction sample was obtained, the regeneration protocol was then performed. A catalyst sample was obtained following the $H_2O + O_2$ regeneration, and then the rest of the catalyst underwent H_2 reduction. Following H_2 reduction, another catalyst sample was obtained for XANES analysis. Figure 2 shows the gas concentrations of H_2S ($NiS + H_2O = H_2S + NiO$) and H_2

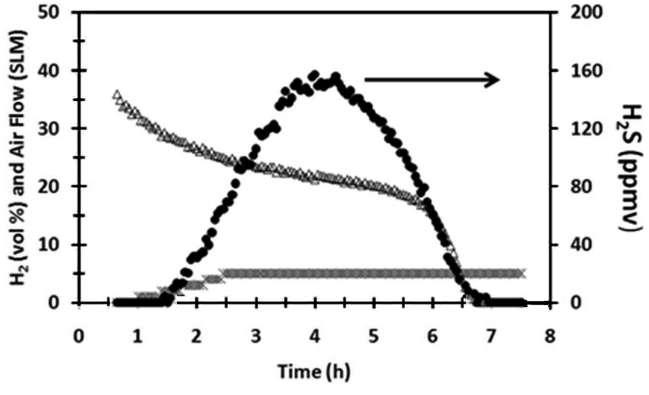

Figure 2. Produced gas concentrations of H_2S (●) and H_2 (Δ), as well as the air flow rate (X), during $H_2O + O_2$ regeneration of postreaction nickel catalyst at 850 °C (dry basis).

($Ni + H_2O = NiO + H_2$) produced during regeneration. The flow rate of air introduced to the reactor is also shown, and it was introduced to help remove any carbon deposits on the catalyst. The regeneration was carried out for 1 h beyond the point when H_2S could not longer be detected eluting from the reactor, which coincides with the decrease in H_2 generation, indicating that the metallic Ni had been oxidized to NiO. Integration of the H_2S leaving the reactor indicated that 0.4 (±0.2) mmol of H_2S/mol Ni left the reactor during each of the regeneration cycles.

XRD of reduced, postreaction, and regenerated samples was conducted and confirmed that the regeneration treatments converted metallic Ni to NiO (with $H_2O + O_2$) and then rereduced NiO to Ni (with H_2).[1] It was observed that the catalyst deactivated with increasing cycle number, as shown by the decrease in maximum CH_4 conversion during each of the ten reaction cycles displayed in Table 2. This loss of activity coincided with the decrease in the amount of reducible Ni as indicated by TPR (Table 2), which we have previously reported and may be correlated to the formation of an irreducible $NiAl_2O_4$ species.[1] Table 2 also shows an increase in the Ni crystallite size with time on-stream, indicating that sintering contributed to some of the loss of activity.

3.2. Sulfur XANES on Fresh and Spent Catalysts. The sulfur XANES spectra of the catalysts used for conditioning of oak-derived syngas are shown in Figure 3, which can be used in conjunction with Figure 1 to visualize the points within the process where the catalysts were sampled. The freshly reduced catalyst sample (Figure 3a) does not show the presence of any sulfur species, which is to be expected because the material had not been exposed to any sulfur-containing gases. After the catalyst had been exposed to syngas from biomass gasification and then collected (Figure 3b), a strong sulfide band (2472 eV) and an additional sulfate band (2482 eV) were observed. Because H_2S can react with metallic nickel to form nickel sulfide, leading to catalyst deactivation, of the presence of a sulfide on the postreaction catalyst confirmed the expected result. The presence of a sulfate band on the postreaction sample likely results from oxidation a sulfide species by H_2O, although it is not clear if the sulfate species are nickel sulfates, magnesium sulfates, potassium sulfates, or a combination of the species. When the catalyst was regenerated using a mixture of H_2O and O_2, sulfur (H_2S) was observed to leave the catalyst reactor (as shown in Figure 2).

When this regenerated catalyst was analyzed by XANES, it revealed that residual sulfur remained on the catalyst sample. The XANES spectrum of this regenerated catalyst (Figure 3c) shows little or no sulfide contribution, indicating that the treatment of the postreaction catalyst nearly fully removed or transformed the sulfides that were present on the catalyst. The sulfate feature in the XANES spectra, however, persisted between the postreaction and regenerated catalyst samples. As was shown with the reaction and regeneration results in Figure 1 and Figure 2, the regeneration protocol can successfully remove sulfur from the catalyst as H_2S, and the catalyst is able to recover a significant amount of its activity. The XANES analysis, however, shows that the $H_2O + O_2$ regeneration protocol can successfully remove sulfides, but residual sulfates remain on the catalyst. These sulfates are likely due to both (i) a portion of sulfates (which was observed on the postreaction sample) remaining on the catalyst and (ii) an oxidative transformation of sulfides to form sulfates. When the regenerated catalyst was subsequently reduced in H_2 (Figure

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Table 2. Maximum CH_4 Conversion, Reducibility As Determined by H_2 Consumption during TPR and Ni Crystallize Size Determined Using XRD and the Scherrer Equation during Each of Ten Reaction Cycles for Pilot-Scale Reforming of Biomass-Derived Syngas[1]

	reaction cycle									
	1	2	3	4	5	6	7	8	9	10
$X_{CH_4,max}$ (%)	91	82	74	76	70	68	60	65	63	58
reducibility (%)	94	88	85	68	59	62		53	53	47
Ni crystallite size (nm)	38(3)	38(3)	40(3)	38(3)	35(2)	42(3)	44(4)	53(5)	46(3)	

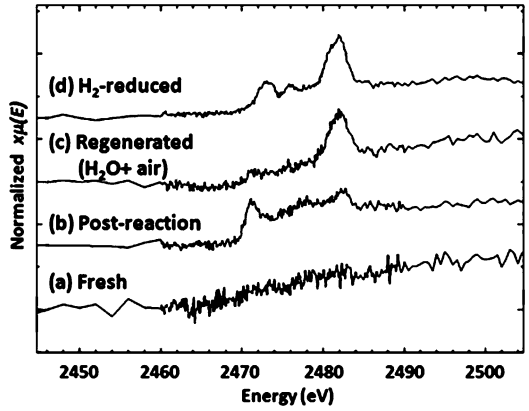

Figure 3. Sulfur K-edge XANES spectra of Ni/Mg/K/Al_2O_3 catalysts used for conditioning of oak-derived syngas at 900 °C and at various stages in the H_2O + O_2 regeneration and H_2-reduction processes at 850 °C.

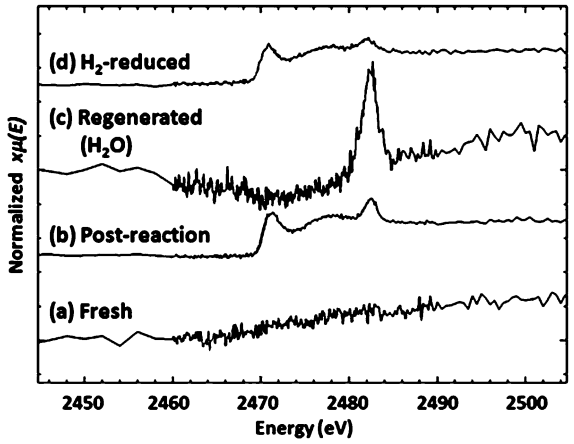

Figure 4. Sulfur K-edge XANES spectra of Ni/Mg/K/Al_2O_3 catalysts used for conditioning a model syngas spiked with H_2S at 900 °C and at various stages in the H_2O regeneration and H_2-reduction processes at 850 °C.

3d) to activate it prior to reaction, there was a partial reduction of the sulfate species to form sulfites (~2477 eV) and sulfides or elemental sulfur (~2473 eV), although the clear presence of sulfates remained.[18] These results indicate that, although sulfur in the form of sulfides is removed from the catalyst through oxidative treatment, a portion of the sulfur may remain as sulfates on the catalyst. A subsequent activation step can then result in readsorption of sulfur as sulfides when nickel becomes reduced.

The pilot-scale regeneration process utilized steam spiked with air to aid in removal of sulfur and carbon deposits on the catalyst, and as such, it was plausible that the air was responsible for the oxidation of sulfides to form sulfates. To test this theory, bench-scale reaction and regeneration experiments were conducted in which the regeneration was carried out in only H_2O, without the addition of O_2. The sulfur XANES spectra from the catalysts collected from these experiments are shown in Figure 4. It should be noted that the "fresh" catalyst spectrum is from the same catalyst for both Figures 3 and 4.

Similar to what was observed on the pilot-scale using biomass-derived syngas, the postreaction sample used on the bench scale showed strong sulfide and sulfate white lines (Figure 4b) after exposure to the model syngas stream. When this catalyst was regenerated using H_2O, the sulfide species were eliminated, though the clear presence of residual sulfates was observed (Figure 4c). The H_2-reduction of the regeneration catalyst was able to reduce some of the sulfates to sulfides (Figure 4d). Comparing spectra b and d of Figure 4 indicates that some sulfur has been removed through the regeneration process due to the higher signal-to-noise on the postreaction sample, but the same types of sulfur species remain. Although the addition of O_2 during the pilot-scale regeneration process could still be involved in the oxidation of sulfides to sulfates, these experiments indicate that the presence of H_2O alone can oxidize sulfides species on the catalyst to form stable sulfates that are difficult to remove.

4. CONCLUSIONS

Direct evidence of the sulfur species found during the reaction and regeneration steps on pilot-scale catalysts used for biomass-derived syngas conditioning was reported for the first time using sulfur K-edge XANES. The regeneration of sulfur-poisoned catalyst using a H_2O + O_2 regeneration protocol is effective at recovering catalytic activity; however, analysis of the catalyst at various stages within the reaction and regeneration protocol using XANES reveals that the treatment does not fully remove sulfur from the catalyst. The residual sulfur is a contributing factor in the incomplete regeneration of the catalyst, although other processes, such as sintering, phase transformation, and attrition, may also be involved. Regeneration by a H_2O + O_2 mixture resulted in (i) sulfur removal from the reactor in the form of H_2S, (ii) mostly complete sulfide removal from the catalyst surface, (iii) formation of sulfates on the catalyst surface, and (iv) oxidation of nickel species to NiO. Subsequent H_2 reduction led to the reduction of NiO to Ni, sulfates were reduced to sulfides, and some catalytic activity was restored. When a H_2O-only regeneration process was utilized, the same types of surface sulfur species were observed, indicating that the addition of O_2 during regeneration had a negligible effect on the chemistry of the sulfur species.

In summary, the regeneration treatment of H_2O + O_2 followed by H_2-reduction was capable of recovering a significant portion of catalyst activity and removing some sulfur from the catalyst bed, but a portion of the sulfur

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remained as a poison, transforming from sulfides to sulfates and back to sulfides in a cyclic process. Because short lifetimes are a concern for catalysts used for conditioning biomass-derived syngas prior to the synthesis of liquid fuels, further understanding of how regeneration affects sulfur species found on the catalyst will lead to improved processes and economics. To optimize the regeneration methods further and to obtain insights into the effectiveness of additional steps, such as decomposition under inert gas flow, it would be useful to use sulfur XANES to determine how new, proposed regeneration methods affect sulfur transformation and how they affect the completeness of sulfur removal.

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Notes

The authors declare no competing financial interest.

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