Deactivation and Regeneration of Ni Catalyst During Steam Reforming of Model Biogas: An experimental investigation

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Abstract

This paper presents detailed study of biogas reforming. Model biogas with different levels of H\textsubscript{2}S is subjected to reforming reaction over supported Ni catalyst in a fixed bed reactor at 700 °C and 800 °C. In order to understand the poisoning effects of H\textsubscript{2}S the reactions have been initially carried out without H\textsubscript{2}S in the feed stream. Three different H\textsubscript{2}S concentrations (20, 50 and 100 ppm) have been considered in the study. The H\textsubscript{2}O to CH\textsubscript{4} ratio is maintained in such a way that CO\textsubscript{2} also participates in the reforming reaction. After performing the poisoning studies, regeneration of the catalyst has been studied using three different techniques i) removal of H\textsubscript{2}S from the feed stream ii) temperature enhancement and iii) steam treatment. Poisoning at low temperature is not recoverable just by removal of H\textsubscript{2}S from the feed stream. However, poisoning at high temperature is easily reversed just by removal of H\textsubscript{2}S from the feed stream. Unlike some previous reports [1, 2], catalyst regeneration is achieved in shorter time frames for all the regeneration techniques attempted.

Keywords: Biogas, Steam Reforming, Catalyst Poisoning, Kinetics, Deactivation, Regeneration

1. Introduction

Bio-gas is an alternate fuel for synthesis gas production containing 50-75% CH\textsubscript{4}, 50-25% CO\textsubscript{2}, 0-10% N\textsubscript{2}, and 0-3% H\textsubscript{2}S. Due to the trivial nature of the anaerobic digestion process by which it is produced it can serve as a decentralized source of energy. The bio-gas thus produced can be converted into synthesis gas either by dry reforming or by a combination of dry and steam reforming using appropriate catalysts [3, 4]. Since the CH\textsubscript{4} to CO\textsubscript{2} ratio in bio-gas is \sim 1.5, dry reforming alone can lead to significant carbon deposition within the reactor [5]. Therefore, it is desirable to mix bio-gas with steam for reforming and generally the H\textsubscript{2}O to CH\textsubscript{4} ratio (S/C) is maintained at 3 to avoid any coke formation [6].

Biogas is an ideal gas for distributed power generation using Solid-Oxide Fuel Cells (SOFC), especially in areas that are not grid connected. The most interesting aspect of biogas fueled high temperature fuel cell system for power generation is the carbon neutral cycle. Although high temperature fuel cells such as SOFC can operate on hydrocarbon fuels without upstream fuel processing [7], in most cases the target fuel is either fully or partially reformed in an upstream fuel processor [8]. In an SOFC plant the fuel processor is connected to the SOFC stack with appropriate heat exchange and steam mixing. However, one of the major challenges in utilizing bio-gas for SOFC application is presence of H\textsubscript{2}S. H\textsubscript{2}S present the bio-gas easily deactivates Ni which is conventionally used in the anode of SOFCs. H\textsubscript{2}S content in the feed gas can be reduced by employing a desulfurization unit, however, this is economically less attractive for small scale distributed power generation using SOFCs.

There are several reports that investigate steam reforming of biogas [9, 10, 3]. However, these studies do not account for the presence of H\textsubscript{2}S, which is generally present in biogas. Biogas reforming without desulfurization will lead to catalyst deactivation due to sulfur poisoning. Sulfur poisoning of Ni and Pt has been studied widely, however, most of the transition metals lose catalytic activity in presence of H\textsubscript{2}S and other sulfur containing compounds [11]. Generally the deactivation of reforming catalyst is exponential in time and deactivation times ranging from 5 to 20 hours have been reported using time on stream analyses [12, 13]. The deactivation rate is faster when the H\textsubscript{2}S concentration is higher [13]. However, there are also reports which show a precipitous drop in the activity of the Ni catalyst on exposure to H\textsubscript{2}S [1].

The objective of this work is to study the deactivation and regeneration of Ni catalyst supported on γ-Al\textsubscript{2}O\textsubscript{3} (Ni/γ-Al\textsubscript{2}O\textsubscript{3}) during steam reforming of biogas containing ppm levels of H\textsubscript{2}S. Although several studies have been reported on the poisoning effect of sulfur on transition metal catalysts, majority of them have been performed using H\textsubscript{2}S diluted in H\textsubscript{2} or CO and H\textsubscript{2}O [14, 12, 15, 16]. Studying the poisoning effect of H\textsubscript{2}S on catalytic surface during reforming of hydrocarbon is more complex due to the competition among various molecules and
radicals for active sites. For instance the saturation coverage of H atoms on a catalytic surface is significantly affected by the partial pressure of CO in the gas mixture. To the best of our knowledge, the report by Ashrafi et al. [13] is the only one that addresses the time on stream effect of H2S during the steam reforming of biogas. Although not dealing with biogas, another report that looks into the effect of sulfur during the steam reforming of CH4 is by Li et al. [1]. However, this study contradicts with the report of Ashrafi et al. According to Li et al. deactivation of Ni/γ-Al2O3 due to H2S is instantaneous and the regeneration is a slow process, where as according to Ashrafi et al. both deactivation and regeneration are slow processes. Nevertheless, the major focus of the work by Li et al. is regeneration methods. According to them, the conventional regeneration methods such as sequential steam, steam-air, steam-hydrogen treatment, and high temperature reaction treatment are ineffective in completely recovering the catalyst activity. Interestingly, in their report the reforming activity of the regenerated catalyst using the conventional method is not stable and falls over time on stream. In the present work, we study the kinetics of deactivation and subsequent regeneration of the catalyst, focusing primarily on the effect of concentration of H2S and the temperature at which the deactivation and regeneration take place.

2. Experimental details

2.1. Catalyst preparation

Initially the γ-Al2O3 (Alfa Aesar) supports (pellets of average length = 5.1 mm and average diameter = 3.3 mm) are calcined in air at 800 °C and held for 4 hr to remove any volatile components present. The nickel metal catalysts supported on γ-Al2O3 are prepared by wet impregnation method using nickel (II) nitrate hexahydrate (Merck, 99% purity) as precursor. Measured quantities of metal precursor equivalent to the desired metal loading (15 wt%) are first dissolved in distilled water of volume equal to or slightly in excess of the total pore volume of the support. The required amount of γ-Al2O3 pellets is then added to the precursor solution and stirred continuously for two hours to ensure that the precursor solution is uniform during the wet impregnation process. The wet materials are subsequently dried overnight at 80 °C followed by calcination at 800 °C in presence of air for 6 h.

2.2. Catalyst characterization

XRD (X-Pert PRO PAN analytical) analysis is conducted for catalyst samples between 20 = 10° to 90° using CuKα radiation (λ=0.15418 nm) at 40 kV and 30 mA. Figure 1 shows XRD patterns of pure γ-Al2O3, calcined Ni/γ-Al2O3, reduced Ni/γ-Al2O3, spent catalyst at 800 °C after stability test without H2S exposure, and spent catalyst at 700 °C exposed to 100 ppm H2S. The presence of NiO is confirmed for calcined Ni/γ-Al2O3 at angles of 37.3° and 66.1°, and an inactive NiAl2O4 crystalline phase at 45.6°. The formation of NiAl2O4 is due to the higher calcination temperature (800 °C). The Ni peaks are observed at 44.6, 51.9 and 76.4 degrees for reduced catalyst and spent catalyst at 800 °C and 700 °C. Reduced Ni/γ-Al2O3 and spent catalysts at 700 °C and 800 °C showed lower peak intensity for NiAl2O4, which is in good agreement with previous literature [17]. The diffraction patterns for NiS and Ni2S2 are not observed for the spent catalyst at 700 °C with 100 ppm H2S exposure even though the catalyst is almost fully poisoned. A similar XRD pattern was observed by Kuhn, et al. [18], for Ni-YSZ sample exposed to 100 ppm H2S. The absence of stable compounds of NiS or Ni2S2 in the XRD pattern is not surprising as these are expected to form only at high concentrations of H2S in the feed. For low concentrations (<100 ppm), it is thought that the formation of chemisorbed S on Ni leads to deactivation [18]. The diffraction peak for graphite carbon at 26.50° is not observed for spent catalyst at 700 °C and 800 °C. γ-Al2O3 showed poor intensity for all the catalysts as shown in Fig. 1 at angles of 37.8, 45.4 and 67.2 degrees.

The BET surface area, pore size distribution and average pore diameter of the catalysts are measured using Micromeritics ASAP 2020 surface and porosity analyzer. In order to remove the moisture and any adsorbed gases, the samples are degassed under vacuum for 6 h at 200 °C. The pore size distribution is calculated from N2 desorption data using the Barrett-Joyner-Halenda (BJH) method. The BET surface area of calcined γ-Al2O3, reduced catalyst, and spent catalysts are shown in Table 1. The surface area of γ-Al2O3 calcined at 800 °C is 206 m2g⁻¹. The calcined and reduced catalysts showed lower surface area compared to γ-Al2O3, probably due to pore blockage. The reduced catalyst showed lower surface area compared to calcined sample due to the agglomeration of Ni particles at higher reduction temperature. The BET surface area for spent catalysts is significantly lower than that of fresh samples.
The temperature programmed reduction (TPR) studies have been carried out using Micrometrics AutoChem II-2920 chemisorption analyzer. A measured amount of fresh catalysts is loaded in U shaped quartz tube and heated to 200 °C for 1 hr in Ar stream (30 ml min$^{-1}$). The samples are then cooled down to 50 °C and the Ar is replaced by 10 vol% H$_2$ in Ar (30 ml min$^{-1}$). The samples are heated from 50 °C to 900 °C at a ramp rate of 10 °C per min. The consumption of H$_2$ is monitored using a thermal conductivity detector (TCD). Figure 2 shows that maximum degree of reduction occurs at 790 °C. The higher reduction temperature indicates the strong interaction of NiO with γ-Al$_2$O$_3$ support. The higher calcination temperatures may also result in the formation of NiAl$_2$O$_4$ and the broad reduction peak may also be due to the reduction NiAl$_2$O$_4$.

To determine the active metal surface area, metal dispersion, and average metal particle size, H$_2$ pulse chemisorption studies have been carried out using Micrometrics AutoChem II-2920 chemisorption analyzer. Measured amount of fresh catalysts is loaded in a quartz tube and reduced with 10 vol.% H$_2$ in Ar (30 ml min$^{-1}$). After reduction the sample is cooled down to 50 °C and Ar flow is continued for another 30 min to remove traces of H$_2$. Following this several pulses of measured quantity of 10 vol.% H$_2$ in Ar are introduced into the reduced catalyst sample until three consecutive similar H$_2$ peaks are obtained. H$_2$ pulse chemisorption results for Ni/γ-Al$_2$O$_3$ reduced at temperature of 800 °C for 15 wt% Ni loading gave 3% metal dispersion, metallic surface area of 19.9 m$^2$g$^{-1}$, and cubic crystallite size of 28.1 nm. This particle size is very close to the value calculated using Scherrer equation, which gives 34.2 nm.

2.3. Steam reforming experiments

Biogas steam reforming experiments were carried out in a fixed bed quartz reactor (20 mm outside diameter and 1 mm wall thickness) maintained at atmospheric pressure. The reactor loaded with 1.5 gm of catalyst pellets diluted with quartz beads (3 mm to 5 mm diameter) was placed in a three zone heating furnace (Applied Test Systems, INC, USA). The catalytic bed was placed in the quartz tube reactor using quartz wool. A schematic representation of the reactor is shown in Fig. 3. The reactor was heated to the desired temperature at a rate of 10 °C per min under N$_2$ flow (99.999% pure, Prax air). Furnace temperature was adjusted to maintain the catalyst bed under isothermal condition. K-type thermocouples were used to measure the reactor temperature. Two Ni-Cr thermocouples were placed at the top and bottom of the catalytic bed to measure the catalyst bed temperature. Prior to the reactions the catalysts were reduced in pure H$_2$ flow (20 mL min$^{-1}$) at 800 °C for 5 hours. Before starting the reaction, water was fed using a calibrated HPLC pump (LabAlliance, USA) through a preheater to the reactor for 5 mins. Pure gases of CH$_4$ (99.999%) and CO$_2$ (99.995%) were fed to the reactor using calibrated mass flow controllers (Bronkhorst High Tech, The Netherlands) with N$_2$ dilution. The gas mixture was heated to 250 °C in a preheat-
All the experiments were repeated to ensure reproducibility.

3. Results and discussion

3.1. Stability tests

Before introducing H₂S to the system to study the deactivation at different H₂S concentrations and temperatures, the biogas steam reforming reactions are performed without H₂S and held at least for 1 hr at steady state. H₂S is then introduced from an N₂ cylinder containing 1052 ppm H₂S. CH₄ (23.8 ml min⁻¹), CO₂ (15.99 ml min⁻¹), N₂(102.4 ml min⁻¹), and H₂O (48.08 ml min⁻¹) are introduced to the reactor. This corresponds to CH₄ to CO₂ ratio of 1.487 and H₂O to CH₄ ratio (S/C) of 2.02. The corresponding inlet mole fractions are CH₄ = 0.125, CO₂ = 0.084, H₂O = 0.252 and N₂ = 0.539. A low S/C ratio is employed to ensure the participation of CO₂ in reforming reactions [9]. Nevertheless, it is worth mentioning here that S/C ratio may have some influence on the chemisorption equilibrium of H₂S at temperatures above 700 °C [2].

### Figure 4:

Conversions of CH₄ and CO₂ during stability test at 800 °C

(a) Time on stream conversion of H₂O, CH₄ and CO₂ during catalyst stability test at 800 °C

(b) Time on stream mole fraction of H₂ and CO during catalyst stability test at 800 °C

In order to ensure that the catalyst does not lose activity over time in non poisoning atmosphere (without H₂S) reforming experiments are performed for 22 hrs at 800 °C. Figure 4(a) shows the conversion of CH₄ and CO₂ on dry basis and H₂O conversion during the catalyst stability test at 800 °C. All data reported in this paper is on dry basis and the lines are just drawn to guide the eye. The reactor exit compositions for the stability test are shown in Fig. 4(b). The constant conversion and product composition implies that the catalyst is stable and the activity remains constant under non-poisoning gas atmosphere. The H₂ to CO ratio in the product gas for the given inlet composition is ~3. The stability test is also carried out at 700 °C. The H₂ to CO ratio at 700 °C is ~2.72 and CO₂ conversion is lower compared to 800 °C, which can be attributed to the shifting of the thermodynamic equilibrium of the reactions involved. Table 2 shows a comparison between equilibrium predictions and the experimental data. The equilibrium composition is calculated using the software DETCHEM by considering CH₄, H₂, CO, CO₂, H₂O and N₂ in the mixture [19]. It can be seen that the conversions and product mole fractions agree well with the equilibrium calculations. Since all the catalysts used in the experiments are prepared in the same batch and since they are stable under non-poisoning gas atmosphere, we can assert that the catalyst deactivation by introducing H₂S to the feed gas is purely due to sulfur poisoning, at least for the time on stream considered in this study.

3.2. Deactivation studies

Catalyst deactivation experiments are performed for two different temperatures and three different H₂S concentrations. Figure 5 shows the deactivation of the catalyst for 20, 50, and 100 ppm H₂S with respect to CH₄+CO₂ concentration at 700 °C. All H₂S concentrations led to almost complete deactivation (98%) of the catalyst, however, the rate at which deactivation occur varies. Higher H₂S concentrations lead to faster deactivation. Figure 6 shows drop in CH₄ conversion as a result of deactivation at 800 °C for different H₂S concentrations. In all cases the catalyst activity dropped, however, did not deactivate fully. The residual activity retained by the catalyst depends on the concentration of H₂S in the feed gas. 100 ppm H₂S concentration in the feed gas led to a final steady state of 34% CH₄ conversion, 50 ppm to 43%, and 20 ppm to 48%. Deactivation rate for 10, 50, and 100 ppm for the two temperatures may also be inferred by comparing Fig. 5 and Fig. 6. It is interesting to notice that for both the temperatures the rate of activity loss (the slope of the curve) before reaching steady state is same for 50 and 100 ppm whereas for 20 ppm the rate of deactivation is much slower at 800 °C compared to 700 °C. For both the temperatures CH₄ conversion is ~98-99% in the absence of H₂S in the feed gas. Therefore, the catalyst deactivation is purely due to sulfur poisoning. The H₂ and CO mole fractions from the

### Figure 5:

CH₄ conversion at 700 °C as a function of time for three different H₂S concentrations.
reactor exit at 700 °C during deactivation for different H₂S concentrations are shown in Fig. 7. Examining Fig. 5 and Fig. 7 leads us to the conclusion that the final activity of the catalyst is independent of the H₂S concentration. In all cases the catalyst retained ~2% of its activity. However, the same is not true for high temperature operation. Fig. 8 shows the exit mole fractions of H₂ and CO at 800 °C. Higher ppm level of H₂S results in low CH₄ conversion and hence low H₂ mole fraction in the product stream. That is at low operating temperatures, the saturation coverage of sulfur on Ni is independent of H₂S concentration. All the H₂S concentrations considered in this study lead to saturation coverages at 700 °C whereas at high temperature, the mechanistics of H₂S adsorption and recombination reaction involving sulfur leads to different saturation coverages of sulfur for different H₂S concentrations.

3.3. Regeneration by H₂S removal

Since chemisorption is a reversible process, surface adsorbed sulfur can be removed by decreasing the sulfur content in the feed stream [2]. For 100 and 50 ppm we have performed the regeneration experiments by removing H₂S from the feed gas (all other gas flow rates remain the same) after reaching their steady state residual activity. For both 100 and 50 ppm the catalyst activity again reached another steady state after H₂S removal (Fig. 6). However, full regeneration could not be achieved. In the case of 50 ppm 95% activity could be recovered, whereas for 100 ppm recovery is only 90%. The time required for regeneration is ~10 h, which is very short compared to the time required for conventional regeneration methods reported by Li et. al [1]. We could not perform regeneration experiments for 20 ppm due to periodic power outages after every 24 hrs. The rate of regeneration is same as rate of deactivation in all cases. For instance from Fig. 6 the deactivation for 100 ppm H₂S takes about 8 hrs and the regeneration also takes approximately the same duration. These results are consistent with the report of Ashraft et al [13]. The catalyst activity loss is mainly due to dissociative adsorption of H₂S on Ni leading to the active sites being covered with sulfur. At high temperature each sulfur atom occupies one adsorption site on Ni [14]. To recover the activity the adsorbed sulfur needs to be removed from the active sites of the catalyst. The surface adsorbed sulfur can participate in recombination reactions with a number of other surface adsorbed species such as H, O, and OH. The recombination products can then desorb from the surface, leaving the surface again capable of promoting surface reactions. The partial recovery of activity would then imply that the adsorbed sulfur is not fully removed by the recombination reactions.

Figure 6: CH₄ conversion at 800 °C as a function of time for three different H₂S concentrations. For 100 ppm H₂S is removed at 8 hrs 40 min and the regeneration is continued until 17 hrs 40 min. For 50 ppm H₂S is removed at 11 hrs 20 min and the regeneration is continued till 21 hrs.

Figure 7: H₂ and CO mole fraction at the reactor exit for different H₂S concentrations at 700 °C.

Figure 8: H₂ and CO mole fraction at the reactor exit for different H₂S concentrations at 800 °C. For 100 ppm H₂S is removed at 8 hrs 40 min and the regeneration is continued until 17 hrs 40 min. For 50 ppm H₂S is removed at 11 hrs 20 min and the regeneration is continued till 21 hrs.
3.4. Regeneration by temperature enhancement

At 800 °C the catalyst activity is recovered by removing H₂S from the feed gas. However, at 700 °C the catalyst activity could not be recovered in the same manner. This means that the kinetics of desorption and/or recombination reactions are not favored at low temperatures. This is further confirmed by temperature stepping at 700 °C which lead to recover the activity. Figure 9 shows the gain in catalytic activity when the temperature is increased from 700 °C to 800 °C. 100 ppm H₂S concentration at 700 °C leads to almost complete deactivation of the catalyst. However, when the temperature is increased to 800 °C, the catalyst started regaining activity and stabilizes at 32% CH₄ conversion, very close to the steady state activity at 800 °C for 100 ppm reported in Fig. 6. This also reconfirms the reproducibility of our experiments. Since chemisorption is exothermic an improved sulfur removal is naturally expected by increasing the temperature [2]. Higher temperature favors the kinetics for desorption reactions and recombination reactions involving adsorbed sulfur species. After reaching the steady state, H₂S is completely removed from the feed gas (all other gas flow rates remain the same) and the catalyst is allowed to regain its activity further. 92% of the activity is recovered by this process. This again corresponds very well with the final activity reported in Fig. 6 for 100 ppm case. The mole fractions of various gases from the reactor exit for the same case are shown in Fig. 10. At steady state before introducing H₂S into the reactor, CH₄ is fully converted and the reactor exit contains ~33% H₂, 9% CO, 9% CO₂ and remaining N₂. As soon as H₂S is introduced to the reactor, the reactants mole fraction starts to increase and the products mole fraction starts to decrease. The mole fraction of CH₄ and CO₂ increases and stabilizes respectively at 15% and 10%. These values corresponds very well to dry inlet mole fraction of CH₄ (16.7%) and CO₂ (11.2%). The 3% H₂ and 1.5% CO at the reactor exit is due to the residual activity (2%) of the catalyst.

3.5. Regeneration by steam treatment

Conventionally, the sulfur poisoned Ni is regenerated by sequential steam, steam air, and steam hydrogen treatment. Since the removal of adsorbed sulfur can be easily achieved by steaming above 650 °C [2] we have attempted the regeneration by treating with H₂O. Once the catalyst is fully deactivated at 700 °C, the feed stream is replaced with H₂O (48.08 ml min⁻¹) diluted in N₂ (102.4 ml min⁻¹) flow for ~5 h. Since steam treatment leads to the formation of NiO the catalyst is further reduced under H₂ flow (20 ml min⁻¹) at 700 °C for 5 h. Total regeneration time is 10 h, which is far shorter than the regeneration time reported by Li et al. and Nielsen [1, 2]. The regenerated catalyst is tested for its activity by performing reforming reaction without H₂S in the feed stream. CH₄ conversion after regeneration is shown in Fig 11. The catalyst showed stable operation for more than 10 hrs whereas Li et al. observed fall in activity of the catalyst regenerated using conventional sequential technique after 10 hrs of operation. Its very likely that the steam treatment regenerates the catalyst by forming SO₂. The oxygen atoms are formed by the dissociative adsorption of H₂O on Ni surface.

4. Conclusions

Ni Catalyst poisoning due to H₂S during the reforming of biogas is studied. The experiments are performed at 700 °C and 800 °C and for three different H₂S concentrations (20, 50, and 100 ppm w.r.t CH₄+CO₂ concentration). At 700 °C, the saturation sulfur coverage is independent of H₂S concentration.
in the feed gas. However, at 800 °C, the saturation coverage of sulfur is dependent on the concentration of H2S. Generally, higher H2S concentrations lead to faster deactivation of the catalyst. The deactivation and regeneration showed exponential behavior on time on stream. At higher H2S concentrations (50 and 100 ppm), the rate of deactivation is found to be independent of the temperature. At 800 °C, the activity of the catalyst is partially recovered just by removing H2 from the feed gas. However, this method did not recover the catalyst activity at 700 °C. Regeneration of the poisoned catalyst at 700 °C required either temperature enhancement or steam treatment. The deactivation and regeneration showed exponential behavior on time on stream. At higher H2S concentrations, the activity of the catalyst which is almost completely poisoned by exposure to 100 ppm H2S at 700 °C is regenerated partially by enhancing the temperature to 800 °C and the catalyst is almost completely regenerated by removing H2 from the feed gas. The same catalyst may also be regenerated by steam treatment. Five hours of steam treatment followed by reduction in H2 for 5 hrs led to almost complete recovery of the catalyst activity. This regeneration time is far shorter than the ones reported in previous literature.

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References

Table 1: BET Analysis of catalyst samples before and after experiments

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<th>Sample</th>
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Table 2: Comparison between equilibrium prediction and experiments

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