Impact of Sulfur Poisoning on the Carbon Deposition over Rh and Ni Catalysts in Steam Reforming of Liquid Hydrocarbons

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Introduction

Due to global resource limitation and increasingly stringent environmental regulations, development of highly efficient and clean devices for fuel conversion is very desired for various vehicles. Consequently, fuel cells (FCs) are attracting extensive attention as they are promising to be used in vehicles to enhance fuel efficiency and reduce emissions[1]. Although considerable progress has been made for FCs-driven vehicles, how to efficiently provide H_2 to FCs remains a bottleneck for the transportation applications. One solution is on-board H_2 storage, which however is rather difficult to be accomplished because of two barriers: i.e., (i) no widespread H_2 refueling infrastructure and (ii) the lack of highly efficient H_2 storage materials. To circumvent this issue, considerable efforts have been made for the on-board H_2 production via steam reforming (SR) of liquid hydrocarbons [1,2].

It has been well known that both Rh and Ni possess high activities towards H_2 production. However, Ni is more prone to carbon deposition compared with Rh[1]. In reforming reactions the Ni metals can be readily covered by considerable carbon deposits, which may encapsulate them to cause catalyst deactivation or diffuse into them to generate filamental carbons that can plug reactors and buildup significant pressure drops[3,4]. Furthermore, inherent sulfur impurities in liquid fuels are another big challenge for reforming catalysts as sulfur is able to strongly interact with the metals to cause their deactivation[4]. As a result, catalyst deactivation resulting from carbon deposition and sulfur poisoning has been identified a significant technical barrier for liquid hydrocarbon reforming.

In spite of enormous published studies regarding H_2 production via various reforming reactions[1-5], little work has been carried out to fundamentally study the impact of sulfur poisoning over the carbon deposition over Rh and Ni catalysts in SR of liquid hydrocarbons. This greatly hinders the applications of Rh and Ni reforming catalysts in on-board H_2 production. The present study thereby focuses on SR of liquid hydrocarbons with/without sulfur over Rh and Ni catalysts loaded on CeO_2-modified Al_2O_3 at 800ºC. The spent catalysts were characterized by temperature-programmed oxidation (TPO) to gain insights on the impact of sulfur poisoning on the carbon deposition over the Rh and Ni catalysts in liquid hydrocarbon reforming.

Experimental

CeO_2-modificed Al_2O_3 (CeAl) support with 20 wt% of CeO_2 loading was prepared by wet-impregnation of $Ce(NO_3)_3$ (Aldrich) onto γ-Al_2O_3 (PURALOX TH 100/150, Sasol, BET: ~150 m^2/g). Afterwards, the mixture solution was dried overnight, followed by calcination at 550°C. The metal (Rh or Ni) was then loaded onto the support at 2 wt% for the Rh catalyst and 10 wt% for the Ni catalyst, respectively. The thus-obtained Rh and Ni catalysts were denoted as RhCeAl and NiCeAl, respectively. SR reactions were conducted at 800°C and 1 atm with a steam-to-carbon ratio of 3.0 and a GHSV of ~2785 hr^{-1}. Both Norpar13 (a model fuel from Exxon Mobile comprising only normal paraffins with an average carbon number of 13) and Norpar13 with 350 ppmw sulfur (referred to as Norpar13(350)) that was prepared by adding 3-methylbenzothiophene into Norpar13 were used as the fuels. Gas products were analyzed by an on-line SRI GC equipped with a TCD. All the reactions were run for around 60 h. The experiments were terminated by increasing the nitrogen flow to 120 ml/min and switching off the fuel and steam valves at the same time. N_2 adsorption-desorption was carried out at liquid-N_2 temperature (77 K) using a Quartchrome Autosorb-1 analyzer to examine the BET (Brunauer-Emmett-Teller method) surface areas of the samples. Each sample was degassed at 200°C under vacuum for 3 h prior to the measurement. The results show that the BET surface area of RhCeAl and NiCeAl is 116.8 and 109.0 m^2/g, respectively. To study the deposited carbons over the spent catalyst, temperature-programmed oxidation (TPO) was performed using a LECO RC-412 multiphase carbon determiner by heating the sample from ambient temperature to 900ºC at a rate of 30ºC/min in UHP O_2. The sulfur content over the spent catalyst after SR of Norpar13(350) was determined with LECO SC-144DR by burning the sample in UHP O_2 at 1350°C.

Results and Discussion

Table 1. H_2 Yields at the Ends of Reactions and Sulfur and Carbon Contents over the Spent Catalysts

Catalysts	Fuel	H_2 yield (%)	Total sulfur (%)	Carbon Deposits (%)
RhCeAl	Norpar13	84.5	-	6
	Norpar13(350)	71.0	0.13	9
NiCeAl	Norpar13	77.8	-	7
	Norpar13(350)	2.8	0.10	123

The fuel conversions for the reactions studied herein were all nearly 100% due to highly effective pyrolysis of the fuels into smaller hydrocarbons at 800°C; therefore, H_2 yields at the ends of SR reactions were used to evaluate the catalyst performances, as shown in Table 1. For SR of Norpar13, the H_2 yields for RhCeAl and NiCeAl were 84.5 and 77.8%, respectively. This demonstrates that the two catalysts were both effective for SR of liquid hydrocarbons in the absence of sulfur. In SR of Norpar13(350) the H_2 yield for NiCeAl significantly decreased to 2.8%, while that for RhCeAl only dropped to 71.0%. The above facts clearly indicate that NiCeAl was much more severely deactivated as compared with RhCeAl in 800ºC-SR of Norpar13(350). As illustrated in Table 1, the sulfur content for RhCeAl (0.13%) is slightly higher than that of NiCeAl (0.10%). This result, along with the catalyst performances in SR of Norpar13/Norpar13(350), strongly suggests that Rh should have higher sulfur-tolerance than Ni at 800ºC.

The carbon amounts over the spent catalysts after the reactions are summarized in Table 1. The two catalysts exhibited relatively lower amounts of deposited carbon after SR of Norpar13, which can be attributed to (1) the high reforming temperature (800°C) at which carbon gasification ($C + H_2O \rightarrow CO + H_2$) can efficiently proceed[3], and (2) the beneficial effect of CeO_2, which can promote steam adsorption to facilitate carbon removal[4,6]. As to SR of Norpar13(350), the carbon deposition over the two catalysts was notably different: RhCeAl remained highly resistant to carbon deposition; on the other hand, a huge amount of carbon was accumulated over NiCeAl because the severe sulfur poisoning of the catalyst could prohibit the carbon gasification reaction[4]. As a consequence, not only severe sulfur poisoning but also abundant carbon deposits are responsible for the deactivation of NiCeAl in 800ºC-SR of Norpar13(350).

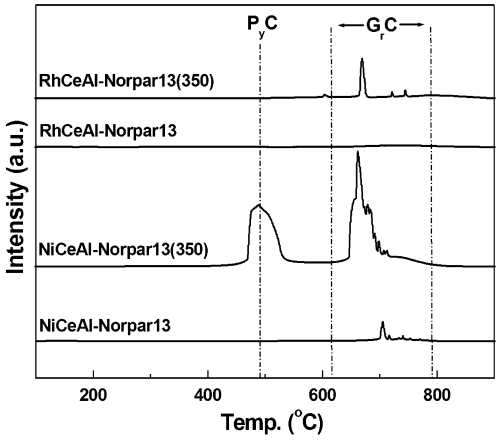

Figure 1. TPO profiles for the spent RhCeAl and NiCeAl catalysts after the reactions (P_yC: pyrolytic carbon; G_rC: graphite carbon).

TPO profiles of the spent RhCeAl and NiCeAl catalysts are shown in Figure 1. After reforming of Norpar13 no intensive carbon peaks were observed for RhCeAl, and a small peak of graphitic carbon occurred at 700°C for NiCeAl[6]. This fact further confirms that the two catalysts possess exceptional carbon-resistance for 800°C-SR of Norpar13. However, as the catalysts were used for SR of Norpar13(350) the TPO profiles were substantially changed, demonstrating that sulfur poisoning can affect not only the amount but also the type of deposited carbon over reforming catalysts. RhCeAl exhibited a peak associated with graphitic carbon; in contrast, two strong peaks could be seen for the spent NiCeAl catalyst, which can be associated with pyrolytic carbon (450-500°C) and graphitic carbon (~700°C), respectively. The pyrolytic carbon originated from gas-phase pyrolysis of heavier hydrocarbons at >600ºC with the formation of carbonaceous intermediates via radical-based polymerization reactions, followed by their condensation over catalyst surfaces[7]. The significant accumulation of pyrolytic carbon and graphite carbon over NiCeAl in SR of Norpar13(350) clarifies that this catalyst was severely deactivated by sulfur and thereby the carbon gasification was dramatically prohibited. The superior sulfur-tolerance of RhCeAl at 800ºC allowed the catalyst to sustain the superior carbon-resistance of Rh, thus making it much more carbon resistant than NiCeAl in 800ºC-SR of Norpar13(350).

Conclusions

The present study investigated the impact the sulfur poisoning on the carbon deposition over Rh and Ni catalysts in SR of liquid fuels with/without sulfur (Norpar13/Norpar13(350)) at 800ºC. Both the catalysts could successfully reform Norpar13 with negligible carbon deposition. For SR of Norpar13(350) the remarkable impact of sulfur poisoning on the carbon deposition could be observed: severe sulfur poisoning of NiCeAl gave rise to abundant carbon deposits (i.e., pyrolytic carbon and graphitic carbon); however, RhCeAl exhibited much lower carbon deposition due to the superior sulfur-resistance of Rh at 800ºC.

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