UNDERSTANDING OF CATALYST DEACTIVATION CAUSED BY SULFUR POISONING AND CARBON DEPOSITION IN STEAM REFORMING OF LIQUID HYDROCARBON FUELS

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ABSTRACT

The present work was conducted to develop a better understanding on the catalyst deactivation in steam reforming of sulfur-containing liquid hydrocarbon fuels for hydrogen production. Steam reforming of Norpar13 (a liquid hydrocarbon fuel from Exxon Mobile) without and with sulfur was performed on various metal catalysts (Rh, Ru, Pt, Pd, and Ni) supported on different materials (Al₂O₃, CeO₂, SiO₂, MgO, and CeO₂-Al₂O₃). A number of characterization techniques were applied to study the physicochemical properties of these catalysts before and after the reactions. Especially, X-ray absorption near edge structure (XANES) spectroscopy was intensively used to investigate the nature of sulfur and carbon species in the used catalysts to reveal the catalyst deactivation mechanism.

Among the tested noble metal catalysts (Rh, Ru, Pt, and Pd), Rh catalyst is the most sulfur tolerant. Al₂O₃ and CeO₂ are much better than SiO₂ and MgO as the supports for the Rh catalyst to reform sulfur-containing hydrocarbons. The good sulfur tolerance of Rh/Al₂O₃ can be attributed to the acidic nature of the Al₂O₃ support and its small Rh crystallites (1-3 nm) as these characteristics facilitate the formation of electron-deficient Rh particles with high sulfur tolerance. The good catalytic performance of Rh/CeO₂ in the presence of sulfur can be ascribed to the promotion effect of CeO₂ on carbon gasification, which significantly reduced the carbon deposition on the Rh/CeO₂ catalyst.

Steam reforming of Norpar13 in the absence and presence of sulfur was further carried out over CeO₂-Al₂O₃ supported monmetallic Ni and Rh and bimetallic Rh-Ni catalysts at 550 and 800 °C. Both monometallic catalysts rapidly deactivated at 550 °C,
and showed poor sulfur tolerance. Although ineffective for the Ni catalyst, increasing the temperature to 800 °C dramatically improved the sulfur tolerance of the Rh catalyst. Sulfur K-edge XANES revealed that metal sulfide and organic sulfide are the dominant sulfur species on the used Ni catalyst, while sulfonate and sulfate predominate on the used Rh catalyst. The superior sulfur tolerance of the Rh/\text{CeO}_2-\text{Al}_2\text{O}_3\) catalyst at 800 °C may be associated with its capability in sulfur oxidation. It is very likely that the oxygen-shielded sulfur structure of sulfonate and sulfate can suppress the poisoning impact of sulfur on Rh through inhibiting direct rhodium-sulfur interaction. Although the Rh-Ni catalyst exhibited better sulfur tolerance than the monometallic ones at 550 °C, its catalytic performance was inferior compared with the Rh catalyst in the sulfur-containing reaction at 800 °C probably due to the severe carbon deposition on the bimetallic catalyst.

The last part of this work focuses on the influence of sulfur on the carbon deposition in steam reforming of liquid hydrocarbon fuels over \text{CeO}_2-\text{Al}_2\text{O}_3 supported monometallic Ni and Rh catalysts at 800 °C. Though abundant carbon deposits can accumulate on the pure \text{CeO}_2-\text{Al}_2\text{O}_3 support due to fuel thermal cracking, the metal addition substantially mitigated the carbon deposition in the sulfur-free reaction. The presence of sulfur increased the carbon deposition on both catalysts, which has a much more significant impact for the Ni catalyst. Our results indicate that (I) the presence of sulfur can suppress carbon gasification and promote the formation of graphitic carbon on reforming catalysts, and (II) the Rh catalyst possesses stronger capability to maintain carbon gasification activity than the Ni catalyst in the presence of sulfur.
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Chapter 1

Introduction

1.1. Background

Hydrogen (H$_2$) has long been a very important feedstock for chemical and petroleum industries [1-6]. Currently, about 44.5 million tons of H$_2$ is produced worldwide every year, and it is being mainly used in the following areas: ammonia production (49%), petroleum refining (37%), and methanol production (8%) [6]. Moreover, H$_2$ is considered as an alternative fuel to fossil fuels as it can be efficiently converted to electricity in fuel cells with few emissions for stationary and transportation applications [1, 5, 7, 8]. Due to the concerns regarding the depletion of fossil fuels and the severe environmental pollution associated with their combustion, H$_2$-driven fuel cells have received considerable attention in the last two decades [1, 5, 7-13]. It is believed that this technology may play a critical role in future generation of electrical power. Unfortunately, free H$_2$ gas rarely exists on earth, and has to be manufactured from compounds like fossil fuels, biomass, and water [5]. As a result, how to make H$_2$ out from these stable compounds is an important research topic in the energy field for a long time [1-3, 5, 14-16]. So far, although various methods such as hydrocarbon pyrolysis, biomass gasification, and water splitting have been developed [3], steam reforming of hydrocarbons remains the most widely used and the most economical one for large-scale H$_2$ production [6]. It is a catalytic reaction between hydrocarbons and steam over supported transition metal catalysts with the formation of H$_2$, CO, and CO$_2$ (Reactions (1))
and (2)) \[3, 5\]. Meanwhile, some parallel reactions (Reactions (3)-(6)) can take place, making steam reforming of hydrocarbons a complex process. Since it is highly endothermic, steam reforming of hydrocarbons is generally operated at 800-1000 °C. Under such high temperatures severe carbon deposition can readily occur to degrade the catalyst performance. Therefore, a high steam-to-carbon ratio (S/C) of ~3 is being used in industry to reduce carbon deposition \[1\].

1. CH\(_4\) + H\(_2\)O \rightarrow CO + 3H\(_2\) (steam reforming)
2. CO + H\(_2\)O \rightarrow CO\(_2\) + H\(_2\) (water-gas-shift)
3. CO + 3H\(_2\) \rightarrow CH\(_4\) + H\(_2\)O (CO methanation)
4. 2CO \rightarrow C + CO\(_2\) (CO disproportionation)
5. CH\(_4\) \rightarrow C + 2H\(_2\) (CH\(_4\) decomposition)
6. C + H\(_2\)O \rightarrow CO + H\(_2\) (carbon gasification)

1.2. Literature review

While natural gas is the most widely used in commercial hydrocarbon reforming, liquid hydrocarbon fuels are preferred in many situations when natural gas is unavailable \[2\]. Moreover, there are remarkably growing interests towards onboard reforming of liquid hydrocarbon fuels (e.g., gasoline, diesel, and jet fuels) for mobile fuel cell power systems used in transportation vehicles \[1, 5, 17-20\]. Generally, steam reforming of liquid hydrocarbon fuels can be catalyzed by base metals (e.g., Ni) and noble metals (e.g., Rh, Ru, Pt, and Pd) supported on metal oxides such as Al\(_2\)O\(_3\) \[17, 18, 21\], CeO\(_2\) \[22, 23\], ZrO\(_2\) \[24-26\], CeO\(_2\)-Al\(_2\)O\(_3\) \[9, 27\], and Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_{1.9}\) \[19\]. Various commercially available liquid hydrocarbon fuels (e.g., gasoline, diesel, and jet fuels) \[9, 17, 21, 26, 28-\]
32] and their surrogates [18, 19, 33-36] have been attempted for H₂ production via reforming reactions. Commercial liquid hydrocarbon fuels are mixtures of higher hydrocarbons (e.g., paraffins, naphthenes and aromatics) with organosulfur compounds (e.g., benzothiophene). The chemical nature of the liquid hydrocarbon fuels poses several technical problems to the fuel reforming process [1, 2, 4, 37-42], which are mainly associated with (I) the presence of organosulfur compounds that can severely deactivate metal catalysts, and (II) the strong tendency of higher hydrocarbons in liquid fuels to generate severe carbon deposition.

### 1.2.1. Sulfur poisoning

Liquid hydrocarbons derived from fossil fuels mostly contain sulfur impurities up to 3000 part per million by weight (ppmw), which cannot be completely removed even upon deep desulfurization treatments [43]. Due to very strong sulfur-metal bonding, supported metal catalysts are therefore susceptible to the presence of sulfur in liquid fuels even at a trace level [18, 44-46]. The bonding of sulfur with metals involves the s and p orbitals of the former and the d orbital of the latter [47]. After examining the chemisorbed sulfur on various metal catalysts, it was revealed that sulfur can withdraw charges from metals and decrease the availability of electrons in their d orbitals [47]. Such a charge transfer can significantly reduce the sticking probabilities and coverage of reactants on metals [48]. Under hydrocarbon reforming conditions, sulfur chemisorbs onto metals to preferentially form surface metal sulfides rather than bulk metal sulfides because S/H₂ ratio is much lower than that required for the formation of the latter [2, 18, 42, 44].
According to previous studies [2, 42], for Ni metal at 500 ºC, sulfur coverage ($\theta_s$) = 0.5 corresponds to the ratio of partial pressure $H_2S/H_2$ as low as $1.6 \times 10^{-12}$. This means that the sulfur impurities will be quantitatively withheld by Ni catalysts until saturation in reforming of liquid hydrocarbon fuels, which can account for their high sensitivity to the presence of sulfur. Due to the inferior sulfur tolerance of Ni, great efforts have been dedicated to noble-metal-based reforming catalysts [17, 19, 22-26, 49-51]. Ferrandon et al. studied the effects of reforming temperature and steam-to-carbon ratio (S/C) on the sulfur tolerance of supported Rh catalysts in gasoline reforming [17]. They claimed that the poisoning effect of sulfur was more pronounced in the reaction at 700 ºC than that at 800 ºC. An increase in S/C from 2 to 3 significantly enhanced the catalyst’s tolerance to sulfur poisoning. Recently, Lu et al. reported that they have developed a sulfur-tolerant Pt catalyst supported on $Ce_{0.8}Gd_{0.2}O_{1.9}$ [19]. The temperature of catalyst calcination was shown to be a crucial factor to attain the superior sulfur tolerance. The catalyst calcined at 800 ºC retained its activity for 100 h on stream in steam reforming of sulfur-containing iso-octane, while the one calcined at 600 ºC obviously lost the activity in the same time period. Based on in situ DRIFTS characterization, they inferred that the calcination treatment at the high temperature gave rise to a strong synergistic effect at the Pt-CeGdO interface, resulting in the formation of electron-deficient Pt sites immune to sulfur poisoning.

In order to further enhance the sulfur tolerance of reforming catalysts, considerable attention has been focused on those with bimetallic formulations. Strohm et al. reported that a Rh-Ni catalyst loaded on $CeO_2-Al_2O_3$ was successful for steam reforming of JP-8 jet fuel containing 22 ppm of sulfur for 72 h with > 95% conversion [9]. Its exceptional
sulfur tolerance compared with the monometallic counterparts was mainly attributed to the intimate Rh-Ni interaction. The presence of Rh facilitated the Ni reduction and maintained its metallic state in an oxidative atmosphere. Ni metals then acted as protective and sacrificial sites to protect Rh from sulfur poisoning. In addition to the Rh-Ni catalyst, a variety of bimetallic reforming catalysts have been developed so far including Rh-Pd [22], Rh-Pt [25, 26], Pt-Pd [29], Pt-Ni [29], Ni-Sr [52], and Ni-Re [53]. Although the mechanisms for their improved sulfur tolerance remain in debate, it is generally accepted that the intimate interaction between two metals can alter their electronic and structural properties. As a result, the reactivity of metals toward sulfur as well as the number of surface active sites present on reforming catalysts will be dramatically affected, allowing bimetallic catalysts to exhibit improved sulfur tolerance as compared with monometallic ones. [54-56].

1.2.2. Carbon deposition

Hydrocarbon steam reforming also involves a high risk of carbon deposition because of rapid pyrolysis of higher hydrocarbons in liquid fuels [2, 5, 37-42]. During hydrocarbon reforming reactions carbon deposits may cover reforming catalysts and block reformer reactors with significant pressure buildup. Therefore, numerous studies have been carried out to study the carbon deposition in hydrocarbon reforming, and various strategies were proposed to solve this issue [2, 37-41, 57-74]. Carbon formation on reforming catalysts is very complex, which can be affected by a number of parameters including reaction temperature, reactant composition, S/C, and the surface and structure properties of reforming catalysts. In general, three types of carbon deposits have been
identified on reforming catalysts: pyrolytic carbon, filamental carbon, and encapsulating carbon [2, 38, 75]. According to Rostrup-Nielsen’s point of view [2], pyrolytic carbon derives from thermal cracking of higher hydrocarbons at temperatures above 600 °C. Encapsulating carbon (gum) is a polymerization film of inert carbon deposits containing C-H bonds. Its formation is mainly observed in reforming of heavy hydrocarbons at low S/C and at temperatures below 500 °C. Filamental carbon is a very destructive carbon form for hydrocarbon reforming over supported Ni catalysts. A commonly accepted mechanism for its growth consists of (I) hydrocarbons decompose on Ni to isolated carbon atoms, (II) these carbon atoms diffuse either on Ni surfaces or through the bulk to reach the nickel-support interface, (III) carbon nucleation at the nickel-support interface leads to the formation of filamental carbon while the Ni particles are lifted up from the support [60, 61, 72, 75, 76]. The carbon concentration gradient between the gas-metal and metal-support interfaces is presumably the driving force for the surface and bulk diffusion of carbon atoms [60, 61]. Compared to Ni, noble metals are highly resistant to the growth of filamentous carbon due to their stronger carbon gasification capability as well as the very low carbon solubility in their bulk [4, 37].

Modification of reforming catalysts by lanthanide elements (i.e., Ce, La, and Yb) and alkalis (i.e., K, Na, Ca, and Mg) is an effective way to suppress the carbon deposition on reforming catalysts as well [38-42, 57]. These promoters can improve steam adsorption and activation, and thereby enhance carbon gasification. Wang and Lu have evaluated the catalytic performances of Ni catalysts supported on Al₂O₃, CeO₂ and CeO₂-Al₂O₃ in methane dry reforming [77], which clearly demonstrated that Ni/CeO₂-Al₂O₃ showed the best performance among the tested catalysts. It was concluded that CeO₂ has a positive
effect on catalytic activity, stability, and carbon suppression when used as a promoter in Ni/Al$_2$O$_3$. The improved carbon resistance of CeO$_2$-promoted catalysts can be largely attributed to the superior oxygen storage capability (OSC) of CeO$_2$ [77-79]. During reforming reactions the lattice oxygen of CeO$_2$ can be released to facilitate carbon gasification with the conversion of Ce$^{4+}$ to Ce$^{3+}$ ($2\text{CeO}_2 \rightarrow \text{Ce}_2\text{O}_3 + \text{O}$). Ce$_2$O$_3$ is unstable and can be easily oxidized back to Ce$^{4+}$ ($\text{Ce}_2\text{O}_3 + \text{H}_2\text{O} \rightarrow 2\text{CeO}_2 + \text{H}_2$) in hydrocarbon steam reforming. Apparently, there exists a cycle of mutual conversion between Ce$^{4+}$ and Ce$^{3+}$, which is beneficial for the steam adsorption and activation. In addition to the promotion effect on carbon gasification, ceria has been proven effective in hindering metal sintering as well. A recent study by Nagai et al. [80] showed that the Pt particles in a Pt catalyst supported on a ceria-based oxide (Ce-Zr-Y mixed oxide) did not sinter after aging treatment at 800 °C in air, while those in a Pt/Al$_2$O$_3$ catalyst did. The mechanism for the inhibition of CeO$_2$ on the Pt particle sintering was explored with the aid of Extended X-ray Absorption Fine Structure (EXAFS) analysis. It was revealed that the Pt-O-Ce bonds formed at the interface of Pt and CeO$_2$ acted as an anchor to inhibit the sintering of Pt particles on the ceria-based oxide.

Supported metal alloy catalysts are another promising option for hydrocarbon reforming with high carbon resistance [63, 65, 66, 70, 71, 75, 81-83]. For instance, Besenbacher et al. found that a Au-Ni alloy catalyst exhibited superior carbon resistance during steam reforming of n-butane [81]. Their DFT calculations suggested that the presence of Au on Ni substantially reduced the chemisorption of carbon atoms on the latter. The beneficial effect of Au on the reduction of carbon deposition on Ni was further confirmed by Chin’s study, which showed that adding 0.5 wt% Au into a Ni catalyst was
effective in pronouncedly reducing the carbon deposition [84]. Recently, Nikolla et al. reported their experimental and theoretical studies on controlling carbon surface chemistry by alloying of Ni with Sn [63, 65, 66, 70, 71]. It was demonstrated that the presence of Sn dramatically enhanced the energy barrier for the formation of C-C bonds, while that for C-O was much less affected. This implies the oxidation of C atoms rather than the C-C bond formation was favored on the Sn-Ni catalyst. The DFT calculations were supported by the lower carbon deposition on the Sn-Ni catalyst compared with the Ni alone catalyst after steam reforming of methane, propane, and iso-octane at 800 °C.
Chapter 2
Motivation, Objective, and Hypotheses

2.1. Motivation

Steam reforming of liquid hydrocarbon fuels is an important catalytic process for \( \text{H}_2 \) production and fuel cell applications. However, catalyst deactivation due to sulfur poisoning and carbon deposition is a major barrier limiting the practical applications of this technology [1, 9, 27, 65, 66, 70, 71, 79, 85-87]. Therefore, developing highly efficient and stable reforming catalysts with superior sulfur tolerance and carbon resistance is desirable. In order to achieve this aim, it is necessary to fundamentally understand how sulfur poison and carbon deposits deactivate reforming catalysts. Up to now, enormous studies have been conducted on hydrocarbon reforming reactions [17-19, 22, 25, 26, 28, 29, 31, 34, 35, 88], but few of them focused on the catalyst deactivation issue. This is probably because many conventional characterization techniques such as XRF, ICP-MS, EDX, and chemical analysis, although being able to determine the presence of sulfur, cannot gain the chemical (e.g., sulfur oxidation state) and structural (bonding of sulfur with metals or other elements such as oxygen and carbon) information of sulfur. Thus little knowledge is available about the nature of the sulfur species in reforming catalysts. In addition, the most widely used tool for analyzing carbon deposits is temperature-programmed oxidation (TPO) [9, 27, 79]. Despite the effectiveness in determining the reactivity of carbon species towards oxygen, it offers very limited information on their molecular structures, which is of critical importance for
understanding the formation and impacts of carbon deposits on reforming catalysts. It is clear that the catalyst deactivation due to sulfur poisoning and carbon deposition in hydrocarbon reforming reactions has not been well explored due largely to lack of adequate characterization of the sulfur and carbon species in the used reforming catalysts. XANES has been widely used to study the sulfur and carbon species in a variety of materials such as petroleum, soil, and coal because of its exceptional capability in providing insights into their chemical states and molecular structures [89-96]. Therefore, this technique was extensively used in the present study to identify the sulfur and carbon species in the used reforming catalysts and investigate their chemical nature. We strongly believe the knowledge obtained from this study will assist the development of highly sulfur-tolerant and carbon-resistant catalysts for steam reforming of sulfur-containing hydrocarbon fuels.

2.2. Objectives

The main objective of the present work is to develop a better understanding on the catalyst deactivation mechanism in steam reforming of sulfur-containing liquid hydrocarbons. The specific objectives include:

(1) To identify the sulfur and carbon species in used reforming catalysts.
(2) To understand the impacts of the sulfur and carbon species on the activity and stability of reforming catalysts
(3) To reveal the influence of sulfur on the structural and chemical properties of carbon deposits on reforming catalysts.
2.3. Hypotheses

(1) Sulfur tolerance of reforming catalysts can be correlated with the sulfur species in them after reforming reactions.

(2) Sulfur poisoning has an impact on the carbon deposition (e.g., carbon gasification) in hydrocarbon reforming.

(3) XANES is effective in studying the chemical nature of sulfur and carbon species in used reforming catalysts.
Chapter 3

Experimental

3.1. Catalyst preparation

High-purity reagent-grade Rh(NO$_3$)$_3$, RuCl$_3$, PtCl$_4$, Pd(NO$_3$)$_2$, Ce(NO$_3$)$_3$, Mg(NO$_3$)$_2$ and SiO$_2$ were purchased from Aldrich Chemicals and used as received. The noble metal catalysts (Rh, Ru, Pt, and Pd) supported on γ-Al$_2$O$_3$ (Sasol PURALOX TH 100/150) were prepared by wet impregnation of the corresponding metal salts onto the Al$_2$O$_3$ support at 2 wt% of metal loading. The CeO$_2$ and MgO supports were fabricated by calcination of Ce(NO$_3$)$_3$ and Mg(NO$_3$)$_2$ at 550 °C for 6 h, respectively. The Rh (2 wt%) catalysts supported on SiO$_2$, CeO$_2$, and MgO were prepared using the same methodology as that of the Al$_2$O$_3$-supported catalysts.

20wt%CeO$_2$-modified Al$_2$O$_3$ (CeO$_2$-Al$_2$O$_3$) support was prepared by wet impregnation of Ce(NO$_3$)$_3$ onto the Al$_2$O$_3$ support, followed by calcination at 550 °C for 6 h. The metal (2 and 10 wt% for Rh and Ni, respectively) was loaded via wet impregnation of the metal nitrate (Rh(NO$_3$)$_3$ or Ni(NO$_3$)$_2$) onto the CeO$_2$-Al$_2$O$_3$ support. Bimetallic Rh-Ni catalyst was prepared via wet co-impregnation of Rh(NO$_3$)$_3$ and Ni(NO$_3$)$_2$ onto the support at the metal loading of 2 and 10 wt% for Rh and Ni, respectively. The as-prepared catalysts were then dried at around 100 °C overnight, followed by calcination at 550 °C for 6 h.
3.2. Reaction conditions

Steam reforming of liquid hydrocarbon fuels was carried out in a fixed-bed flow reactor system, as shown in Figure 3-1. Approximately 1 g of catalyst with particle sizes of 18-35 mesh (0.5-1 mm) was placed in the center of a stainless steel tube (0.54 inch o.d., 0.375 inch i.d., 24 inch long) with the rest of tube being packed with α-alumina beads. The reforming reactions in this work were performed at 550 and 800 ºC. Prior to the reactions, the catalysts were reduced by UHP hydrogen (20 ml/min) at 550 and 800 ºC for the low- and high-temperature reaction, respectively. Both water and fuel were pumped via HPLC pumps through a pre-heater and then into the reactor at volumetric flow rates of 4.08 and 1.38 mL/h, respectively, for a steam-to-carbon molar ratio (S/C) of 3:1 and feed weight hourly space velocity (WHSV) of 5.1 h⁻¹. The fuel employed in this study was sulfur-free Norpar13, a liquid hydrocarbon (Exxon Mobil) comprising only normal paraffins with an average carbon number of 13. The experiments with sulfur were carried out by doping the Norpar13 fuel with 3-methylbenzothiophene (3-MBT) for an equivalent 350 parts per million (ppm) of sulfur (by weight). Hydrogen production rate (HPR), which is defined as HPR = \frac{\text{moles of } H_2 \text{ produced per minute}}{\text{grams of hydrocarbons fed}} , was calculated to evaluate the catalyst performance. The reforming reactions were terminated by switching off the fuel and steam at the same time, and N₂ was flowing while the reactor was cooling down. The spent catalysts were then recovered and stored at room temperature for further analysis. As control experiments, non-catalytic thermal cracking of Norpar13 at 550 and 800 ºC was also performed in the absence of catalysts while keeping all the other conditions the same. In order to do experimental uncertainty analyses, catalytic tests on
selected samples were repeated at least three times. The error analyses on these experimental data were done by using a data processing software ORIGIN. The same methodology was also applicable to the error analyses on the contents of carbon and sulfur on the used reforming catalysts.

3.3. Catalyst characterization

3.3.1. Characterization of fresh catalysts

N$_2$ adsorption-desorption was carried out at liquid N$_2$ temperature with a Quartchrome Autosorb-1 analyzer to examine the BET (Brunauer-Emmett-Teller method) surface area ($S_{BET}$). Each sample was degassed by heating at 200 °C under vacuum prior to the measurement.

H$_2$ temperature-programmed reduction (H$_2$-TPR) was conducted on a Micrometrics TPR/TPD AutoChem 2910 with 5% H$_2$ in Ar at a temperature ramp of 5°C/min. H$_2$ chemisorption was conducted using the same device to measure the metal dispersion of the fresh catalysts. For the Al$_2$O$_3$-supported noble metals (Rh, Ru, Pt, and Pd) and the Rh catalysts supported on different materials (Al$_2$O$_3$, CeO$_2$, SiO$_2$, and MgO), they were reduced in hydrogen to 800 °C for 1 h, followed by cooling to 50 °C under Ar, then pulsing with 24.3% H$_2$ in Ar till saturation. A “sequential H$_2$ pulse chemisorption” method has been developed to separately determine the dispersion of Rh and Ni in the bimetallic Rh-Ni catalyst [9, 97]. The RhO$_x$ species in the bimetallic catalyst were reduced in H$_2$ to 280 °C, followed by cooling down to 50 °C under Ar. Then 24% H$_2$ in
Ar was pulsed for the measurement of Rh dispersion. Immediately after that, the sample was heated up to 500 °C in the presence of H₂ to reduce the NiO species. Then after cooling to 50 °C under Ar, 24% H₂ in Ar was pulsed again to measure the dispersion of Ni metal by deducting the contribution of Rh metal. It was shown that at 280 °C in H₂, only RhOₓ would be reduced with little reduction of NiO [9, 97]. The metal dispersion was calculated by assuming the chemisorption stoichiometry of one hydrogen atom per surface metal atom. The inverse of the metal dispersion data, 1/D, provides an estimation of the average metal particle size [10, 98].

In-situ X-ray photoelectron spectroscopy (XPS) measurements of the unreduced and reduced Rh catalysts supported on Al₂O₃ and CeO₂ were performed on a Physical Electronics Quantum 2000 Scanning ESCA microprobe located at Environmental Molecular Sciences Laboratory in the Pacific Northwest National Laboratory. The fresh catalyst sample was loaded in a quartz reactor and reduced under a 10% H₂/He mixture (100 cc/min in total) at 800 °C for 1 h before cooling to room temperature. The quartz reactor is connected to the XPS analytical chamber such that the reduced sample can be transferred into the chamber without air exposure. The XPS instrument uses a focused monochromatic Al-Kα X-ray (1486.7 eV) source for excitation and a spherical section analyzer. The X-ray beam used for this data was a 105-W, 100-µm X-ray beam spot rastered over a 1.4 × 0.2 mm rectangle on the sample. Electrons of 1 eV, 20 µA, and low-energy Ar⁺ ions were used to avoid the charging problem on the catalysts during XPS analysis. The binding energy were referenced using 916.7 and 74.7 eV for the Ce 3dₓ/₂ 4f₀ and Al 2p for the Rh/CeO₂ and Rh/Al₂O₃, respectively.
3.3.2. Characterization of used catalysts

The sulfur content in the used catalysts was determined by LECO SC 144DR. The sample was burnt in a pure oxygen environment at 1350 °C, resulting in a complete conversion of sulfur to SO$_2$. An IR cell was used to measure its concentration, based on which the sulfur content was determined. To measure the carbon amount in the used catalysts, TPO was performed using a LECO RC-412 multiphase carbon determiner with UHP oxygen passed over the sample as it was heated from ambient temperature to 900 °C at a rate of 30 °C/min. The temperature-programmed hydrogenation (TPH) experiments were conducted in a flow apparatus on a Micrometrics 2910 Autochem analyzer. In a typical TPH experiment, about 0.1 g of sample was loaded in a U-shaped quartz cell on a small amount of quartz wool plug. The sample was pretreated in Ar (50 ml/min) at 100 °C for 30 min, and then cooled down to 60 °C. Then the TPH profile was collected in a flow of 5% H$_2$/Ar (50 ml/min) while heating the sample at a ramp rate of 10 °C/min to 900 °C. Methane generated by carbon hydrogenation was monitored by a mass spectrometer (AMETEK Dycor DM200M).

XPS analyses on used catalysts were performed on a Kratos Analytical Axis Ultra using an X-ray source of monochromatic alumina (1486.6 eV) at 280 W, with pass energies of 80 eV (survey) and 20 eV (high-resolution) with step sizes of 0.5 and 0.1 eV, respectively. The catalyst powders were pressed into 5 × 5 mm 3M double-sided tape using a mortar and pestle and visualized by a stereomicroscope to ensure complete and uniform coverage. Prior to the analysis, oxide samples were dried overnight in an oven at 120 °C under atmospheric pressure. After drying, all samples were immediately stored in a container and mounted for analysis. Sample height positions were set from an O 1s
signal at 529 eV after changing the lateral coordinates such that the measured signals from the sample powders were maximized, thus minimizing any possible signal from the 3M double-sided tape. The tape was measured independently, and the characteristic shape of the C 1s line was not found when compared with the C 1s line collected during sampling. As a reference, we used the C 1s signal of the adventitious carbon (carbon of any surface adsorbed), which we fixed at 285 eV. XPS quantification was performed by applying the appropriate relative sensitivity factors (RSFs) and spectrometer transmission function for the Kratos instrument to the integrated peak areas. These RSFs take into consideration the X-ray cross-section and average attenuation length and instrumental factors related to X-ray source position, sample position, and spectrometer position. The spectrometer transmission function was corrected to an NPL calibration standard for the particular pass energy, magnification lens, aperture and iris settings, and transmission function of the spectrometer. The average sampling depth set on the C 1s line from an alumina powder was 30 Å. A survey scan was initially recorded for the sample to identify the elements present. Composition as well as chemical states were determined from the charge-corrected high resolution scans.

Sulfur K-edge XANES measurements of sulfur poisoned catalysts were performed at Beamline 9-BM/XOR of the Advanced Photon Source (APS) at Argonne National Laboratory. The storage ring was operated with an electron beam of 7 GeV and an electron current of 100 mA in a top-up mode. The monochromator was double-crystal Si(111), and the XANES spectra were collected in fluorescence mode with a Si DRIFT 4-element detector (Vortex). Air absorption was controlled by the use of helium purging in the incident flight path and the sample chamber, which were
separated by a 5 micron thick polycarbonate window. The monochromator crystals were Si(111) with an energy resolution of approximately 0.3 eV at 2.5 keV. Harmonics were rejected by use of a Rh-coated flat mirror in the experimental station. The beam was focused to a spot size of approximately 1 mm in the horizontal and vertical directions by the use of a Rh-coated toroidal mirror. A small amount of well-ground sample was evenly spread over a sulfur-free tape. Energy calibration was accomplished by setting the edge energy of elemental sulfur to 2472.0 eV. To establish the relationship between the edge energy and oxidation state, reference compounds were measured as received from Alfa Aesar (Ce$_2$(III)S$_3$, NiS, NiS$_2$, elemental sulfur, Na$_2$SO$_3$) and Sigma (NiSO$_4$, Ce(III)$_2$(SO$_4$)$_3$, Ce(IV)(SO$_4$)$_2$, 5-methylbenzothiophene, and dibenzothiophene). Up to 5 scans were collected and averaged to improve the signal to noise ratio.

Carbon K-edge XANES spectra were collected in total electron yield (TEY) mode at the Montana State University Nanostructures X-ray Materials Characterization Facility located at Beamline U4B of the National Synchrotron Light Source, Brookhaven National Laboratory, Upton, NY. A description of the experimental setup is available elsewhere [99]. The storage ring was operated with an electron beam of 800 MeV and an average electron current of 600 mA. A reference spectrum was always simultaneously collected for energy alignment. For sample preparation, the used catalyst was uniformly pressed onto a copper tape, and the sample was densely packed so that no visible crack or gap existed. The sample thickness was roughly tenths of millimeters, which assured that no interference from the adhesive was possible. XANES data were processed using Athena [100].
Scanning transmission X-ray microscopy (STXM) was performed on the Beamline X1A1 located in the National Synchrotron Light Source at Brookhaven National Laboratory, Upton, NY. Complete details on the design, operation, and capabilities of the microscope were described elsewhere [101, 102]. The STXM experiments were operated inside a He purge enclosure at room temperature and atmospheric pressure. The X-ray beam was focused to a size of 50 nm × 50 nm, and spectra were acquired in an energy range from 270 to 310 eV. STXM images were analyzed using a software written by Jacobsen et al. [103], which allows us to extract carbon XANES spectra at different locations within a sample.

Transmission electron microscopy (TEM) was performed on a Philips (FEI) EM420T (Tungsten emitter at 120 keV) with energy-dispersive X-ray spectroscopy (EDX). The images of high-resolution TEM and scanning transmission electron microscopy (STEM) of the used catalysts upon the reaction with sulfur were recorded by JEOL 2010F at 200 kV accelerating voltage. In a typical TEM sample preparation, the used catalyst was well dispersed in ethanol, and several drops of the suspension were deposited on a copper grid.
**Figure 3-1.** Schematic diagram of the reforming reactor.
Chapter 4
Comparative Study on the Sulfur Tolerance of Supported Noble Metal Catalysis in Steam Reforming of Liquid Hydrocarbon Fuel

Abstract

In order to clarify the impacts of metal and support on the sulfur tolerance of reforming catalysts, Al₂O₃-supported noble metals (Rh, Ru, Pt, and Pd) and Rh catalysts on different supports (Al₂O₃, CeO₂, SiO₂, and MgO) were tested by steam reforming of Norpar13 without and with sulfur at 800 °C. The reaction results indicate that (I) Rh/Al₂O₃ is the most sulfur tolerant among the Al₂O₃-supported noble metal catalysts, and (II) Al₂O₃ and CeO₂ are much better than SiO₂ and MgO as the supports for Rh catalyst to reform sulfur-containing hydrocarbons. High-resolution TEM/STEM characterization demonstrates that the Rh particles in Rh/Al₂O₃ were highly dispersed and smaller (mostly 1-3 nm) compared with those in the other Al₂O₃-supported noble metal catalysts. Sulfur K-edge XANES shows that the formation of sulfonate and sulfate is preferred on Rh/Al₂O₃ in the reaction with sulfur, being notably different from the other noble metal catalysts on which metal sulfides and organic sulfides dominate. The superior sulfur tolerance of Rh/Al₂O₃ may be attributed to the well-dispersed Rh particles and the formation of electron-deficient Rh particles with high sulfur tolerance. The good catalytic performance of Rh/CeO₂ in the presence of sulfur can be ascribed mainly to the promotion effect of CeO₂ on carbon gasification, leading to very low carbon deposition on the Rh/CeO₂ catalyst.
4.1. Introduction

Many previous studies regarding hydrocarbon reforming have demonstrated that noble metal catalysts generally possess good sulfur tolerance and carbon-resistance [17-19, 22, 23, 33, 49]. Owing to their potentially strong resistance to sulfur poisoning and carbon deposition, supported noble metal catalysts are being intensively studied and developed in fuel processing field for H₂ production and fuel cell applications. In the present study, two series of catalysts: Al₂O₃-supported noble metals (Rh, Ru, Pt, and Pd), and Rh catalysts on different supports (Al₂O₃, CeO₂, SiO₂, and MgO) were prepared and tested for steam reforming of hydrocarbon fuels in the absence and presence of sulfur at 800 °C. The goal is to explore the impacts of metal and support on the sulfur tolerance of supported noble metal catalysts in hydrocarbon reforming. In addition to fresh catalyst characterization using BET, H₂-TPR, and H₂ chemisorption, high-resolution TEM/STEM and sulfur K-edge XANES were employed to characterize the metal particle sizes and to identify the sulfur species in the used catalysts upon the reactions with sulfur, respectively. Combination of the catalyst performances and the characterization results clearly demonstrates that both metals and supports can profoundly affect the sulfur tolerance of supported noble metal catalysts in steam reforming of hydrocarbons with sulfur.
4.2. Results

4.2.1. Al$_2$O$_3$-supported noble metal catalysts

The hydrogen production rates (HPR) for the Al$_2$O$_3$-supported noble metal catalysts (Rh, Ru, Pt, and Pd) upon reforming of Norpar13 and Norpar13 doped with 350 ppmw sulfur (refer to as Norpar13(350)) for 55 h are exhibited in Figure 4-1. For the sulfur-free cases, the H$_2$ production over the Rh, Ru, and Pt catalysts is comparable, which is slightly higher than that of Pd. This observation is consistent with previous studies illustrating that Pd is less reactive than the other noble metals (e.g., Rh, Ru, and Pt) in hydrocarbon reforming [98, 104]. Although the presence of sulfur deactivated all the Al$_2$O$_3$-supported noble metal catalysts in Norpar13(350) reforming to some extent, the activity drop for Rh/Al$_2$O$_3$ is the lowest (see Table 4-1). This fact shows that Rh/Al$_2$O$_3$ possesses better sulfur tolerance than the other Al$_2$O$_3$-supported noble metals in steam reforming of sulfur-containing hydrocarbons at 800 ºC.

The carbon amounts in the used Al$_2$O$_3$-supported noble metal catalysts after the reactions without and with sulfur for 55 h are presented in Figure 4-2. Compared with the sulfur-free reaction, the carbon deposition dramatically increased upon Norpar13(350) reforming, which is especially significant for the Ru, Pt, and Pd catalysts. Figure 4-3 exhibits the sulfur contents in the used noble metal catalysts after Norpar13(350) reforming for 55 h. It is interesting to note that the sulfur content in Rh/Al$_2$O$_3$ is about 2-3 times higher than those in the Ru, Pt, and Pd catalysts, though its catalytic performance is
the best among all the Al₂O₃-supported noble metal catalysts for Norpar13(350) reforming.

Figure 4-4 presents the TEM and Z-contrast (STEM) images of the used noble metal catalysts upon Norpar13(350) reforming for 55 h. It can be seen that the Rh particles highly dispersed on Al₂O₃ in a range of 1-3 nm. This observation is consistent with previous studies demonstrating that Rh prefers to homogeneously distribute on Al₂O₃ [105-107]. It was found that rhodium atoms in Rh/Al₂O₃ can strongly interact with the oxygen ions in the Al₂O₃ support, which is capable of effectively stabilizing Rh particles against their sintering [105, 106]. Beck et al.[108] used EXAFS to characterize a Rh catalyst supported on Al₂O₃, and demonstrated that the Rh particles in this catalyst are in a range of 1-2 nm. In contrast, much larger metal particles in a range of 10-25 nm can be clearly seen in the other Al₂O₃-supported noble metal catalysts. Compared with Rh/Al₂O₃, the dispersion of other noble metals (Ru, Pt, and Pd) on Al₂O₃ appears to be lower, which has been well demonstrated by previous studies as well [22, 23, 80, 105, 108, 109]. In Nagai et al.’s study, it was shown that the Pt particles in a Pt/Al₂O₃ catalyst are mostly larger than 10 nm after 800 ºC aging in air for 5 h [80]. Zhao et al. reported that the Ru particle sizes of Ru/Al₂O₃ upon calcination at 500 ºC are between 10 and 15 nm [109].

The metal particle sizes obtained from TEM agrees well with the results of H₂ chemisorption. As summarized in Table 4-1, no measurable H₂ uptakes can be detected for the Ru and Pd catalysts, implying that the metal particles in these two catalysts are not well dispersed on Al₂O₃ and their particle sizes should be pretty large upon 800 ºC reduction. Combining the above-mentioned facts, we suggest that the metal dispersion of the Al₂O₃-supported noble metal catalysts follows an order of Rh > Pt > Ru ≈ Pd.
In order to gain insight into the pronouncedly different sulfur tolerance of the Al$_2$O$_3$-supported Rh, Ru, Pt, and Pd catalysts, sulfur K-edge XANES was carried out to identify the sulfur species in these used catalysts after Norpar13(350) reforming for 55 h, as shown in Figure 4-5. With respect to the Rh/Al$_2$O$_3$ catalyst, four sulfur species can be observed, which are metal sulfide (Rh-S) at 2472 eV, organic sulfide (-C-S-C-) at 2475 eV, sulfonate (C$_x$H$_y$-SO$_2$O$^-$) at 2481 eV, and sulfate (SO$_4^{2-}$) at 2483 eV [92, 110]. Although the same sulfur species can be observed with the other used Al$_2$O$_3$-supported noble metal catalysts, their relative abundances are dramatically different from that of Rh/Al$_2$O$_3$. Apparently, the Ru, Pt, and Pd catalysts show strong peaks of organic sulfides, but with notably weaker peaks of metal sulfide, sulfonate, and sulfate. We believe that the organic sulfides should largely derive from the deposition of the organic sulfur compound (3-MBT) in the fuel and its pyrolysis fragments containing -C-S-C- on the catalysts. It seems that the formation of organic sulfides is closely correlated with abundant carbon deposits, which can cover reforming catalysts to hinder desorption of organic sulfides. Therefore, the much more severe carbon deposition on the Ru, Pt, and Pd catalysts upon Norpar13(350) reforming than that on Rh/Al$_2$O$_3$ may account for the strong XANES peaks of organic sulfides in the formers rather than in the latter. Moreover, the excessive carbon deposits may cover the metal surfaces of the Ru, Pt, and Pd catalysts such that sulfur adsorption on the metals as well as the formation of the oxidized sulfur species will be suppressed. These postulations may explain the weak peaks of metal sulfide, sulfonate, and sulfate in the sulfur XANES spectra of the used Ru, Pt, and Pd catalysts.
4.2.2. Rh catalysts on different supports

The Rh catalysts on different supports (Al$_2$O$_3$, CeO$_2$, SiO$_2$, and MgO) were studied to evaluate the effect of support on the sulfur tolerance of Rh. Figure 4-6 displays the TPR profiles for the Rh catalysts on the different supports. Rh/Al$_2$O$_3$ shows a very broad profile up to 600 °C due to the reduction of Rh$_2$O$_3$. The rhodium reduction for Rh/SiO$_2$ and Rh/MgO is accomplished at lower temperatures around 200 and 400 °C, respectively. Rh/CeO$_2$ exhibits two peaks at 150 and 200 °C as a result of the reduction of Rh$_2$O$_3$ and CeO$_2$, respectively [10]. Since the reduction of CeO$_2$ alone generally takes place at temperatures higher than 400 °C [78], it appears that Rh is able to facilitate the reduction of CeO$_2$. This is very likely due to the facile H$_2$ dissociation on Rh, followed by spillover of H species onto CeO$_2$ [10, 78]. Compared with the other Rh catalysts, the reduction peak in Rh/Al$_2$O$_3$ is much broader. This may be due to the intimate interaction between rhodium and alumina, thus making Rh reduction difficult [107, 108, 111].

Figure 4-7 presents the catalytic performances of the Rh catalysts on the different supports after reforming of Norpar13 and Norpar13(350) for 55 h. In the case of Norpar13 reforming, the Rh catalysts supported on Al$_2$O$_3$, CeO$_2$, and MgO exhibit similar H$_2$ production, which is slightly higher than Rh/SiO$_2$. With the presence of sulfur, both Rh/SiO$_2$ and Rh/MgO significantly deactivated, while the activity drops for Rh/Al$_2$O$_3$ and Rh/CeO$_2$ are much less significant (refer to Table 4-1). The pronouncedly different catalytic performances of these Rh catalysts in Norpar13(350) reforming reflect the crucial role of support in determining the sulfur tolerance of Rh catalysts in hydrocarbon reforming.
The carbon amounts on the used Rh catalysts after reforming of Norpar13 and Norpar13(350) for 55 h are presented in Figure 4-8. In the absence of sulfur, the carbon deposition on Rh/SiO₂ is much more severe than those on the other Rh catalysts. The excessive carbon deposits on Rh/SiO₂ may account for its slight deactivation in reforming of sulfur-free Norpar13. Evidently, the carbon amounts on the used Rh catalysts after Norpar13(350) reforming are higher than those after Norpar13 reforming, which is also true for the Al₂O₃-supported noble metal catalysts (Figure 4-2). It is therefore clear that the presence of sulfur can enhance the carbon deposition on reforming catalysts. Our recent work studied the sulfur poisoning mechanism of a Ni-based catalyst in steam reforming of hydrocarbons at 800 ºC [112]. It was found that sulfur is capable of degrading the capability of reforming catalysts in carbon gasification and then giving rise to severe carbon deposition. Figure 4-9 exhibits the sulfur contents in the used Rh catalysts on the different supports after Norpar13(350) reforming for 55 h. In parallel with what we have observed with the Al₂O₃-supported noble metal catalysts, the sulfur content in Rh/Al₂O₃ is apparently higher than those in the other Rh catalysts after Norpar13(350) reforming.

Figure 4-10 presents the TEM and Z-contrast (STEM) images of the used Rh catalysts supported on CeO₂, SiO₂, and MgO after Norpar13(350) reforming for 55 h. Rh particles in a range of 5-15 nm can be clearly seen on those supports, which is obviously larger than those of Rh/Al₂O₃ (1-3 nm). The formation of large Rh particles on supports such as CeO₂, SiO₂, and MgO has been well documented in literature [50, 113, 114]. For example, Hennings and Reimert observed that the metal particle sizes of Rh/CeO₂ after steam reforming of natural gas at 800 ºC are around 10 nm [50]. Sadi et al.’s study
regarding the morphological changes of Rh/SiO$_2$ in a reducing atmosphere indicated that the Rh particles on SiO$_2$ are largely in a range of 30-40 nm [113]. The very larger Rh particles on SiO$_2$ can be explained by weak interaction between Rh and SiO$_2$ such that Rh tends to agglomerate to form large particles. Accordingly, it can be inferred that Al$_2$O$_3$ is such a support that can effectively stabilize Rh to attain smaller particle sizes compared with the other supports investigated in this study.

Sulfur K-edge XANES spectra of the used Rh catalysts after Norpar13(350) reforming for 55 h are shown in Figure 4-11. Again, the peaks of the oxidized sulfur species (sulfonate and sulfate) for Rh/Al$_2$O$_3$ are much stronger than those of the other Rh catalysts. In addition, both Rh/MgO and Rh/SiO$_2$ exhibit an intensive peak of organic sulfides, which is not the case for Rh/Al$_2$O$_3$ and Rh/CeO$_2$. Again, their peak intensities of metal sulfide, sulfonate, and sulfate are weak due very likely to the severe carbon deposition on these two catalysts upon Norpar13(350) reforming.

4.3. Discussion

Both the reaction data and the characterization results presented in this work shed light on the remarkable effects of metal and support on the sulfur tolerance of supported noble metal catalysts in steam reforming of sulfur-containing liquid hydrocarbon fuel. Among the tested Al$_2$O$_3$-supported noble metal catalysts, Rh/Al$_2$O$_3$ exhibits the best sulfur tolerance. As to the different supports, Al$_2$O$_3$ and CeO$_2$ are the promising ones for Rh catalyst to reform hydrocarbons in the presence of sulfur. Generally, sulfur poisoning of reforming catalysts is influenced by various parameters such as the physicochemical properties of metal and support (e.g., the dispersion and electronic structure of metal as
well as the acidic property of support) [44, 46, 47, 74, 115-120]. In the following, the impacts of metal and support on the sulfur tolerance of supported metal catalysts in steam reforming of hydrocarbons will be discussed in terms of these parameters.

**4.3.1. Best sulfur tolerance of Rh among the noble metal catalysts**

The results of H$_2$ chemisorption and TEM show that Rh/Al$_2$O$_3$ has the highest metal dispersion among the Al$_2$O$_3$-supported noble metal catalysts. This is very likely due to the intimate interaction between Rh and Al$_2$O$_3$, which is a well-known phenomenon for Al$_2$O$_3$-supported Rh catalysts [105-108, 111]. The mechanism for the strong interaction between Rh and Al$_2$O$_3$ remains unclear, and various hypotheses have been proposed, including (I) the generation of a spinel rhodium-alumina structure through diffusion of Rh into Al$_2$O$_3$ bulk [111], (II) covering Rh by a layer of Al$_2$O$_3$ [107], and (III) formation of non-stoichiometric rhodium oxides (e.g., RhO$_x$) that are capable of strongly interacting with Al$_2$O$_3$ [108]. Due to the highest metal dispersion, the number of metal sites in Rh/Al$_2$O$_3$ available for sulfur adsorption is expected to be higher than those in the other noble metal catalysts. This is one of plausible reasons to explain the good sulfur tolerance of Rh/Al$_2$O$_3$.

Sulfur poisoning of supported metal catalysts can be attributed to the strong chemisorptive sulfur adsorption on metals, through which sulfur withdraws electrons from metals and decreases the density of states (DOS) around their Fermi levels [44, 46, 47, 74]. The magnitude of such an adverse electronic effect of sulfur strongly depends on the nature of metals. Previous studies [47, 121, 122] have verified that the tendency of Rh to lose its electrons upon sulfur adsorption is lower than most transition metals [47, 121,
122]. For example, recent work has demonstrated that sulfur is able to incur a reduction of ca. 25% in the DOS near the Fermi level of Rh, whereas that for Pt and Pd is much more significant (ca. 50-55%) [121, 122]. Therefore, it is also reasonable to correlate the good sulfur tolerance of Rh with its strong resistance to the sulfur-induced electron withdrawal.

Sulfur K-edge XANES spectra of the used noble metal catalysts (Figure 4-5) indicates that the formation of sulfonate and sulfate prevailed on Rh/Al₂O₃. It has been proposed that sulfonate and sulfate is less poisoning than metal sulfide because their oxygen-shielded sulfur structure can hinder direct sulfur-metal interactions, thus reducing the poisoning effect of sulfur on metals [44, 46, 74]. Besides, previous studies regarding sulfur poisoning of supported metal catalysts have indicated that oxidized sulfur species on metals are unstable and tend to migrate onto supports [123-126]. This implies that the Al₂O₃ support in Rh/Al₂O₃ may act as a sulfur trap to accommodate the oxidized sulfur species and then protect Rh from sulfur poisoning. The possible sulfur accumulation on the Al₂O₃ support can interpret the fact that why Rh/Al₂O₃ with the highest sulfur content among all the tested catalysts still exhibited good catalytic performance in Norpar13(350) reforming.

**4.3.2. Significant support effect on the sulfur tolerance of Rh**

With respect to the effect of support on the sulfur tolerance of supported metal catalysts, there is a general agreement that those on acidic supports have better sulfur tolerance [115-117, 119, 120, 127, 128]. This is because acidic supports favor the formation of electron-deficient metals as a result of electron transfer from metals to
acidic supports [115, 117-120, 129, 130]. Tang et al. reported that the binding energy of Pd 3d$_{5/2}$ for strongly acidic Pd/Beta-H (335.5 eV) is higher than that for weaker acidic Pd/Al-MCM-41 (335.0 eV), which well supports the formation of electron-deficient metals on acidic supports [120]. Furthermore, Miller et al. compared the sulfur adsorption on Pt catalysts supported on acidic and alkaline zeolites. They claimed that the ratio of S to Pt is lower for the one on the acidic zeolite, indicative of suppressed sulfur adsorption on electron-deficient metals [117]. This is probably because of the difficulty to withdraw electrons from electron-deficient metals by sulfur, thus weakening the interaction between sulfur and metals [117, 127, 129]. Moreover, it has been suggested that smaller metal particles generally have better sulfur tolerance as metals become electron-deficient if their particle sizes decrease [131-133]. Sheu et al. [133] investigated the sulfur tolerance of Pd catalysts loaded on SiO$_2$, TiO$_2$, and TiO$_2$-grafted SiO$_2$ in tetralin hydrogenation. The authors claimed that the Pd catalyst on TiO$_2$-grafted SiO$_2$ was the most sulfur tolerant, which was ascribed to the retardation effect of TiO$_2$ modification on the growth of Pd crystallites, resulting in the formation of electron-deficient Pd particles.

The good sulfur tolerance of Rh/Al$_2$O$_3$ in Norpar13(350) reforming may be attributed to the smaller Rh particles and the acidic Al$_2$O$_3$ support, both of which may aid in the formation of electron-deficient Rh particles with improved sulfur tolerance. In order to confirm this hypodissertation, XPS was carried out measure the binding energy (B.E.) of the fresh Rh catalysts supported on Al$_2$O$_3$ and CeO$_2$. As shown in Figure 4-12, The B.E. for the unreduced and reduced Rh/CeO$_2$ catalysts is 309.0 (Rh$^{3+}$) and 307.0 (Rh$^0$) eV, respectively [97]. Remarkable B.E. shifts to high energy are observed for the unreduced (309.8 eV) and reduced (307.6 eV) Rh/Al$_2$O$_3$ catalysts compared with the
Rh/CeO$_2$ catalyst and Rh metal standard (see Table 4-2). These XPS results proved the formation of electron-deficient Rh particles on the Al$_2$O$_3$ support. Due to the weaker interaction between sulfur and electron-deficient metals [47, 117, 129], the bonding between the adsorbed sulfur and the Rh particles in Rh/Al$_2$O$_3$ may be readily broken, followed by sulfur oxidation induced by the surface oxygen species derived from steam in our reforming reactions. It is possible that the preferred formation of the oxidized sulfur species on Rh/Al$_2$O$_3$ is related to the formation electron-deficient Rh particles on Al$_2$O$_3$.

Despite SiO$_2$ is also a known acidic support like Al$_2$O$_3$, the sulfur tolerance of Rh/SiO$_2$ is worse than that of Rh/Al$_2$O$_3$. This contrast can be partially attributed to the larger Rh particles in Rh/SiO$_2$. Moreover, the high carbon contents on Rh/SiO$_2$ in Norpar13 reforming in the absence and presence of sulfur is believed to be another important reason for its inferior catalytic performance. As to the MgO support, it is an alkaline material, which is supposed not to favor the formation of electron-deficient Rh particles. Furthermore, the TEM result indicates the fairly large Rh particles on the MgO support. As a result, Rh/MgO exhibited poor sulfur tolerance in Norpar13(350) reforming.

It is very interesting to note that, although CeO$_2$ is not an acidic support and the Rh particles on Rh/CeO$_2$ are larger than those on Rh/Al$_2$O$_3$, the two catalysts show very similar catalytic performance in Norpar13(350) reforming. This can be attributed to the strong oxygen storage capability of CeO$_2$ that enables the facile release of its surface oxygen species to facilitate carbon gasification [10, 77-79, 134]. Therefore, the amounts of carbon deposits on the used Rh/CeO$_2$ catalysts upon Norpar13 reforming without and with sulfur are much lower compared with those supported on Al$_2$O$_3$, SiO$_2$, and MgO.
(Figure 4-8). Unlike the Rh catalysts on SiO$_2$ and MgO, there is no intensive XANES peak of organic sulfides observed for Rh/CeO$_2$ after Norpar13(350) reforming. This is because its low carbon deposition did not favor the accumulation of organic sulfides. Another interesting phenomena concerning Rh/CeO$_2$ is no detectable H$_2$ adsorbed on it in H$_2$ chemisorption (Table 4-1), which is most likely due to the strong metal-support interaction (SMSI) between Rh and CeO$_2$ [135, 136]. For CeO$_2$-supported metal catalysts under a strong reducing atmosphere, CeO$_2$ can be reduced CeO$_{2-x}$, followed by migration onto metals to cover their surfaces and thereby impede H$_2$ chemisorption [135, 136]. Interestingly, Rh/CeO$_2$ exhibited good catalytic performance in our hydrocarbon reforming reactions, revealing that the Rh particles in this catalyst should be well exposed in the reactions. According to previous literature [137], such an inconsistency may be because the oxygen species existing in steam reforming of hydrocarbons are able to oxidize CeO$_{2-x}$ back to CeO$_2$, therefore recovering the buried Rh particles. This hypodissertation is supported by the TEM image of the used Rh/CeO$_2$ catalyst (Figure 4-10) showing no evidence of ceria existing on the Rh particles.

4.4. Conclusions

The present study clearly demonstrated that both metal and support play key roles in determining the sulfur tolerance of supported noble metal catalysts in steam reforming of sulfur-containing hydrocarbon fuel. Among the Al$_2$O$_3$-supported noble metal catalysts (Rh, Ru, Pt, and Pd), Rh/Al$_2$O$_3$ shows the best sulfur tolerance. CeO$_2$ and Al$_2$O$_3$ are much better than SiO$_2$ and MgO as the supports for Rh catalyst to reform sulfur-containing hydrocarbons. The superior sulfur tolerance of Rh/Al$_2$O$_3$ can be associated with the well-
dispersed Rh particles and the formation of electron-deficient Rh particles with high sulfur tolerance. Sulfur K-edge XANES indicated that the formation of sulfonate and sulfate preferred on Rh/Al₂O₃. Their oxygen-shield sulfur structure may hinder direct Rh-S interaction and thereby suppress the poisoning effect of sulfur. The good catalytic performance of Rh/CeO₂ in the reaction with sulfur can be mainly attributed to the pronounced promotion effect of CeO₂ on carbon gasification, leading to the very low carbon deposition on this catalyst.
Table 4-1. The physical properties of the fresh Al₂O₃-supported noble metal catalysts (Rh, Ru, Pt, and Pd) and the fresh Rh catalysts on the different supports (Al₂O₃, CeO₂, SiO₂, and MgO)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>S_{BET} (m²/g_{cat})</th>
<th>Pore Vol. (cm³/g)</th>
<th>Dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/Al₂O₃</td>
<td>148.3</td>
<td>0.77</td>
<td>83.6</td>
</tr>
<tr>
<td>Ru/Al₂O₃</td>
<td>136.1</td>
<td>0.76</td>
<td>N.D.</td>
</tr>
<tr>
<td>Pt/Al₂O₃</td>
<td>137.8</td>
<td>0.81</td>
<td>62.4</td>
</tr>
<tr>
<td>Pd/Al₂O₃</td>
<td>134.3</td>
<td>0.69</td>
<td>N.D.</td>
</tr>
<tr>
<td>Rh/CeO₂</td>
<td>92.9</td>
<td>0.18</td>
<td>N.D.</td>
</tr>
<tr>
<td>Rh/SiO₂</td>
<td>378.6</td>
<td>0.29</td>
<td>44.3</td>
</tr>
<tr>
<td>Rh/MgO</td>
<td>36.7</td>
<td>0.08</td>
<td>58.7</td>
</tr>
</tbody>
</table>

*Not detectable. No reliable H₂ chemisorption after 800 °C reduction pretreatment due very likely to significant metal agglomeration into larger particles, as evidenced by TEM images shown in Figures 4-4 and 4-10.

b Not detectable. No reliable H₂ chemisorption after 800 °C reduction pretreatment due very likely to strong metal-support interaction in Rh/CeO₂, which may make Rh surface covered by reduced ceria species.
Table 4-2. Rh 3d XPS data of unreduced and reduced (10H₂/He, 800 °C) Rh/Al₂O₃ and Rh/CeO₂

<table>
<thead>
<tr>
<th>Samples</th>
<th>Pretreatment</th>
<th>Rh 3dₓ/ᵧ (eV)</th>
<th>FWHM</th>
<th>Rh 3dₓ/ᵧ (eV)</th>
<th>FWHM</th>
<th>ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/Al₂O₃</td>
<td>Unreduced</td>
<td>309.8</td>
<td>2.8</td>
<td>314.6</td>
<td>2.7</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>Reduced</td>
<td>307.6</td>
<td>1.5</td>
<td>312.3</td>
<td>1.8</td>
<td>4.7</td>
</tr>
<tr>
<td>Rh/CeO₂</td>
<td>Unreduced</td>
<td>309.0</td>
<td>1.4</td>
<td>313.9</td>
<td>1.8</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>Reduced</td>
<td>307.0</td>
<td>1.1</td>
<td>311.8</td>
<td>1.4</td>
<td>4.8</td>
</tr>
<tr>
<td>Rh foil</td>
<td></td>
<td>307.0</td>
<td>N/A</td>
<td>312.0</td>
<td>N/A</td>
<td>5.0</td>
</tr>
<tr>
<td>Rh₂O₃</td>
<td></td>
<td>308.8</td>
<td>N/A</td>
<td>313.6</td>
<td>N/A</td>
<td>4.8</td>
</tr>
</tbody>
</table>

* spin–orbit coupling energy.

b Not available

c reference [97]
Figure 4-1. Comparison of the catalytic performances of Al₂O₃-supported Rh, Ru, Pd, and Pt catalysts in steam reforming of Norpar13 and Norpar13 doped with 350 ppmw sulfur (Norpar13(350)) at 800 ºC for 55 h. The number in the parentheses represents the percentage of activity drop for the Al₂O₃-supported Rh, Ru, Pd, and Pt catalysts in the reaction with sulfur compared with the sulfur-free reaction upon 55 h on stream.
Figure 4-2. The carbon amounts in the used Al₂O₃-supported Rh, Ru, Pd, and Pt catalysts after steam reforming of Norpar13 and Norpar13 doped with 350 ppmw sulfur (Norpar13(350)) at 800 °C for 55 h.
Figure 4-3. The sulfur contents in the used Al$_2$O$_3$-supported Rh, Ru, Pd, and Pt catalysts after steam reforming of Norpar13 doped with 350 ppmw sulfur (Norpar13(350)) at 800 °C for 55 h.
Figure 4-4. High-resolution TEM and Z-contrast (STEM) images of the used Al₂O₃-supported Rh, Ru, Pd, and Pt catalysts after steam reforming of Norpar13 doped with 350 ppmw sulfur (Norpar13(350)) at 800 ºC for 55 h. The brighter spots in the Z-contrast (STEM) images represent metal particles.
Figure 4-5. Sulfur K-edge XANES spectra of the used Al₂O₃-supported Rh, Ru, Pd, and Pt catalysts after steam reforming of Norpar13 doped with 350 ppmw sulfur (Norpar13(350)) at 800 °C for 55 h.
Figure 4-6. TPR profiles of the fresh Rh catalysts supported on Al$_2$O$_3$, CeO$_2$, SiO$_2$, and MgO.
Figure 4-7. Comparison of the catalytic performances of the Rh catalysts supported on Al$_2$O$_3$, CeO$_2$, SiO$_2$, and MgO in steam reforming of Norpar13 and Norpar13 doped with 350 ppmw sulfur (Norpar13(350)) at 800 °C for 55 h. The number in the parenthesis represents the percentage of activity drop for the Rh catalysts supported on Al$_2$O$_3$, CeO$_2$, SiO$_2$, and MgO in the reaction with sulfur compared with the sulfur-free reaction upon 55 h on stream.
Figure 4-8. The carbon amounts in the used Rh catalysts supported on Al₂O₃, CeO₂, SiO₂, and MgO after steam reforming of Norpar13 and Norpar13 doped with 350 ppmw sulfur (Norpar13(350)) at 800 ºC for 55 h.
Figure 4-9. The sulfur amounts in the used Rh catalysts supported on $\text{Al}_2\text{O}_3$, $\text{CeO}_2$, $\text{SiO}_2$, and $\text{MgO}$ after steam reforming of Norpar13 doped with 350 ppmw sulfur (Norpar13(350)) at 800 °C for 55 h.
Figure 4-10. High-resolution TEM and Z-contrast (STEM) images of the used Rh catalysts supported on CeO$_2$, SiO$_2$, and MgO after steam reforming of Norpar13 doped with 350 ppmw sulfur (Norpar13(350)) at 800 ºC for 55 h. The brighter spots in the Z-contrast (STEM) images represent metal particles. For Rh/CeO$_2$, d-space analysis confirms a Rh particle supported on CeO$_2$. It is difficult to differentiate Rh particles from CeO$_2$ in the Z-contrast (STEM) image of the used Rh/CeO$_2$ catalyst as cerium is a very heavy element.
Figure 4-11. Sulfur K-edge XANES spectra of the used Rh catalysts supported on Al$_2$O$_3$, CeO$_2$, SiO$_2$, and MgO after steam reforming of Norpar13 doped with 350 ppmw sulfur (Norpar13(350)) at 800 ºC for 55 h.
Figure 4-12. Rh 3d XPS spectra of the unreduced and reduced (800 °C) Rh catalysts supported on Al$_2$O$_3$ and CeO$_2$. 
Chapter 5
Sulfur Poisoning of CeO$_2$-Al$_2$O$_3$-Supported Mono- and Bi-metallic Ni and Rh Catalysts in Steam Reforming of Liquid Hydrocarbons at Low and High Temperatures

Abstract
Steam reforming of liquid hydrocarbons was performed over CeO$_2$-Al$_2$O$_3$ supported monometallic Ni and Rh and bimetallic Rh-Ni catalysts at 550 and 800 °C. XANES and XPS were used to identify the sulfur species in the used catalysts and to study their impacts on the metal surface properties, respectively. It was found that both monometallic catalysts rapidly deactivated at 550 °C, and showed poor sulfur tolerance. Although ineffective for the Ni catalyst, increasing the temperature to 800 °C dramatically improved the sulfur tolerance of the Rh catalyst. XANES revealed that metal sulfide and organic sulfide are the dominant sulfur species on the used Ni catalyst, while sulfonate and sulfate predominate on the Rh catalyst. The presence of sulfur induced severe carbon deposition on the Ni catalyst at 800 °C. The superior sulfur tolerance of the Rh catalyst at 800 °C may be associated with its capability in sulfur oxidation. It is likely that the oxygen-shielded sulfur structure of sulfonate and sulfate can suppress the poisoning impact of sulfur on Rh through inhibiting direct rhodium-sulfur interaction. Moreover, XPS indicated that the metal surface properties of the Rh catalysts after the reaction without and with sulfur at 800 °C are similar, suggesting that sulfur poisoning on Rh was mitigated under the high-temperature condition. Although the Rh-Ni catalyst exhibited better sulfur tolerance than the monometallic catalysts at 550 °C, its catalytic...
performance was inferior compared with the Rh catalyst in the sulfur-containing reaction at 800 °C probably due to the severe carbon deposition on the bimetallic catalyst.

5.1. Introduction

Fuel cells are electrochemical devices for efficient and environmentally benign conversion of fuels such as hydrogen (H\textsubscript{2}) into electricity [1]. One of their potential applications is to be used in transportation vehicles as auxiliary power units (APUs) to save energy and reduce pollutant emissions [8, 12, 138]. Of various fuel cells, proton exchange membrane fuel cells (PEMFCs) and solid oxide fuel cells (SOFCs) are considered good candidates for such an application [1, 7, 13]. To effectively supply H\textsubscript{2} to the mobile fuel cell power systems many approaches have been attempted so far [6]. One of them is on-board H\textsubscript{2} production via steam reforming of liquid hydrocarbons [1, 6, 7, 13]. Generally, hydrocarbon steam reforming is operated at high temperatures (> 700 °C) for converting hydrocarbons to H\textsubscript{2}, CO, and CO\textsubscript{2}, which can be directly fed into SOFCs. Excessive CO up to 20% may be generated in high-temperature steam reforming (HTSR) [88]. Unfortunately, PEMFCs are very sensitive to CO because of its poisoning effect on their anodes [1]. Therefore, costly and cumbersome downstream treatments are imperative for deep CO removal for PEMFCs, which dramatically add to the cost and complexity of the fuel processing system [1]. In this context, low-temperature (450-650 °C) steam reforming (LTSR) is a better choice for PEMFCs as it can dramatically reduce the CO formation [1, 9, 10, 97]. The foregoing information clearly indicates that HTSR and LTSR have their own unique features, and therefore are suitable for different fuel cell
applications. This triggers our interest in a comparative study on steam reforming of liquid hydrocarbons at different temperatures.

Hydrocarbon steam reforming generally employs transition metal catalysts (e.g., Ni and Rh) supported on metal oxides such as Al₂O₃ [17, 18, 21, 79, 139, 140], CeO₂ [22, 23, 141, 142], and CeO₂-Al₂O₃ [9, 27, 77]. Reforming of various liquid hydrocarbon fuels (e.g., gasoline, diesel, and jet fuels) [9, 17, 21, 26, 28-32] and their surrogates [18, 19, 33-36] has been extensively studied. For the liquid hydrocarbon fuels derived from fossil fuels, they often contain organic sulfur impurities whose content may be up to 3000 ppmw (ppm by weight) [43]. It has been well documented that sulfur can deactivate metal catalysts even at a trace level [18, 44-46].

Although base metals such as nickel are cost-effective, their sulfur tolerance is lower when compared with noble metals. As a result, considerable attention has been focused on noble-metal-based reforming catalysts [17, 19, 20, 22-26, 33, 49-51, 88]. Hennings et al. compared the catalytic performances of Rh, Pt, Ru, and Ni in hydrocarbon steam reforming in the presence of sulfur at 800 °C, and reported that Rh shows the best sulfur tolerance [50]. A very similar conclusion has also been drawn in a recent study about reforming of n-tetradecane in the presence of sulfur [33]. Moreover, it was found that bimetallic catalysts are generally more active and stable than monometallic ones for hydrocarbon reforming. For example, Strohm et al. [9] developed a sulfur-tolerant Rh-Ni catalyst, which allowed for successful low-temperature (~520 °C) reforming of a JP-8 jet fuel containing 22 ppm sulfur for 72 h with >95% fuel conversion.

In spite of many studies available concerning liquid hydrocarbon reforming [17, 19, 22-24, 26, 31, 33-35, 49, 88], sulfur poisoning of reforming catalysts has not been well
studied from a mechanistic point of view. Therefore, the objective of the present work is to
develop a better understanding on sulfur poisoning of supported metal catalysts in liquid hydrocarbon steam reforming. Monometallic Ni and Rh as well as bimetallic Rh-Ni catalysts supported on CeO₂ modified Al₂O₃ were evaluated for steam reforming of liquid hydrocarbons without and with sulfur at 550 and 800 °C. A variety of characterization techniques involving H₂-TPR, H₂-chemisorption, chemical analysis, XPS, and XANES were applied to study the physicochemical properties of the fresh and used catalysts. With the aid of XANES and XPS the sulfur species in the used catalysts as well as their impacts on the catalyst surface properties were investigated. Particular attention was paid to interpret the catalyst sulfur tolerance in terms of the formation of different sulfur species.

5.2. Results and Discussion

5.2.1. Physical properties

Table 5-1 summarizes the physic-chemical properties of the catalytic materials studied. The Al₂O₃ support has a surface area of 144 m²/g and a pore volume of 0.81 cm³/g, while those for the CeO₂-Al₂O₃ support are 121 m²/g and 0.63 cm³/g, respectively. Impregnation of the metals onto CeO₂-Al₂O₃ did not notably alter the textural property of the CeO₂-Al₂O₃ support (117 m²/g and 0.57 cm³/g for Rh/CeO₂-Al₂O₃, 109 m²/g and 0.54 cm³/g for Ni/CeO₂-Al₂O₃, and 102 m²/g and 0.49 cm³/g for Rh-Ni/CeO₂-Al₂O₃).

H₂-TPR profiles of the supports and the catalysts are presented in Figure 5-1. Since no reduction is detectable for the Al₂O₃ up to 850 °C due to its thermally stable
characteristics, the observed H₂ consumption between 300 and 850 ºC in the case of CeO₂-Al₂O₃ can be attributed to the reduction of ceria. A sharp reduction peak appears at ca. 100 ºC with a shoulder at ca. 250 ºC for Rh/CeO₂-Al₂O₃, which is due to the reduction of Rh₂O₃ as well as CeO₂ [10], respectively. Comparison of the reduction profiles of CeO₂-Al₂O₃ and Rh/CeO₂-Al₂O₃ indicates that the presence of rhodium enhances the ceria reduction, most likely because of hydrogen spillover from rhodium to ceria [10, 143]. Ni/CeO₂-Al₂O₃ exhibits a broad peak from 400 to 850 ºC dominantly stemming from the reduction of NiO in close interaction with the Al₂O₃ support [144]. Besides, the likelihood of ceria reduction in this temperature range may exist. For Rh-Ni/CeO₂-Al₂O₃ two peaks are observed at ca. 100 and 450 ºC, which can be mainly attributed to the reduction of Rh₂O₃ and NiO [9, 10], respectively. Compared with Ni/CeO₂-Al₂O₃, it is apparent that the nickel reduction temperature for the bimetallic catalyst is lower, illustrating that the presence of Rh facilitates the nickel reduction [9, 10].

5.2.2. Reforming reactions

Non-catalytic thermal cracking of Norpar13 in the absence of reforming catalysts was first carried out in the flow reactor to assess the impact of the reforming temperature on the fuel conversion. It was found that the fuel was completely cracked with the generation of smaller gaseous hydrocarbons at 800 ºC, whereas the fuel was essentially intact at 550 ºC. Afterwards, reforming of Norpar13 doped with 350 ppm sulfur by weight (Norpar13(350)) at 800 ºC over the Al₂O₃ and CeO₂-Al₂O₃ supports was conducted to evaluate the support impact on H₂ production. As can be seen in Table 5-2, the gas product compositions are very close to that observed in the fuel cracking
experiment at the same temperature, suggesting that the supports alone are not effective for catalytic hydrocarbon reforming. In all the above-mentioned cases negligible H$_2$ was generated, which indicates that H$_2$ production is ineffective in the absence of reforming catalysts.

H$_2$ production rates (HPR) in the reactions without and with sulfur at 550 and 800 ºC are displayed in Figures 5-2 and 5-3, respectively. Most reactions were run for 55 h, except Norpar13(350) reforming at 550 ºC that was operated for 30 h. No deactivation sign was observed for Rh/CeO$_2$-Al$_2$O$_3$ in the absence of sulfur since it exhibited stable HPRs for Norpar13 reforming at the two temperatures. For Norpar13 reforming over Ni/CeO$_2$-Al$_2$O$_3$ at 550 ºC, the HPR slowly decreased with time on stream; however, at 800 ºC the HPR is rather stable and comparable to that for Rh/CeO$_2$-Al$_2$O$_3$ under the same condition.

In the case of Norpar13(350) reforming, the HPR rapidly decreased for both Rh/CeO$_2$-Al$_2$O$_3$ and Ni/CeO$_2$-Al$_2$O$_3$ at 550 ºC, demonstrating their poor sulfur tolerance at the low temperature. Interestingly, with increasing the temperature to 800 ºC the HPR with Rh/CeO$_2$-Al$_2$O$_3$ only decreased by 10% from ca. 0.18 to 0.16 mol/g$_{fuel}$-min, and a little CH$_4$ (ca. 1-2%) was detected without C$_2$+ hydrocarbons in the gas products (Table 5-2). In contrast, Ni/CeO$_2$-Al$_2$O$_3$ completely lost its activity within 55 h, which is reflected by the formation of abundant lower hydrocarbons with a composition very close to that observed in the fuel thermal cracking experiment. Taking the catalytic performance of the monometallic catalysts with sulfur-containing fuel into account, we deduce that Rh/CeO$_2$-Al$_2$O$_3$ became highly sulfur tolerant upon increasing temperature to
800 °C, while Ni/CeO$_2$-Al$_2$O$_3$ was still severely poisoned in Norpar13(350) reforming at 800 °C.

The catalytic performances of Rh-Ni/CeO$_2$-Al$_2$O$_3$ for Norpar13(350) reforming at 550 and 800 °C are also shown in Figure 5-3. It is evident that the activity drop of Rh-Ni/CeO$_2$-Al$_2$O$_3$ at 550 °C is slower than those of the monometallic Rh and Ni catalysts. This indicates that the bimetallic catalyst possesses better sulfur tolerance at 550 °C. Strohm et al. [9] attributed the enhanced sulfur tolerance of Rh-Ni/CeO$_2$-Al$_2$O$_3$ to the intimate Rh-Ni interaction, which can protect Rh from sulfur poisoning. It is very interesting to note that at 800 °C, the activity of the bimetallic catalyst is lower than that of monometallic Rh/CeO$_2$-Al$_2$O$_3$ after 30 h on stream for Norpar13(350) reforming. Unlike the case of Norpar13(350) reforming at 550 °C, no beneficial effect of Ni addition to Rh was observed with the bimetallic catalyst for the high-temperature (800 °C) reforming of the sulfur-containing feed Norpar13(350).

5.2.3. Used catalyst characterization

5.2.3.1. Carbon deposition

The carbon contents in the used supports and catalysts are presented in Figure 5-4. All the reported carbon data were obtained from the used catalysts after 55 h on stream, except for Norpar13(350) reforming at 550 °C, where the reactions were terminated at 30 h (time on stream). The carbon deposition on Al$_2$O$_3$ (0.98 g/g$_{cat}$) and CeO$_2$-Al$_2$O$_3$ (0.79 g/g$_{cat}$) after Norpar13(350) at 800 °C is high as a consequence of the fuel cracking, which
can lead to the formation of abundant pyrolytic carbon [38-40, 42]. The lower carbon deposition on CeO$_2$-Al$_2$O$_3$ indicates the positive effect of ceria in reducing carbon deposition on reforming catalysts. This is likely due to the steam activation over ceria to provide oxygen, which facilitates gasification of surface carbon species [77-79].

Upon Norpar13 reforming at 550 and 800 °C, 0.03 and 0.06 g/g$_{\text{cat}}$ of carbon was deposited on Rh/CeO$_2$-Al$_2$O$_3$, respectively. For the reaction with sulfur, the carbon amount on Rh/CeO$_2$-Al$_2$O$_3$ is 0.20 g/g$_{\text{cat}}$ at 550 °C, and further raising the temperature to 800 °C led to a decline in carbon to 0.13 g/g$_{\text{cat}}$. The carbon amount on Ni/CeO$_2$-Al$_2$O$_3$ (0.66 g/g$_{\text{cat}}$) after Norpar13 reforming at 550 °C is about twenty times higher than that on Rh/CeO$_2$-Al$_2$O$_3$ in the same reaction, showing the susceptibility of nickel to carbon formation which is consistent with the literature [58, 65, 70, 71]. The severe carbon deposition may account for the progressive deactivation of Ni/CeO$_2$-Al$_2$O$_3$ in Norpar13 reforming at 550 °C. With increasing temperature to 800 °C the carbon amount significantly declined to 0.06 g/g$_{\text{cat}}$, reflecting that higher reforming temperature favored the carbon removal from Ni/CeO$_2$-Al$_2$O$_3$ in the absence of sulfur. However, in the presence of sulfur the carbon deposition dramatically increased upon elevating the temperature of reforming (1.23 g/g$_{\text{cat}}$ at 800 °C vs 0.32 g/g$_{\text{cat}}$ at 550 °C) on Ni/CeO$_2$-Al$_2$O$_3$. This trend clearly shows that sulfur poisoning significantly degraded the reforming activity of Ni such that fuel cracking led to excessive carbon deposits. Note that both Rh/CeO$_2$-Al$_2$O$_3$ and Ni/CeO$_2$-Al$_2$O$_3$ are carbon resistant in the sulfur-free reaction at 800 °C, while the carbon amount on the latter is remarkably higher after Norpar13(350) reforming at 800 °C. This pronounced distinction further confirms the
superior sulfur tolerance of Rh at 800 °C such that the presence of sulfur did not result in severe carbon deposition on Rh/CeO$_2$-Al$_2$O$_3$.

It is worthwhile to mention that the carbon deposition on Rh-Ni/CeO$_2$-Al$_2$O$_3$ (0.59 g/g$_{cat}$) is much higher than that on Rh/CeO$_2$-Al$_2$O$_3$ (0.13 g/g$_{cat}$) after Norpar13(350) reforming at 800 °C. This fact reveals that the presence of Ni resulted in severe carbon deposition on the bimetallic catalyst during the high-temperature reaction with sulfur. This may be due to the sulfur poisoning of the Ni in the bimetallic catalyst, as observed in the case of Norpar13(350) reforming over Ni/CeO$_2$-Al$_2$O$_3$ at 800 °C. It is possible that the abundant carbon deposits notably covered the bimetallic catalyst surfaces to induce its deactivation. Hence, compared with Rh/CeO$_2$-Al$_2$O$_3$, the inferior catalytic performance of Rh-Ni/CeO$_2$-Al$_2$O$_3$ in Norpar13(350) reforming at 800 °C is due most likely to the sulfur poisoning of Ni and severe carbon deposition.

### 5.2.3.2. Sulfur content

Figure **5-5** presents the sulfur amounts in the used catalysts after Norpar13(350) reforming at 550 and 800 °C for 30 and 55 h, respectively. For comparison, those in the used supports after Norpar13(350) reforming at 800 °C for 55 h are shown as well. The sulfur contents in the used Al$_2$O$_3$ and CeO$_2$-Al$_2$O$_3$ supports are 0.29 and 0.18 mg/g$_{cat}$, respectively. It is apparent that the sulfur content on Ni/CeO$_2$-Al$_2$O$_3$ notably increased with raising temperature (0.42 and 0.96 mg/g$_{cat}$ for 550 and 800 °C, respectively). Interestingly, a reverse trend is observed with Rh/CeO$_2$-Al$_2$O$_3$, i.e., its sulfur content declined from 2.40 mg/g$_{cat}$ at 550 °C to 1.36 mg/g$_{cat}$ at 800 °C. This implies that the sulfur accumulation on Rh/CeO$_2$-Al$_2$O$_3$ is relatively unfavorable at the higher temperature, in
agreement with Ferrandon’s study [17]. The sulfur content in Rh-Ni/CeO$_2$-Al$_2$O$_3$ is 4.71 and 1.37 mg/g$_{cat}$ at 550 and 800 °C, respectively. The significantly higher sulfur content in Rh-Ni/CeO$_2$-Al$_2$O$_3$ at 550 °C can be attributed to the dramatically enhanced Ni dispersion in the presence of Rh (Table 5-1), which allows for more surface nickel sites for sulfur adsorption.

5.2.3.3. XPS

Since XPS is a powerful tool in material surface characterization, it was first carried out to study the chemical nature of the sulfur species in the used catalysts as well as the impacts of sulfur poisoning on the surface properties of the Rh and Ni catalysts. As shown in Figure 5-6, the S 2p XPS spectra do not show any sulfur signals. This may be attributed to the followings: (I) the sulfur contents in the used catalysts are low, and (II) carbon deposits covered some sulfur species. It is apparent that no useful information regarding the sulfur species in the used catalysts can be extracted from the XPS characterization of sulfur species. The elemental composition of the used Rh and Ni catalyst is determined by XPS, as shown in Table 5-3.

Figure 5-7 shows the Rh 3d and Ni 2p XPS spectra for used Rh/CeO$_2$-Al$_2$O$_3$ and Ni/CeO$_2$-Al$_2$O$_3$ after the reactions without and with sulfur at 550 and 800 °C for 30 and 55 h, respectively. The used Rh catalysts after Norpar13 reforming at 550 and 800 °C and Norpar13(350) reforming at 800 °C exhibit a Rh 3d$_{5/2}$ peak at ca. 308.0 eV, indicative of the existence of Rh$^+$ [97]. Interestingly, for Norpar13(350) reforming at 550 °C the XPS peak of Rh 3d$_{5/2}$ occurs at ca. 309.2 eV with a shoulder at 308.0 eV as a result of the coexistence of Rh$^{3+}$ and Rh$^+$ [97]. Recently, Kugai’s work regarding in-situ XPS study on
supported Rh catalysts has verified that Rh$_2$O$_3$ (Rh$^{3+}$) can be fully reduced to Rh$^0$ at around 400 ºC, while Rh$^0$ was oxidized back to Rh$^+$ rather than Rh$^{3+}$ upon air exposure [97]. Accordingly, it is very likely that the formation of Rh$^+$ in the used Rh catalysts was due to the air exposure of the used catalysts during the sample storage. However, the formation of Rh$^{3+}$ in Norpar13(350) reforming at 550 ºC should not result from the air oxidation, but rather from sulfur poisoning of Rh (e.g., the formation of Rh$_2$S$_3$ and Rh$_2$(SO$_4$)$_3$) [145, 146]. The much weaker XPS peak of Rh$^{3+}$ in Rh/CeO$_2$-Al$_2$O$_3$ after Norpar13(350) reforming at 800 ºC, compared with the Rh catalyst upon the reaction with sulfur at 550 ºC, implies that the sulfur poisoning on Rh was mitigated or weakened dramatically at the higher temperature.

With respect to the used Ni catalysts after Norpar13 reforming at 550 and 800 ºC, the Ni 2p$_{3/2}$ peak occurs at ca. 855.5 eV, suggesting the formation of NiO due most likely to the catalyst exposure to air [97]. For Norpar13(350) reforming at 550 and 800 ºC the Ni 2p$_{3/2}$ peak notably shifts to ca. 856.1 eV, which can be associated with sulfur poisoning of nickel such as the formation of nickel sulfide [86].

According the above-mentioned XPS results, it seems that increasing the temperature facilitates the sulfur removal from Rh, while sulfur retained on Ni at 800 ºC. Wang’s study concerning sulfidation of noble metals has indicated that rhodium sulfide is unstable at temperatures > 300 ºC, leading to significant sulfur removal from rhodium [146]. However, the adsorbed sulfur on nickel is refractory even at 800 ºC [147]. Based on Hepola’s report [148], a monolayer of adsorbed sulfur remains on Ni even at 950 ºC. The pronouncedly different thermal stability of sulfur on the two metals may interpret
why the high-temperature operation can alleviate the sulfur poisoning on Rh, while it did not work for Ni.

5.2.3.4. Sulfur XANES

Given the ineffectiveness of XPS in probing the sulfur species in the used catalysts, sulfur K-edge XANES was conducted on the used catalysts after Norpar13(350) reforming at 550 (30 h on stream) and 800 ºC (55 h on stream). As shown in Figure 5-8a, the Al₂O₃ and CeO₂-Al₂O₃ supports exhibit almost the same spectra after Norpar13(350) reforming at 800 ºC, both presenting a sharp peak at ca. 2475 eV with a broad one centered at ca. 2483 eV, corresponding to organic sulfides (-C-S-C-) and sulfate (SO₄²⁻) [92, 110], respectively. The organic sulfides may derive from the deposition of the organosulfur compound (3-MBT) in the fuel and its cracking products containing -C-S-C- on the supports.

Figure 5-8b shows the sulfur XANES spectra of Rh/CeO₂-Al₂O₃ and Ni/CeO₂-Al₂O₃ after the reactions with sulfur at 550 and 800 ºC for 30 and 55 h, respectively. The peak at ca. 2472 eV is visible for all of them, indicative of the formation of metal sulfide [110]. Nickel sulfide is the only major sulfur species for Ni/CeO₂-Al₂O₃ at 550 ºC. In addition to the nickel sulfide, organic sulfides and oxidized sulfur species emerged after the reaction at 800 ºC. Note that the carbon amount in Ni/CeO₂-Al₂O₃ after Norpar13(350) reforming at 800 ºC is much higher than that at 550 ºC (Figure 5-4). Hence, the observation of organic sulfides on Ni/CeO₂-Al₂O₃ at 800 ºC but not on that at 550 ºC hints that their formation may be closely associated with the severe pyrolytic carbon
deposition at the higher temperature. This may be because carbon deposits can cover the organic sulfides to hinder their removal from catalyst surfaces.

It is worthy to note that the sulfur XANES spectra of Rh/CeO$_2$-Al$_2$O$_3$ are dramatically different from those of Ni/CeO$_2$-Al$_2$O$_3$. Apart from the rhodium sulfide, the major sulfur species on Rh/CeO$_2$-Al$_2$O$_3$ are sulfonate and sulfate. The much stronger peaks of the oxidized sulfur species for Rh/CeO$_2$-Al$_2$O$_3$ than that for Ni/CeO$_2$-Al$_2$O$_3$ clearly indicate that the sulfur oxidation is preferred in the presence of Rh. It is worthwhile to mention that no organic sulfides are observed with Rh/CeO$_2$-Al$_2$O$_3$ at 800 ºC. One possible reason is due to its low carbon deposition after the reaction with sulfur at 800 ºC such that the accumulation of organic sulfides was not preferred. Recall that increasing the reforming temperature significantly reduced the sulfur content in Rh/CeO$_2$-Al$_2$O$_3$ (Figure 5-5), which can be associated with the thermodynamically unfavorable chemisorption of sulfur on metals as well as the enhanced decomposition of the oxidized sulfur species at the high temperature [126, 149, 150].

Figure 5-8c exhibits the sulfur XANES spectra of Rh-Ni/CeO$_2$-Al$_2$O$_3$ after Norpar13(350) reforming at 550 and 800 ºC for 30 and 55 h, respectively. Apparently, metal sulfide, sulfonate, and sulfate can be identified in the used bimetallic catalysts. The observation of organic sulfides in Rh-Ni/CeO$_2$-Al$_2$O$_3$ after the high-temperature reaction confirms that severe pyrolytic carbon deposition is associated with the formation of organic sulfides.

The dynamic nature of the sulfur chemistry on the catalyst surface can be well illustrated by time series of sulfur K-edge XANES spectra of the sulfur poisoned Rh and Ni catalyst as shown in Figure 5-9. Qualitatively, for the used Ni catalysts, the
relative abundance of all three major sulfur species, metal sulfide (or nickel sulfide), organic sulfide and sulfate, is changing with time. In contrast, the sulfur K-edge XANES spectra of the used Rh catalysts are essentially the same, which all present peaks deriving from rhodium sulfide, sulfonate, and sulfate in comparable peaks intensities.

In order to correlate catalyst deactivation with sulfur poisoning and carbon deposition, a parameter for relative activity loss, Degree of Catalyst Deactivation (DCD) at any reaction time, is defined as follows:

\[
DCD = \frac{\text{HPR without sulfur} - \text{HPR with sulfur}}{\text{HPR without sulfur}} \times 100\%.
\]

Under the reaction conditions “HPR without sulfur” is a constant for the Ni catalyst, thus DCD gives the extent of catalyst deactivation due to the presence of sulfur. To show a clear correlation between catalyst deactivation and other variables, the carbon deposition and metal sulfide are presented in “catalyst deactivation domain” other than time domain. Figure 5-10 shows the evolution of metal sulfide and carbon deposition on the Ni catalyst due to sulfur poisoning with DCD. With increasing DCD the carbon deposition increases linearly while the amount of metal sulfide actually decreases in general. The result shows a clear correlation between the carbon deposition (not metal sulfide) and the DCD. Note that an extrapolation of the carbon line does not pass the origin but intercepts the DCD axis at about 35%, implying there are two sequential catalyst deactivation processes involved. If we assume under our reaction conditions carbon deposition and the formation of metal sulfide are the only two factors responsible for catalyst deactivation, it can be further inferred that in less than 5 hrs the formation of nickel sulfide (which is the
only major sulfur species present at the beginning, see Fig. 3) has caused the loss of about one third of the steam reforming activity of the Ni catalyst, and subsequently two thirds of the activity is gradually being lost in another 50 hrs due to the carbon deposition.

5.2.4. Superior sulfur tolerance of Rh at 800 °C

The profoundly different performances of the monometallic Rh and Ni catalysts in the sulfur-containing reaction at 800 °C demonstrate that Rh is much more sulfur tolerant than Ni at the high temperature. Despite such a distinction has been documented previously, little is known about the mechanism behind this phenomenon [33, 50]. A possible reason is that many conventional characterization techniques (e.g., EDX, XRF, and ICP-MS), though being able to determine the presence of sulfur, cannot derive its chemical (e.g., sulfur oxidation state) and structural (bonding of sulfur with metals or other elements such as oxygen and carbon) information. Moreover, XPS, which is powerful in surface chemical analysis, is not effective in probing the sulfur species in the used reforming catalysts as well.

It is important to note that the present work clearly demonstrates the advantages of using XANES technique for reliably differentiating various sulfur species on catalyst surface at trace levels [112]. The sulfur XANES results allow us to infer that the distinct sulfur tolerance of the two catalysts at 800 °C may closely correlate with the formation of different sulfur species. It was found that sulfur oxidation to sulfonate and sulfate is preferred on Rh/CeO$_2$-Al$_2$O$_3$, whereas the formation of metal sulfide and organic sulfide predominate on Ni/CeO$_2$-Al$_2$O$_3$. The observed sulfur oxidation on rhodium is consistent with Nomoto’s study clarifying that coadsorption of (CH$_3$)$_2$S and H$_2$O on Rh(100)
provoked the formation of S-O bonds [151]. Moreover, Yagi et al. have illustrated the conversion of (CH₃)₂S to sulfate on a rhodium membrane in the presence of oxygen [152].

The formation of different sulfur species on the Rh and Ni catalysts may be attributed to the following. First, the oxygen surface mobility on rhodium is about several orders of magnitude higher than that on nickel [153]. It therefore can be envisioned that the strong oxygen surface mobility on rhodium would enhance the sulfur oxidation. Second, the sulfide formation on nickel is highly favored compared with that on rhodium in terms of the notably different free energy of formation with respect to their metal sulfides (ΔG°ᵣ = -65.7 and -3.1 kJ/mol for nickel and rhodium sulfide, respectively) [44]. Similarly, Lakhapatri et al. claimed that a S-Ni bond is much stronger than a S-Rh bond because of the larger electronegativity difference between nickel and sulfur than that between rhodium and sulfur (χₕₗ₈ = 2.58, χₕₗ₉ = 2.28, and χₕₗ₁ = 1.91) [18]. This implies that a S-Rh bond should be more easily broken as compared with a S-Ni bond.

Sulfur poisoning of metal catalysts is due to the presence of unshared electrons in sulfur, through which strong sulfur-metal interaction forms [44, 46, 47, 74]. Previous studies have revealed that the chemisorptive sulfur adsorption on metals is very detrimental because the direct metal-sulfur interaction can adversely affect multiple metal sites in the proximity of sulfur [47]. For example, Erley and Wagner pointed out that a sulfur atom is capable of blocking about nine CO adsorption sites on Ni(111) [45]. Feibelman’s calculation further confirmed that the strong poisoning effect of a sulfur atom on the electronic structure of metals exceeds its nearest metal neighbors [48]. According to Joyner and Pendry [154], the poisoning range for a sulfur atom is 5-7 Å, meaning that it can negatively affect at least ten close-packed metal surface atoms [155].
Due to such a long-range adverse electronic impact, the direct chemisorptive metal-sulfur interaction reduces the availability of metal $d$-electrons and suppresses the sticking probability and coverage of other reactants on metals [48]. In the case of Ni/CeO$_2$-Al$_2$O$_3$, the formation of nickel sulfide (direct nickel-sulfur interaction) can inhibit the hydrocarbon adsorption and activation on nickel metal sites. Furthermore, the presence of sulfur may hinder the dissociation of steam into surface oxygen species (i.e., O and OH) and lower their mobility so that the interactions between carbon and surface oxygen species for carbon gasification will be suppressed. As a result, sulfur poisoning of Ni/CeO$_2$-Al$_2$O$_3$ may impede the hydrocarbon reforming reaction and give rise to severe carbon deposition at 800 °C. We believe that the blocking of nickel metal sites by sulfur and carbon is responsible for the severe deactivation of Ni/CeO$_2$-Al$_2$O$_3$ in Norpar13(350) at 800 °C.

It has been known that the poisoning effect of sulfur strongly depends on its electronic configuration [46, 74, 124, 156, 157]. It can be expected that the poisoning effect of sulfur on metals would be attenuated if it is shielded by other elements (e.g., oxygen) such that no unshared electrons of sulfur are available for the direct sulfur-metal interaction [46, 74]. Some researchers have reported that oxidized sulfur species like sulfate are much less deleterious than metal sulfide to metal catalysts as their oxygen-shielded sulfur structure can prohibit the direct sulfur-metal interaction. As a consequence, we speculate that the effective sulfur oxidation to sulfonate and sulfate on Rh/CeO$_2$-Al$_2$O$_3$ may play a crucial role in its superior sulfur tolerance at 800 °C. This inference is in harmony with Chen’s study reporting the distinct tolerance of Pt catalysts supported on TiO$_2$ and Al$_2$O$_3$ towards H$_2$S poisoning [156]. Compared with the Pt/Al$_2$O$_3$
that was poisoned due to the rapid formation of Pt-S, the Pt/TiO$_2$ was relatively sulfur resistant since the labile lattice oxygen in TiO$_2$ can attack sulfur to form sulfate. Furthermore, Wakita et al. reported that the deactivated Pt/Al$_2$O$_3$ catalyst because of the formation of metal sulfides during CO preferential oxidation was regenerable by calcination of the used catalyst at 175 ºC. It was indicated that such a treatment broke the Pt-S interaction with converting S$^{2-}$ to S$^{6+}$ [124]. A very similar conclusion has also been drawn by An and Deng [157], who investigated the mechanism of sulfur poisoning of Pt and Pd catalysts supported on Al$_2$O$_3$ in H$_2$-O$_2$ reaction. They concluded that sulfur poisoning of the metal catalysts resulted from S$^{2-}$, but barely related to S$^{6+}$.

The very similar Rh XPS spectra of Rh/CeO$_2$-Al$_2$O$_3$ after the reaction without and with sulfur at 800 ºC imply that the poisoning effect of sulfur on rhodium was significantly eliminated at the high temperature. Such a result suggests that during Norpar13(350) reforming over Rh/CeO$_2$-Al$_2$O$_3$ at 800 ºC the oxidized sulfur species formed on rhodium can be effectively removed. The pronounced decomposition of the oxidized sulfur species on rhodium at > 400 ºC has been proven by Wang et al. [146]. Moreover, the abundant H$_2$ in the reaction can attack the sulfur species on rhodium to facilitate their removal with the formation of H$_2$S [19, 26, 125, 157]. In addition, for supported metal catalysts the oxidized sulfur species on metals generally possess lower thermal stability compared with those on the support [125, 126, 146, 158]. As such, there might exist a driving force for the oxidized sulfur species on rhodium to migrate onto the support [50, 123, 159]. We thereby anticipate that the possible migration of the oxidized sulfur species onto the CeO$_2$-Al$_2$O$_3$ support may also contribute to the superior sulfur
tolerance of Rh/CeO$_2$-Al$_2$O$_3$ at 800 °C since the support can act as a sulfur trap to protect rhodium from sulfur poisoning in this case.

The catalytic performance of Rh/CeO$_2$-Al$_2$O$_3$ was stable in the reaction with sulfur at 800 °C. Moreover, the XPS characterization result revealed that the rhodium surface properties after the reactions with and without sulfur at 800 °C are very similar. These facts suggest that the high temperature condition may result in fast kinetics for the aforementioned sulfur cleanup processes (e.g., breaking of sulfur-metal bond, sulfur oxidation, decomposition of the oxidized sulfur species, and their potential migration onto the support), thus ensuring clean rhodium metal sites available for the reaction. In contrast, the sulfur cleanup seems to be slower at 550 °C, which may cause the sulfur accumulation on rhodium, as evidenced by the observation of Rh$^{3+}$ (Rh$_2$S$_3$ and Rh$_2$(SO$_4$)$_3$) in Rh/CeO$_2$-Al$_2$O$_3$ after Norpar13(350) reforming at 550 °C by XPS. Moreover, we did observe that the sulfur content in Rh/CeO$_2$-Al$_2$O$_3$ is higher at 550 °C. Therefore, Rh/CeO$_2$-Al$_2$O$_3$ exhibited inferior performance in the low-temperature reaction of sulfur-containing fuel.

5.3. Conclusions

The following conclusions could be drawn from this study:

(1) Both Rh and Ni monometallic catalysts exhibited poor sulfur tolerance for steam reforming of liquid hydrocarbons containing 350 ppm sulfur by weight at 550 °C. Increasing the temperature to 800 °C significantly improved the sulfur tolerance of the Rh catalyst, while the Ni catalyst was still severely deactivated at 800 °C.
(2) XANES revealed that metal sulfide and organic sulfide are dominant in the Ni catalyst, while sulfonate and sulfate predominate in the Rh catalyst. Their dramatically different sulfur tolerance at 800 °C may be correlated with the formation of different sulfur species. Abundant carbon species were deposited on the Ni catalyst after the high-temperature reaction with sulfur, which may be because the formation of nickel sulfide suppressed carbon gasification. The severe Ni catalyst deactivation in the reaction with sulfur at 800 °C can be attributed to the blocking of nickel metal sites by sulfur and carbon. XPS result suggests that that sulfur poisoning on the Rh catalyst can be effectively mitigated by increasing reforming temperature to 800 °C. The superior sulfur tolerance of Rh at the high temperature is tentatively attributed to the followings: (I) sulfur oxidation and the oxygen-shielded sulfur structure of sulfonate and sulfate may inhibit direct rhodium-sulfur interaction, and (II) the decomposition of the oxidized sulfur species as well as their possible migration onto the support may protect Rh from sulfur poisoning.

(3) The Rh-Ni catalyst exhibited better sulfur tolerance than the monometallic ones at 550 °C because of the protection effect of Ni on Rh. However, no such a beneficial effect was observed for the bimetallic catalyst at 800 °C. Excessive carbon species were deposited on the Rh-Ni bimetallic catalyst after the reaction with sulfur at 800 °C. The presence of Ni led to enhanced carbon deposition on the Rh-Ni catalyst in reforming of sulfur-containing hydrocarbons at 800 °C. The severe carbon deposition on the Rh-Ni bimetallic catalyst may be mainly caused by sulfur-poisoning of Ni to form metal sulfide which led to accumulation of pyrolytic carbon deposits in the reaction with sulfur at 800 °C.
Table 5-1. Physicochemical properties of the materials prepared in this study

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal loading (wt%)</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>Pore vol. (cm$^3$/g)</th>
<th>Metal dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>---</td>
<td>144</td>
<td>0.81</td>
<td>---</td>
</tr>
<tr>
<td>CeO$_2$-Al$_2$O$_3$</td>
<td>---</td>
<td>121</td>
<td>0.63</td>
<td>---</td>
</tr>
<tr>
<td>Rh/CeO$_2$-Al$_2$O$_3$</td>
<td>2</td>
<td>116</td>
<td>0.57</td>
<td>49.3</td>
</tr>
<tr>
<td>Ni/CeO$_2$-Al$_2$O$_3$</td>
<td>10</td>
<td>109</td>
<td>0.54</td>
<td>2.7</td>
</tr>
<tr>
<td>Rh-Ni/CeO$_2$-Al$_2$O$_3$</td>
<td>2(Rh)/10(Ni)</td>
<td>102</td>
<td>0.49</td>
<td>32.5(Rh)/8.2(Ni)</td>
</tr>
</tbody>
</table>
Table 5-2. Product selectivity in the reforming reactions at 800 °C after 55 h on stream

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Fuel</th>
<th>Gas product selectivity (%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂</td>
<td>CH₄</td>
<td>CO</td>
<td>CO₂</td>
<td>C₂ +</td>
</tr>
<tr>
<td>Fuel cracking (no catalyst)</td>
<td>Norpar13</td>
<td>14.9</td>
<td>20.3</td>
<td>2.9</td>
<td>0</td>
<td>61.9</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Norpar13(350)</td>
<td>16.9</td>
<td>21.7</td>
<td>1.8</td>
<td>0.3</td>
<td>59.3</td>
</tr>
<tr>
<td>CeO₂–Al₂O₃</td>
<td>Norpar13(350)</td>
<td>19.1</td>
<td>17.3</td>
<td>5.3</td>
<td>2.1</td>
<td>56.2</td>
</tr>
<tr>
<td>Rh/CeO₂–Al₂O₃</td>
<td>Norpar13</td>
<td>71.7</td>
<td>0</td>
<td>18.6</td>
<td>9.7</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>Norpar13(350)</td>
<td>65.1</td>
<td>1.5</td>
<td>17.8</td>
<td>15.6</td>
<td>0</td>
</tr>
<tr>
<td>Ni/CeO₂–Al₂O₃</td>
<td>Norpar13</td>
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</tr>
<tr>
<td></td>
<td>Norpar13(350)</td>
<td>15.6</td>
<td>21.5</td>
<td>0.8</td>
<td>0</td>
<td>62.1</td>
</tr>
</tbody>
</table>
Table 5-3. XPS surface elemental compositions (atom% and wt% (the values in parentheses are wt%)) of the used Rh and Ni catalysts upon steam reforming of liquid hydrocarbons (Norpar13) without and with sulfur at 550 and 800 °C.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>T (°C)</th>
<th>Al</th>
<th>O</th>
<th>Ce</th>
<th>C</th>
<th>Rh</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/CeO$_2$-Al$_2$O$_3$</td>
<td>Norpar13</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td></td>
<td>32.94</td>
<td>58.47</td>
<td>0.84</td>
<td>7.51</td>
<td>0.24</td>
<td>N/A*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(43.19)</td>
<td>(45.47)</td>
<td>(5.74)</td>
<td>(4.38)</td>
<td>(1.21)</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td></td>
<td>29.66</td>
<td>11.20</td>
<td>1.59</td>
<td>17.21</td>
<td>0.34</td>
<td>N/A*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(38.40)</td>
<td>(39.30)</td>
<td>(10.70)</td>
<td>(9.92)</td>
<td>(1.67)</td>
<td></td>
</tr>
<tr>
<td>Norpar13(350)</td>
<td>550</td>
<td>18.36</td>
<td>31.15</td>
<td>0.29</td>
<td>50.00</td>
<td>0.20</td>
<td>N/A*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(29.93)</td>
<td>(30.11)</td>
<td>(2.43)</td>
<td>(36.28)</td>
<td>(1.25)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>800</td>
<td>29.20</td>
<td>53.47</td>
<td>1.53</td>
<td>15.49</td>
<td>0.31</td>
<td>N/A*</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(37.96)</td>
<td>(41.22)</td>
<td>(10.34)</td>
<td>(8.97)</td>
<td>(1.52)</td>
<td></td>
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<tr>
<td>Ni/CeO$_2$-Al$_2$O$_3$</td>
<td>Norpar13</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>550</td>
<td></td>
<td>16.69</td>
<td>33.82</td>
<td>0.29</td>
<td>47.86</td>
<td>N/A*</td>
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</tr>
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<td></td>
<td></td>
<td>(26.70)</td>
<td>(32.09)</td>
<td>(2.39)</td>
<td>(34.10)</td>
<td>(4.71)</td>
<td></td>
</tr>
<tr>
<td>800</td>
<td></td>
<td>30.83</td>
<td>52.18</td>
<td>1.69</td>
<td>13.91</td>
<td>N/A*</td>
<td>1.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(38.68)</td>
<td>(38.81)</td>
<td>(11.02)</td>
<td>(7.79)</td>
<td>(3.69)</td>
<td></td>
</tr>
<tr>
<td>Norpar13(350)</td>
<td>550</td>
<td>11.1</td>
<td>16.89</td>
<td>0.09</td>
<td>71.25</td>
<td>N/A*</td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(20.47)</td>
<td>(18.32)</td>
<td>(0.87)</td>
<td>(58.02)</td>
<td>(2.32)</td>
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<tr>
<td></td>
<td>800</td>
<td>7.41</td>
<td>21.10</td>
<td>0.54</td>
<td>70.35</td>
<td>N/A*</td>
<td>0.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(13.39)</td>
<td>(22.61)</td>
<td>(5.11)</td>
<td>(56.58)</td>
<td>(2.31)</td>
<td></td>
</tr>
</tbody>
</table>

* All the catalysts were tested on stream for 55 h, except those with sulfur (steam reforming of Norpar13(350)) at 550 °C were run for 30 h.

b Not Available
Figure 5-1. TPR profiles of $\text{Al}_2\text{O}_3$, $\text{CeO}_2$-$\text{Al}_2\text{O}_3$, $\text{Rh/ CeO}_2$-$\text{Al}_2\text{O}_3$, $\text{Ni/ CeO}_2$-$\text{Al}_2\text{O}_3$, and $\text{Rh-Ni/ CeO}_2$-$\text{Al}_2\text{O}_3$. 
Figure 5-2. Hydrogen production rate (HPR) for steam reforming of Norpar13 over Rh/CeO$_2$-Al$_2$O$_3$ and Ni/CeO$_2$-Al$_2$O$_3$. Conditions: 1 g of catalyst; WHSV = 5.1 h$^{-1}$; S/C = 3.
Figure 5-3. Hydrogen production rate (HPR) for steam reforming of Norpar13 doped with 350 ppm sulfur by weight over Rh/CeO$_2$-Al$_2$O$_3$, Ni/CeO$_2$-Al$_2$O$_3$, and Rh-Ni/CeO$_2$-Al$_2$O$_3$. Conditions: 1 g of catalyst; WHSV = 5.1 h$^{-1}$; S/C = 3.
Figure 5-4. The amount of carbon on the used supports (Al₂O₃ and CeO₂-Al₂O₃) and catalysts (Rh/CeO₂-Al₂O₃, Ni/CeO₂-Al₂O₃, and Rh-Ni/CeO₂-Al₂O₃) after steam reforming of Norpar13 and Norpar13 doped with 350 ppm sulfur by weight at 550 and 800 °C. The reaction time for reforming of Norpar13 with 350 ppm sulfur at 550 °C is 30 h, while that is 55 h for all the other cases.
Figure 5-5. Sulfur content in the used supports (Al$_2$O$_3$ and CeO$_2$-Al$_2$O$_3$) and catalysts (Rh/CeO$_2$-Al$_2$O$_3$, Ni/CeO$_2$-Al$_2$O$_3$, and Rh-Ni/CeO$_2$-Al$_2$O$_3$) after steam reforming of Norpar13 with 350 ppm sulfur by weight at 550 and 800 °C for 30 and 55 h, respectively.
Figure 5-6. S 2p XPS spectra of the used Rh/CeO$_2$-Al$_2$O$_3$ and Ni/CeO$_2$-Al$_2$O$_3$ catalysts after steam reforming of Norpar13 with 350 ppm sulfur by weight at 550 and 800 °C for 30 and 55 h, respectively.
Figure 5-7. Rh 3d and Ni 2p XPS spectra for the used Rh/CeO$_2$-Al$_2$O$_3$ and Ni/CeO$_2$-Al$_2$O$_3$ catalysts after the steam reforming reactions without and with sulfur at 550 and 800 ºC. (a) Norpar13 reforming at 550 ºC for 55 h, (b) Norpar13 reforming at 800 ºC for 55 h, (c) reforming of Norpar13 with 350 ppm sulfur by weight at 550 ºC for 30 h, (d) reforming of Norpar13 with 350 ppm sulfur by weight at 800 ºC for 55 h.
Figure 5-8. Sulfur K-edge XANES spectra of (a) the used supports Al₂O₃ and CeO₂-Al₂O₃ after steam reforming of Norpar13 with 350 ppm sulfur by weight at 800 ºC for 55 h, (b) Rh/CeO₂-Al₂O₃ and Ni/CeO₂-Al₂O₃, and (c) Rh-Ni/CeO₂-Al₂O₃ after steam reforming of Norpar13 with 350 ppm sulfur by weight at 550 and 800 ºC for 30 and 55 h, respectively.
Figure 5-9. Time series of sulfur K-edge XANES spectra of the used Rh/CeO$_2$-Al$_2$O$_3$ and Ni/CeO$_2$-Al$_2$O$_3$ catalysts after steam reforming of Norpar13 with 350 ppm sulfur at 800 °C.
Figure 5-10. Amount of metal sulfide (open circle) and carbon deposition (solid square) due to sulfur poisoning on the 10wt% Ni/\text{CeO}_2-\text{Al}_2\text{O}_3 catalyst with the degree of catalyst deactivation.
Chapter 6

Influence of Sulfur on the Carbon Deposition in Steam Reforming of Liquid Hydrocarbons over CeO$_2$-Al$_2$O$_3$ Supported Ni and Rh Catalysts

Abstract

This study was performed to elucidate the influence of sulfur on the carbon deposition in steam reforming of liquid hydrocarbons over CeO$_2$-Al$_2$O$_3$ supported Ni and Rh catalysts at 800 ºC. The characteristics of the carbon deposits on the used catalysts upon the reactions without and with sulfur were investigated by TPO, TEM, STXM, TPH, XANES, and SEM. Though abundant carbon deposits can accumulate on the pure CeO$_2$-Al$_2$O$_3$ support due to fuel thermal cracking, the addition of Ni or Rh metal greatly reduced the carbon deposition in the sulfur-free reaction. The presence of sulfur increased the carbon deposition on both catalysts, which has a much more significant impact for the Ni catalyst. Carbon XANES study on the used catalysts revealed that graphitic carbon was dominant in the presence of sulfur, while oxidized carbon species (quinone-like carbon, carboxyl and carbonate) prevailed without sulfur. Meanwhile, the formation of carboxyl and carbonate more dramatically dropped on the Ni catalyst than that on the Rh catalyst. Our results strongly suggest that (I) the presence of sulfur can suppress carbon gasification and promote the formation of graphitic carbon on reforming catalysts due mainly to its poisoning effect on metals, and (II) Rh catalyst possesses stronger capability to maintain carbon gasification activity than Ni catalyst in the presence of sulfur.
6.1. Introduction

Catalyst deactivation resulting from carbon deposition is one of major challenges for hydrocarbon reforming technology [38-40]. The carbon deposition in reforming reactions is determined by two competitive processes: carbon formation and carbon gasification. Hydrocarbon decomposition \( (C_mH_n \rightarrow mC + n/2 H_2, \Delta H_{298}^\circ = 188 \text{ kJ/mol for complete decomposition of } n-C_7H_{16} \) and CO disproportionation \( (2CO \rightarrow C + CO_2, \Delta H_{298}^\circ = -172 \text{ kJ/mol}) \) are two well-known pathways leading to the carbon problem [38-40]. The former can be either catalytic (metal-catalyzed hydrocarbon decomposition) or non-catalytic (thermal cracking), and is thermodynamically favorable at high temperatures. In contrast, CO disproportionation is suppressed with increasing reforming temperature because of its exothermic characteristic [38, 160]. Consequently, hydrocarbon decomposition is considered as the predominant pathway for the carbon formation in high-temperature (> 700 ºC) hydrocarbon reforming [160, 161]. The carbon species deposited on reforming catalysts can be gasified into carbon oxides with the aid of steam (i.e., carbon gasification) in steam reforming of hydrocarbons [5]. If carbon formation is kinetically slower than carbon gasification, carbon species can be effectively removed from reforming catalysts; however, if the former is faster, carbon build-up will occur [38, 40, 112].

The goal of the present study is to clarify the impact of sulfur on the carbon deposition in steam reforming of liquid hydrocarbon fuels. We comparatively study the carbon deposition on CeO\(_2\)-Al\(_2\)O\(_3\) supported Ni and Rh catalysts upon steam reforming of Norpar13 without and with sulfur at 800 ºC. The total amount, speciation, reactivity, structure, and morphology of the carbon deposits on the used catalysts were investigated by different techniques including TPO, TEM, STXM, TPH, XANES, and SEM.
characterization results clearly demonstrated that sulfur can profoundly affect the carbon deposition on reforming catalysts, and the extent of sulfur poisoning on the carbon gasification on the Ni and Rh catalysts is different.

6.2. Results

6.2.1. Carbon deposition on the support

For hydrocarbon reforming at 800 °C, non-catalytic homogeneous fuel thermal cracking is expected to be significant, which may result in significant accumulation of pyrolytic carbon on reforming catalysts [42]. In order to evaluate its impact on the carbon deposition in this study, steam reforming of sulfur-free Nopar13 and Nopar13 doped with 3-methylbenzothiophene for an equivalent 350 parts per million (ppm) of sulfur by weight (Nopar13(350)) over the CeO$_2$-Al$_2$O$_3$ support at 800 °C was carried out in the flow reactor for 55 h. The carbon amounts on the used supports were determined to be significant (0.83 and 0.79 g/g$_{\text{cat}}$ for reforming of Norpar13 and Nopar13(350), respectively). The TPO profile (Figure 6-1a) in either case shows an intensive peak between 600 and 800 °C as a result of burning off of the carbon deposits on the support. Carbon K-edge XANES was performed to study the structure of the carbon deposits on the used supports. This technique is very powerful in providing fingerprint information of various carbonaceous materials (e.g., aromatics, carboxyl, and carbonate) as their XANES spectra are considerably different [93, 95, 96]. The carbon XANES spectra of the used supports (Figure 6-1b) are very similar to each other. They both exhibit an intensive peak at 285.2 eV with a plateau starting at 291.5 eV, corresponding to $\pi^*$
transition and $\sigma^*$ exciton of aromatic carbon, respectively [95, 96]. The observation of these two features at the same time suggests that the carbon deposits on the used pure supports are graphitic, as indicated by the graphite spectrum exhibited in Figure 6-1b [94, 96]. Moreover, a weak peak occurs at 288.3 eV as a result of the formation of carboxyl groups (COOH) [95]. Fanning and Vanke [162] have reported that oxidation of carbon black by an O$_2$/Ar mixture occurred only at temperatures higher than 350 ºC. Their result suggests that the oxidation of the carbon deposits on the used reforming catalysts due to air exposure is unlikely. Therefore, the formation of carboxyl groups should have taken place in hydrocarbon reforming due to the reaction between the carbon deposits and steam (i.e., carbon gasification). The above-mentioned results of TPO and XANES show that sulfur did not notably affect the carbon deposition on the support alone, which was derived from mostly non-catalytic homogeneous fuel thermal cracking at high temperature and not influenced by sulfur.

### 6.2.2. Properties of the carbon deposits on the used catalysts

As reported early, for steam reforming of Norpar13 and Norpar13(350) at 800 ºC for 55 h, the monometallic Ni and Rh catalysts were found to be effective without any deactivation in the absence of sulfur within the test time. However, the situation is remarkably different in the sulfur-containing reaction: the Ni catalyst completely lost its activity within 55 h on stream, whereas the activity drop of the Rh catalyst was only about 10% during the same period of time. The subsequent carbon analysis determined that the carbon amounts on the used catalysts upon Norpar13 reforming were both close to ca. 0.06 g/g$_{\text{cat}}$. The presence of sulfur significantly promoted the carbon deposition on
the Ni catalyst (ca. 1.23 g/g cat), while the increase in the carbon deposition on the Rh catalyst (0.13 g/g cat) was much smaller. TEM images of the used catalysts after 55 h of Norpar13(350) reforming are presented in Figure 6-2. Large carbon deposits (confirmed by EDX) can be easily identified on the Ni catalyst, which however is not the case for the Rh catalyst. This contrast further confirms the higher carbon amount on the Ni catalyst than that on the Rh catalyst in the presence of sulfur.

6.2.2.1. Carbon distribution

STXM in Figure 6-3 shows the carbon distribution on the used Ni and Rh catalysts after the reactions without and with sulfur. The principle of STXM is similar to TEM; one of major distinctions between these two techniques is that they use different detection sources (X-ray and electron for STXM and TEM, respectively). A stack of images can be collected by scanning a sample area in an X-ray energy range (from 270 to 310 eV in this study). The darker areas in the images arise from X-ray absorption by the used catalysts, while the lighter areas are due to background. Data processing allows for the construction of XANES spectra at any given points within the scanned area. For each sample in Figure 6-3, four representative points (50 nm × 50 nm) are selected within a catalyst particle, and their corresponding carbon K-edge XANES spectra are shown as well. It is apparent that, after the sulfur-free reaction, no strong carbon signal is detected for both Ni and Rh catalysts, being consistent with the low carbon deposition in the absence of sulfur. For Norpar13(350) reforming, no intensive carbon signal is observed for the Rh catalyst as well, while the strong features of graphitic carbon can be clearly seen for the Ni catalyst. Evidently, the STXM results illustrate that (I) the carbon contents on both catalysts were
low in the absence of sulfur, and (II) upon the reaction with sulfur, the Ni catalyst surfaces were significantly covered by graphitic carbon, while the carbon coverage on the Rh catalyst remained low.

TPO profiles of the used catalysts after the reactions without and with sulfur for 55 h are shown in Figure 6-4. The carbon deposits formed on the used Ni and Rh catalysts without sulfur are oxidized between 600 and 800 °C, which is also the case for the Rh catalyst upon the reaction with sulfur. In contrast, two intensive peaks are observed at ca. 490 and 660 °C for the carbon deposits on the Ni catalyst with sulfur. The observed low- and high-temperature peaks from the used Ni catalyst after Norpar13(350) reforming most likely derived from the carbon deposits on the Ni and the CeO$_2$-Al$_2$O$_3$ support, respectively. Such assignments are not only supported by the TPO results of the used CeO$_2$-Al$_2$O$_3$ support revealing that the oxidation of the carbon deposits on the support occurs at temperatures between 600 and 800 °C, but also in agreement with previous studies reporting that the oxidation temperature for the carbon deposits on metals is lower than that for those on supports [18, 33, 163, 164]. For example, Shekhawat et al. observed two TPO peaks at ca. 550 and 700 °C in their study regarding catalytic partial oxidation of n-tetradecane over Pt/Al$_2$O$_3$. They attributed the low- and high-temperature peaks to the carbon deposited on Pt and Al$_2$O$_3$, respectively [33]. The easier carbon oxidation on metals may be because they are able to facilitate carbon oxidation, which agrees with the well-known fact that metals are good catalysts for hydrocarbon combustion [165-167].
6.2.2.2. Reactivity of carbon deposits

As shown in Figure 6-5, TPH was carried out to study the reactivity of the carbon deposits on the used Ni and Rh catalysts after reforming of Norpar13 and Norpar13(350) for 55 h. After the reaction without sulfur, both Ni and Rh catalysts exhibit strong CH\textsubscript{4} signals as a result of effective carbon hydrogenation reaction (C + 2H\textsubscript{2} → CH\textsubscript{4}) on their surfaces. Upon the reaction with sulfur, CH\textsubscript{4} signals for the Rh catalyst remain strong. On the contrary, those are much weaker for the used Ni catalyst, whereas its carbon content is about ten times higher than that on the Rh catalyst. This distinction implies that the carbon deposits on the Ni catalyst are much more refractory than those on the Rh catalyst in the presence of sulfur. From DFT calculations regarding the carbon deposition on nickel-based reforming catalysts, Xu et al. have reported that large graphitic carbon islands are the most stable form of carbon on reforming catalysts, and their formation requires high carbon coverage [67-69]. It is very likely that the high carbon amount on the Ni catalyst after the sulfur-containing reaction favored the formation of refractory graphitic carbon islands, which may account for the negligible generation of CH\textsubscript{4} in the TPH of the used Ni catalyst with sulfur. Due to the low carbon deposition on the two catalysts after the sulfur-free reaction and on the Rh catalyst after the reaction with sulfur, the formation of graphitic carbon islands may be limited, leading its carbon deposits to be relatively reactive compared with those on the Ni catalyst upon Norpar13(350) reforming. Moreover, owing to the much lower carbon deposition, it is reasonable to rationalize that less metal surfaces were covered by carbon. Therefore, H\textsubscript{2} dissociation (H\textsubscript{2} → 2H) on the metals and the subsequent reaction between C and H are expected to be more favorable. This may be another possible reason for the notable
formation of CH₄ from the used Ni and Rh catalysts after Norpar13 reforming and the used Rh catalyst upon Norpar13(350) reforming. These TPH results further confirm the much more severe carbon deposition on the Ni catalyst in the presence of sulfur. As a result, the carbon deposits may form very stable graphitic carbon islands, and significantly cover the Ni catalyst surfaces.

6.2.2.3. Carbon structure and carbon gasification

Carbon K-edge XANES spectra of the used catalysts after reforming of Norpar13 and Norpar13(350) for 55 h are shown in Figure 6-6. A major peak at 284.8 eV observed in the sulfur-free case can be ascribed to quinone-like carbon such as benzoquinone type [96]. For the used catalysts upon Norpar13(350) reforming, the quinone peak is weaker while the graphitic characteristics (the peak at 285.2 eV together with a plateau starting at 291.5 eV) become very strong. Apparently, the presence of sulfur can promote the formation of graphitic carbon. The carboxyl groups at 288.3 eV can be detected for all the used catalysts, though the peak intensities are weaker in the presence of sulfur. Moreover, a small peak at 290.2 eV, corresponding to carbonate groups (CO₃²⁻) [168-170], is observed for the Rh catalyst after reforming of Norpar13 and Norpar13(350) as well as the Ni catalyst after Norpar13 reforming. However, its presence becomes difficult to be observed with the Ni catalyst upon Norpar13(350) reforming. It is very likely that both carboxyl and carbonate are intermediates of carbon gasification in steam reforming of hydrocarbons, as suggested by previous literature [162, 170-174]. Almarri’s study regarding TPD investigation of oxygen-containing functional groups on carbon-based adsorbents has reported that carboxyl groups are not stable because of their low
decomposition temperatures between 230 and 270 °C [175]. Recently, Senanayake et al. reported that carbonate groups can readily decompose at ambient temperatures on CeO$_x$/Au catalysts in water-gas-shift reaction [170]. Under the reforming temperature (800 °C) the facile decomposition of both carboxyl and carbonate can be expected to give rise to effective carbon removal from reforming catalysts. For all the carbon XANES spectra, the peaks between 293 and 295 eV are from the ceria (M$_{4,5}$ edge) in the support. These peaks are strong for the Rh catalyst whether sulfur is present or not. On the contrary, they become rather weak for the Ni catalyst after the reaction with sulfur. It thereby suggests that the carbon deposits significantly cover the Ni catalyst surfaces, in good agreement with the STXM and TPO results, and then prevented the ceria in the support from being detected by XANES.

As shown in Figure 6-7, the oxidized carbon species (quinone-like carbon, carboxyl, and carbonate) were predominant in the absence of sulfur, while graphitic carbon prevailed on the used catalysts after the reaction with sulfur. Moreover, the peak heights of carboxyl and carbonate decreased when the fuel contained sulfur. These facts are strong evidence of sulfur poisoning effect on carbon gasification, which may be because sulfur poisoning hinders the steam dissociation into highly reactive surface oxygen species (O and OH), lower their mobility on reforming catalysts, and thus inhibit the interactions between carbon deposits and the surface oxygen species [176, 177].

In order to gain more insight into the dynamic impact of sulfur on carbon deposition, the two catalysts were further tested for Norpar13(350) reforming at different time on stream (5, 15, and 30 h) for comparison with the results at 55 h. As shown in Figure 6-8, the carbon amount on the used Ni catalyst increases much more significantly than that on
the used Rh catalyst with time on stream, further confirming the pronounced promotion
effect of sulfur on the carbon deposition on the former. Figure 6-9 shows time series of
carbon XANES spectra of the used Ni and Rh catalysts after Norpar13(350) reforming.
For the Ni catalyst, four carbon peaks including quinine-like carbon, aromatic carbon,
carboxyl, and carbonate are present at 5 h. As the reaction proceeds, the aromatic carbon
peak becomes increasingly stronger, and meanwhile the peaks of carboxyl and carbonate
progressively decrease. It seems that the presence of sulfur suppressed the carbon
gasification while dramatically promoting the formation of aromatic carbon on the Ni
catalyst. In the case of the Rh catalyst, only the quinine-like carbon species are detectable
over 5 h on stream. Afterwards, the peak at 285.2 eV and the plateau starting at 291.5 eV
appear, indicating the formation of graphitic carbon on the Rh catalyst with time on
stream. Unlike the Ni catalyst case, the spectrum shape and peak intensities of carboxyl
and carbonate for the used Rh catalyst after 15, 30, and 55 h on stream are very similar,
implying that the poisoning effect of sulfur on the carbon gasification on the Rh catalyst
is not as significant as that on the Ni catalyst. This deduction is corroborated by Figure 6-
10, which compares the normalized peak intensities of carboxyl, carbonate, and aromatics
for the Ni and Rh catalysts upon Norpar13(350) reforming at different time on stream.
Obviously, the peak intensities for both carboxyl and carbonate rapid decrease in the case
of the Ni catalyst, while the peak intensity of carboxyl is essentially constant and that of
carbonate slightly decreases with time on stream for the Rh catalyst. Meanwhile, it
should be noted that the increase of aromatics over the Ni catalyst is faster than that over
the Rh catalyst with time on stream, further confirming the more abundant accumulation
of aromatic carbon deposits on the former in the reforming reaction with sulfur-containing feed.

6.2.2.4. Suppressed formation of filamental carbon

Figure 6-11 shows the SEM images of the used Ni catalysts after the reactions without and with sulfur. In both cases no filamental carbon was observed, although it is a very common type of carbon for nickel-based reforming catalysts. Moreover, the TEM image of the used Ni catalyst after Norpar13(350) reforming (Figure 6-2) also did not show any evidence of filamental carbon. We therefore infer that the formation of filamental carbon is not favorable on the CeO$_2$-Al$_2$O$_3$-supported Ni catalyst under the reforming conditions employed in this study. The suppressed filamental carbon in the case of Norpar13 reforming can be attributed to the effective carbon gasification in the absence of sulfur [160]. It is interesting to note that the excessive carbon deposits on the Ni catalyst after Norpar13(350) reforming did not lead to filamental carbon, which may be tentatively ascribed to the presence of sulfur. Rostrup-Nielsen’s study regarding carbon-free methane steam reforming over sulfur-passivated nickel catalysts has illustrated the inhibition effect of sulfur on the growth of filamental carbon [178]. It has been well established that the step-edge sites of Ni are critical for the formation of filamental carbon. This is because carbon atoms prefer to adsorb on the step-edge sites and diffuse from these sites to the nickel-support interface for the growth of filamental carbon [42, 75, 179]. However, the step-edge sites are also the favorable sites for sulfur adsorption [2, 42, 75]. It is reasonable to believe that the sulfur atoms adsorbed on the
step-edge sites can interrupt the adsorption and diffusion of carbon atoms on Ni such that the formation of filamental carbon is suppressed.

### 6.3. Discussion

#### 6.3.1. The roles of metals in carbon gasification

The abundant carbon deposits on the CeO$_2$-Al$_2$O$_3$ support after the reactions without and with sulfur clearly demonstrate that the support alone is ineffective in carbon gasification, though ceria is a good promoter for reducing the carbon deposition on reforming catalysts because of its superior oxygen storage capability (OSC) [9, 77, 79, 134]. In contrast, the much lower carbon deposition on the used Ni and Rh catalysts after the sulfur-free reaction clarifies the critical roles of metals in carbon removal. It is very likely that metal particles and/or the metal-support boundaries are the active sites to catalyze carbon gasification, as suggested by previous studies [164, 180]. A bifunctional mechanism has been proposed for steam reforming of hydrocarbons over supported metal reforming catalysts, i.e., metal and support are the preferential site for the adsorption and activation of hydrocarbons and steam, respectively [164, 180]. Our previous studies [10, 181] have clearly demonstrated that metals can enhance the reduction of ceria support (Ce$^{4+}$ → Ce$^{3+}$) probably because they serve as the active sites for dissociative H$_2$ chemisorption and subsequent spillover to the ceria. Thus-generated Ce$^{3+}$ species are anticipated to be greatly beneficial for the steam adsorption and activation, which can be represented by the following equation: H$_2$O + Ce$_2$O$_3$ $\rightarrow$ 2CeO$_2$ + H$_2$ [10]. In addition, Song et al. have shown that the presence of metals can enhance the oxygen mobility of
ceria to achieve rapid carbon gasification [134]. In the present study, the metals may not only directly participate in carbon gasification, but also synergistically cooperate with the ceria to enhance the carbon gasification on the CeO$_2$-Al$_2$O$_3$ support. It appears that the CeO$_2$-Al$_2$O$_3$ support may also play an important role for attaining the low carbon deposition on the Ni and Rh catalyst in the sulfur-free reaction.

As demonstrated by TPO (Figure 6-4), the carbon deposition on the used Ni and Rh catalysts after Norpar13 reforming mainly took place on the support rather than on the metals. In steam reforming of hydrocarbons, various carbon species, which are generated through either metal-catalyzed hydrocarbon decomposition or non-catalytic fuel thermal cracking, will preferentially adsorb on the metals based on the aforementioned bifunctional mechanism of steam reforming reactions [164, 180]. Without sulfur, rapid carbon gasification can keep the metal surfaces clean and available for hydrocarbon reforming. The exceptional catalyst performance in Norpar13 reforming is evidence supporting that the metal surfaces were well exposed in the reaction without sulfur. The carbon deposits on the CeO$_2$-Al$_2$O$_3$ support in the Ni and Rh catalysts should arise from fuel thermal cracking, as observed in the case of the pure CeO$_2$-Al$_2$O$_3$ support upon the reactions without and with sulfur. The significantly reduced carbon deposition on the support in the presence of Ni or Rh upon Norpar13 reforming may be due to the following: (I) the preferential adsorption of hydrocarbons on the metals can suppress their accumulation on the support, (II) the interaction of support and metals can enhance the steam adsorption and activation on the support, thus making the carbon gasification on the catalyst more effective, and (III) the carbon deposit precursors on the support may potentially migrate to the metals where they can be rapidly gasified.
6.3.2. The impact of sulfur on carbon deposition

In steam reforming of hydrocarbons, the carbon species initially deposited on reforming catalysts may be gasified by the surface oxygen species (O and OH derived from steam dissociation on reforming catalysts) to form carboxyl and carbonate, the decomposition of which will lead to effective carbon gasification [39, 40]. Another possibility is that these carbon species undergo various reactions (e.g., cyclization, dehydrogenation, aromatization) to generate aromatic species [39, 74]. Subsequently, they may either react with the surface oxygen species to generate quinone-like carbon species, or further condense to form polynuclear aromatic carbon with graphitic nature if the efficiency of carbon gasification is not sufficiently high. It has been shown that the decomposition temperature of quinone-like carbon is between 700 and 800 °C, while graphitic carbon is much more refractory [38, 75, 175, 182-184]. Many studies have claimed that quinone-like carbon species are the intermediates of carbon gasification [162, 183, 184]. Furthermore, it is possible that the oxygen groups in the quinone-like carbon species can hinder the condensation between the aromatic rings such that the formation of polynuclear graphitic carbon will be suppressed. Therefore, it can be deduced that quinone-like carbon is more favorable for carbon gasification than graphitic carbon.

Both the low carbon deposition and the major formation of the oxidized carbon species (quinone-like carbon, carboxyl, and carbonate) on the used Ni and Rh catalysts upon Norpar13 reforming clearly demonstrate the effective carbon gasification in the absence of sulfur. In contrast, the increased total carbon amount and the predominant formation of graphitic carbon upon Norpar13(350) reforming indicates that the presence
of sulfur can retard the carbon gasification on reforming catalysts. Due to the critical role of metals in carbon gasification, we deduce that the negative impact of sulfur on the carbon deposition on reforming catalysts may largely originate from its poisoning effect on metals. Sulfur may cover the metal surfaces and block the metal-support boundary sites such that carbon gasification will be dramatically suppressed or even prohibited. Moreover, sulfur may react with the CeO$_2$-Al$_2$O$_3$ support to form stable compounds (e.g., Al$_2$(SO$_4$)$_3$, Ce$_2$SO$_2$, Ce$_2$(SO$_4$)$_3$, and Ce(SO$_4$)$_2$) [185], thus eliminating the support’s capability in carbon gasification.

The observation of the low- and high-temperature TPO peaks in the case of Norpar13(350) reforming over the Ni catalyst (Figure 6-4) strongly suggests that its surfaces (not only the support but also the Ni sites) were largely covered by carbon, being consistent with the results of STXM (Figure 6-3). This is to say, the abundant carbon deposits on the Ni catalyst upon the reaction with sulfur may prevent the surface active Ni sites from interacting with the reactants (hydrocarbons and steam), which is believed to be a major reason for its severe deactivation in Norpar13(350) reforming [112]. On the contrary, the carbon deposition on the Rh catalyst in the presence of sulfur was much lower and mainly occurred on the support. Such remarkably different carbon deposition on the two catalysts upon Norpar13(350) reforming is most likely because Rh possesses stronger capability to maintain carbon gasification activity than Ni in the presence of sulfur, as can be inferred from Figure 6-10. Our previous study [112] has identified the sulfur species in the used Ni and Rh catalyst after Norpar13(350) reforming. It was found that oxidized sulfur species (i.e., sulfonate and sulfate) prevailed on the Rh catalyst, while metal sulfide and organic sulfide were the major sulfur species on the Ni catalyst. There
might exist close correlations between the pronouncedly different carbon deposition with sulfur and the formation of different sulfur species on the two catalysts. Further work is needed to look into how the formation of the different sulfur species affects the physicochemical properties of the metals, which may allow us to gain more insight into the mechanism regarding sulfur poisoning effect on the carbon deposition on reforming catalysts.

### 6.4. Conclusions

The various characterization results shown in this study clearly demonstrate that sulfur can profoundly affect the carbon deposition in steam reforming of liquid hydrocarbons, and the extent of sulfur poisoning on the carbon gasification on the Ni and Rh catalysts is different. Compared with the pure CeO$_2$-Al$_2$O$_3$ support, the very low carbon deposition on both catalysts in the reaction without sulfur suggests that metals in the catalyst play a critical role in carbon gasification on reforming catalysts. The metals may not only directly participate in carbon gasification, but also synergistically cooperate with the CeO$_2$-Al$_2$O$_3$ support to enhance its carbon gasification capability. The presence of sulfur increased the carbon deposition on both catalysts, which has a much more significant impact on the Ni catalyst. The carbon deposits remarkably covered the Ni catalyst and may prevent its surfaces from hydrocarbon reforming, which is believed to be the major reason causing its severe deactivation in the reaction with sulfur. Carbon XANES studies indicate that the presence of sulfur can suppress carbon gasification and promote the formation of graphitic carbon on reforming catalysts due mainly to its poisoning effect on metals, and Rh possesses stronger capability to maintain carbon
gasification activity than Ni in the reaction with sulfur. In spite of abundant carbon deposits, no filamental carbon was observed on the Ni catalyst in the sulfur-containing reaction probably because sulfur adsorption of Ni can hinder its growth.
Figure 6-1. TPO profiles (a) and XANES spectra (b) of the used CeO$_2$-Al$_2$O$_3$ support after reforming of Norpar13 and Norpar13(350) at 800 °C for 55 h. For comparison, the spectrum of a pure graphite is also included.
Figure 6-2. TEM images of the used 10wt%Ni/CeO$_2$-Al$_2$O$_3$ and 2wt%Rh/CeO$_2$-Al$_2$O$_3$ catalysts after Norpar13(350) reforming at 800 ºC for 55 h.
Figure 6-3. Carbon K-edge spectra (obtained from STXM) of the used 2wt%Rh/CeO$_2$-Al$_2$O$_3$ and 10wt%Ni/CeO$_2$-Al$_2$O$_3$ catalysts supported on CeO$_2$-Al$_2$O$_3$ after Norpar13 and Norpar13(350) reforming at 800 ºC for 55 h. The insets show the STXM images of the used catalysts at 282 eV. The red points are representative areas (50 nm × 50 nm) for studying the carbon species on the used catalysts.
Figure 6-4. TPO profiles of the used 2wt%Rh/CeO$_2$-Al$_2$O$_3$ after reforming of Norpar13 (a) and Norpar13(350) (b) at 800 °C for 55 h, and 10wt%Ni/CeO$_2$-Al$_2$O$_3$ after reforming of Norpar13 (c) and Norpar13(350) (d) at 800 °C for 55 h. For comparison, the TPO profile of the used CeO$_2$-Al$_2$O$_3$ support (e) after reforming of Norpar13 at 800 °C for 55 h is also included.
Figure 6-5. TPH (temperature-programmed hydrogenation) of the used 2wt%Rh/\text{CeO}_2-\text{Al}_2\text{O}_3 and 10wt%Ni/\text{CeO}_2-\text{Al}_2\text{O}_3 after Norpar13 and Norpar13 (350) reforming at 800 °C for 55 h.
Figure 6-6. Carbon K-edge XANES spectra of the used 2wt%Rh/CeO2-Al2O3 and 10wt%Ni/CeO2-Al2O3 catalysts after reforming of Norpar13 and Norpar13 (350) at 800 °C for 55 h.
Figure 6-7. XANES peak heights of the different carbon species identified in Figure 6 as well as the carbon amounts for the used Ni and Rh catalysts upon reforming of Norpar13 and Norpar13(350) at 800 °C for 55 h.
Figure 6-8. Carbon amount on the used 2wt%Rh/CeO$_2$-Al$_2$O$_3$ and 10wt%Ni/CeO$_2$-Al$_2$O$_3$ catalysts upon Norpar13 (350) reforming at different time on stream.
Figure 6-9. Carbon K-edge XANES for the used 2wt%Rh/CeO$_2$-Al$_2$O$_3$ and 10wt%Ni/CeO$_2$-Al$_2$O$_3$ catalysts upon Norpar 13(350) reforming at the different reaction time on stream.
Figure 6-10. Normalized peak intensities (normalized the peaks for the Ni catalyst and the Rh catalyst to those at 5 and 15 h, respectively) of carboxyl, carbonate, and aromatics for the used 2wt%Rh/CeO$_2$-Al$_2$O$_3$ and 10wt%Ni/CeO$_2$-Al$_2$O$_3$ catalysts upon Norpar13(350) reforming at the different time on stream.
Figure 6-11. SEM images of the used 10wt%Ni/CeO$_2$-Al$_2$O$_3$ catalysts after reforming of Norpar13 (a) and Norpar13(350) (b) at 800 °C for 55 h.
Chapter 7

Summary and conclusions

This dissertation focuses on investigating the catalyst deactivation due to sulfur poisoning and carbon deposition in steam reforming of sulfur-containing liquid hydrocarbon fuels. A variety of reforming catalysts (Al$_2$O$_3$-supported Rh, Ru, Pt, and Pd catalysts, Rh catalysts supported on Al$_2$O$_3$, CeO$_2$, SiO$_2$, and MgO, and mono-/bi-metallic Rh and Ni catalysts supported on CeO$_2$-Al$_2$O$_3$) were developed and tested. Different analytical techniques were applied to investigate the physicochemical properties of these catalysts before and after the steam reforming reactions. In order to develop a better understanding on the catalyst deactivation mechanism in hydrocarbon reforming in the presence of sulfur, XANES was extensively used in this work to reveal the nature (e.g., the oxidation state, the binding structure, and the relative abundance) of the sulfur and carbon species in the used catalysts.

Among the Al$_2$O$_3$-supported noble metal catalysts (Rh, Ru, Pt, and Pd), the Rh catalyst shows the best sulfur tolerance. Al$_2$O$_3$ and CeO$_2$ are much better than SiO$_2$ and MgO as the supports for Rh to reform sulfur-containing hydrocarbons. The superior sulfur tolerance of Rh/Al$_2$O$_3$ may be associated with the well-dispersed Rh particles and the formation of electron-deficient Rh particles with high sulfur tolerance. Sulfur K-edge XANES indicated that the formation of sulfonate and sulfate only preferred on Rh/Al$_2$O$_3$. The good catalytic performance of Rh/CeO$_2$ in the presence of sulfur can be ascribed mainly to the promotion effect of CeO$_2$ on carbon gasification, leading to very low carbon deposition on the Rh/CeO$_2$ catalyst.
The experimental results regarding steam reforming of liquid hydrocarbon fuels over CeO$_2$-Al$_2$O$_3$-supported mono- and bi-metallic Rh and Ni catalysts at low and high temperatures allowed us to observe following facts: (1) that both the monometallic ones exhibited poor sulfur tolerance at 550 °C, and (2) increasing the temperature to 800 °C significantly improved the sulfur tolerance of the Rh catalyst, while the Ni catalyst was still severely deactivated at 800 °C. Sulfur K-edge XANES revealed that metal sulfide and organic sulfide are dominant in the Ni catalyst (as well as the Al$_2$O$_3$-supported Ru, Pt, Pd catalysts), while sulfonate and sulfate predominate in the Rh catalyst. Their dramatically different sulfur tolerance at 800 °C may be correlated with the formation of different sulfur species. Abundant carbon species were deposited on the Ni catalyst after the high-temperature reaction with sulfur, which may be because the formation of nickel sulfide suppressed carbon gasification. The severe Ni catalyst deactivation in the reaction with sulfur at 800 °C can be attributed to the blocking of nickel metal sites by sulfur and carbon. XPS result suggests that sulfur poisoning on the Rh catalyst can be effectively mitigated by increasing reforming temperature to 800 °C. The superior sulfur tolerance of the Rh catalyst at the high temperature is tentatively attributed to the followings: (I) sulfur oxidation and the oxygen-shielded sulfur structure of sulfonate and sulfate may inhibit direct rhodium-sulfur interaction, and (II) the decomposition of the oxidized sulfur species as well as their possible migration onto the support may protect Rh from sulfur poisoning. The Rh-Ni catalyst exhibited better sulfur tolerance than the monometallic ones at 550 °C because of the protection effect of Ni on Rh. However, no such a beneficial effect was observed for the bimetallic catalyst at 800 °C. Excessive carbon species were deposited on the Rh-Ni bimetallic catalyst after the reaction with
sulfur at 800 °C. The presence of Ni led to enhanced carbon deposition on the Rh-Ni catalyst in reforming of sulfur-containing hydrocarbons at 800 °C. The severe carbon deposition on the Rh-Ni bimetallic catalyst may be mainly caused by sulfur-poisoning of Ni to form metal sulfide which led to accumulation of pyrolytic carbon deposits in the reaction with sulfur at 800 °C.

The last part of this work clearly demonstrates that sulfur can profoundly affect the carbon deposition in steam reforming of liquid hydrocarbon fuels, and the extent of sulfur poisoning on the carbon gasification on the Ni and Rh catalysts supported on CeO$_2$-Al$_2$O$_3$ is very different. Compared with the pure CeO$_2$-Al$_2$O$_3$ support, the very low carbon deposition on both catalysts in the reaction without sulfur suggests that metals in the catalyst play a critical role in carbon gasification on reforming catalysts. The metals may not only directly participate in carbon gasification, but also synergistically cooperate with the ceria in the CeO$_2$-Al$_2$O$_3$ support to enhance its carbon gasification capability. The presence of sulfur increased the carbon deposition on both catalysts, which has a much more significant impact on the Ni catalyst. Carbon K-edge XANES studies indicate that the presence of sulfur can suppress carbon gasification and promote the formation of graphitic carbon on reforming catalysts due mainly to its poisoning effect on metals, and the Rh catalyst possesses stronger capability to maintain carbon gasification activity than the Ni catalyst in the reaction with sulfur.

The main conclusions that can be drawn from the present work include: (1) the metal type and reaction temperature have major impacts on the nature of sulfur species in reforming catalysts and their sulfur tolerance, (2) the deactivation of Ni-based reforming catalysts in high-temperature (800 °C) reforming of liquid hydrocarbon fuels in the
presence of sulfur can be largely attributed to its severe carbon deposition, (3) the presence of sulfur can suppress carbon gasification and promote the formation of graphitic carbon on reforming catalysts, and (4) the Rh catalyst has better sulfur tolerance and carbon resistance than the other noble metal and Ni catalysts in the high-temperature steam reforming of hydrocarbon fuels.
Chapter 8

Future Work

The present study has fundamentally studied the catalyst deactivation issue in steam reforming of sulfur-containing liquid hydrocarbon fuels. In order to develop a new generation of highly sulfur tolerant and carbon resistant reforming catalysts, the followings are recommended for future work:

(1) It would be very important to study the sulfur and carbon chemistry over reforming catalysts under real hydrocarbon reforming conditions (e.g., high reaction temperatures in the presence of hydrocarbons, steam, and sulfur impurities). This will allow us to gain more insights into the catalyst deactivation mechanism in liquid hydrocarbon steam reforming.

(2) Although this study has investigated the influence of sulfur on the carbon deposition on reforming catalysts during liquid hydrocarbon reforming, the effect of carbon on sulfur poisoning of reforming catalysts has not been well studied. Therefore, following work is suggested to study this issue: (1) to exam the impact of different hydrocarbons (e.g., paraffin and aromatics) on sulfur poisoning of reforming catalysts, (2) to control the carbon deposition on reforming catalysts by changing reaction parameters such as reaction time and
steam-to-carbon ratio, which will allow us to fundamentally study how carbon deposits affect the sulfur poisoning.
Appendix A

Catalyst Preparation Procedure

Calculations

There are two major steps for catalyst preparation. The first step is to prepare the support, and the second step is to load active metals onto the prepared support. In this study we use the wet impregnation method in both steps for simplicity and time savings. Prior to all steps of preparation, appropriate calculations must first be conducted. For our case, we prepare catalysts in terms of wt% of material added to the catalyst. For example, to prepare a support with A wt% CeO$_2$ on $\gamma$-Al$_2$O$_3$ (CeAl), the following calculation is used to determine how much starting material to use. Here we use ceria nitrate as CeO$_2$ precursor. The molecular weight of different elements and compounds are listed below in the right.

\[
\begin{align*}
X \text{ g } \gamma\text{-Al}_2\text{O}_3 & \quad Y \text{ g } \text{Ce(NO}_3)_3\cdot6\text{H}_2\text{O} \\
\frac{172.11 \times Y}{434.23} \text{ g CeO}_2
\end{align*}
\]

\[
\Rightarrow \frac{172.11 \times Y}{434.23} / X = A / (100 - A)
\]

\[
\Rightarrow Y = \frac{434.23 \times A \times X}{172.11 \times (100 - A)}
\]

This will calculate the weight of ceria nitrate that would be needed to make a catalyst of A wt% CeO$_2$ on X grams of $\gamma$-alumina.

<table>
<thead>
<tr>
<th>Molecular Weight</th>
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<tbody>
<tr>
<td>Ni</td>
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<td>O</td>
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<tr>
<td>N</td>
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<tr>
<td>Rh</td>
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<tr>
<td>Ce</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>CeO$_2$</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
</tr>
<tr>
<td>Ni(NO$_3$)$_2$\cdot6$\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>Ce(NO$_3$)$_3$\cdot6$\text{H}_2\text{O}$</td>
</tr>
</tbody>
</table>
For the loading of the metals we can conduct similar calculations. Instead of basing everything on the amount of alumina, we are now basing it on the weight of the support material. For example to load B wt% Rh and C wt% Ni on 20%CeAl we need to perform the calculations for both the Rh and the Ni. For the Rh, we use a 10% wt/wt solution of Rh nitrate in nitric acid solution (Sigma-Aldrich Co.). This number is the wt% of Rh (on a metal basis) not how much Rh-nitrate is dissolved in the solution. For the Ni, we use nickel nitrate as precursor. Thus the calculation would be as follows for the B wt%Rh-C wt%Ni/CeAl catalyst.

\[
\text{Calculations:} \quad \begin{aligned}
X \text{ g CeAl} & \quad Y \text{ g Rh(NO}_3\text{)}_3 \quad (10\text{ wt}\%\text{Rh}) \\
0.1 \times Y & \text{ g Rh} \\
\Rightarrow Y & = \frac{10 \times B \times X}{100 - B - C} \\
\Rightarrow Z & = \frac{290.81 \times C \times X}{58.69 \times (100 - B - C)} \\
Z & \text{ g Ni(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \\
& \frac{58.69 \times Z}{290.81} \text{ g Ni}
\end{aligned}
\]

This will yield the weight of Rh nitrate in nitric acid solution and the weight of nickel nitrate that are needed to make a catalyst of B wt% Rh and C wt% Ni on X grams of CeAl support.

**Support Preparation**

Weigh out the gamma alumina. We usually use 6 grams at a time. Put the 6 grams of alumina into a 150 mL beaker and slowly add distilled water and stir it until we get a nice homogeneous suspension. Try to use minimal amount of water. Once the mixture is made, we need to keep it stirring while we prepare ceria solution otherwise it will cake-up. Make sure stirring is nice and smooth to keep the alumina in a suspension. Weigh out the appropriate amounts of ceria nitrate. Take the ceria nitrate and dissolve it in distilled
water. Make sure all the solid is dissolved prior to moving on to the next step. Take the prepared solution and slowly inject it into the stirring alumina solution. Typically we use a pipette and slowly (a few drops at a time) inject one pipette full then wait until it all mixes through. Continue until all of the solution is added to the alumina, then rinse the vial with the ceria nitrate solution a few times with water and added it to the alumina.

Keep an eye on the stirring solution to make sure the stir bar does not get hung-up. Allow the water to evaporate off. Try to allow the solution to dry completely while stirring and heating at around 100 °C. Once the solution gets dry, lower the stirring rate to keep the powder from floating. Once the solution is dry, remove it from the container and dry overnight at around 100 °C then calcine the support at 550 °C using a temperature ramp of about 1 °C/min and a hold at 550 °C for 6 hours.

**Metal Loading**

Take the prepared support and add some water until a solution is made (just like what we do with the alumina for the ceria loading). Weigh out the appropriate amounts of metal nitrates. Make a solution of the metal nitrates in water (one solution not separate solutions). It is typically difficult to get all of the nickel nitrate to dissolve completely in a small amount of water, so we can slightly heat it until it is all dissolved. Put all metal nitrates in a water solution together to make one solution. Before pipetting the metal nitrates solution into the support solution, make sure all the metal nitrates are dissolved and the metal solution is homogeneous. Slowly pipette the metal nitrates solution into the stirring support solution. Pretty much adding the metal to the support is in the exact same procedure as adding the ceria nitrate to the alumina as discussed above. Once the mixture
is dried overnight at around 100 °C, calcine it at a ramp of 1 °C/min and a hold at 550 °C for 6 hours.

**Pelletizing**

Fill the dye with about 1 cm of catalyst powder. Compress the powder in the press until the pressure gauge reads slightly over 6000. Allow this to sit for at least one minute followed by adding pressure to keep the gauge slightly over 6000. Remove the dye from the press and then remove the formed pellet from the dye. Grind the pellet and sift using the proper mesh plates. Keep repeating until all the powder is in pellet form.
Appendix B

Properties of Norpar13 liquid hydrocarbon fuel

Certificate of Analysis

ExxonMobil Chemical

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<tr>
<td>Specific Gravity @ 15.6/15.6°C</td>
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<td>Color, Saybolt</td>
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<td>Refractive Index @ 25°C</td>
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</tr>
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<td>Passes</td>
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<td>Odor</td>
<td>Passes</td>
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</tr>
<tr>
<td>Sulfur Content, ppm</td>
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</tbody>
</table>

Figure B-1. Summary of the properties of Norpar13 liquid hydrocarbon fuel.
Appendix C

Sulfur K-edge XANES spectra of sulfur standards

Figure C-1. Sulfur standards. Top: sulfur K-edge XANES spectra (showing white line); Bottom: first derivative of the sulfur K-edge XANES spectra (showing edge energy). It can be seen that the XANES spectra of the various sulfur standards are significantly different from each other.
Appendix D

Curving fitting on Rh 3d XPS peaks

Figure D-1. Deconvolution of Rh 3d XPS spectra of the used Rh catalysts after steam reforming of liquid hydrocarbons (Norpar13) without and with sulfur at 550 and 800 °C. All the reactions at were operated on stream for 55 h, except those with sulfur (steam reforming of Norpar13(350)) at 550 °C were run for 30 h. Black: original Rh 3d XPS spectra; Red: Rh⁺; Blue: Rh³⁺.
Appendix E

Additional sulfur K-edge XANES spectra

![Graph showing sulfur K-edge XANES spectra for CeAl_Norpar13(350)_800°C with different time on steam.]

Figure E-1. Sulfur K-edge XANES spectra of the pure CeO$_2$(20wt%)-Al$_2$O$_3$ support after steam reforming of Norpar13 with 350 ppm sulfur at 800 °C with different time on steam. Reforming conditions: 1 g of catalyst, S/C =3.
Figure E-2. Sulfur K-edge XANES spectra of the pure CeO$_2$(20wt%)-Al$_2$O$_3$ support after steam reforming of Norpar13 with 350 ppm sulfur at 550 °C for 55 h. Reforming conditions: 1 g of catalyst, S/C = 3.
Figure E-3. Sulfur K-edge XANES spectra of the pure CeO₂, Al₂O₃, and CeO₂(20wt%)-Al₂O₃ supports after steam reforming of Norpar13 with 350 ppm sulfur at 800 °C for 55 h. Reforming conditions: 1 g of catalyst, S/C =3.
Figure E-4. Sulfur K-edge XANES spectra of the pure CeO$_2$, Al$_2$O$_3$, MgO, and SiO$_2$ supports after steam reforming of Norpar13 with 350 ppm sulfur at 800 °C for 55 h. Reforming conditions: 1 g of catalyst, S/C =3.
Figure E-5. Sulfur K-edge XANES spectra of the Rh catalysts without and with ceria modification after steam reforming of Norpar13 with 350 ppm sulfur at 800 °C for 55 h. Reforming conditions: 1 g of catalyst, S/C =3.
Figure E-6. Sulfur K-edge XANES spectra of the Ni catalysts without and with ceria modification after steam reforming of Norpar13 with 350 ppm sulfur at 800 °C for 55 h. Reforming conditions: 1 g of catalyst, S/C =3.
Figure E-7. Sulfur K-edge XANES spectra of the Rh and Ni catalysts supported on CeO$_2$(20wt%)-Al$_2$O$_3$ with different metal loadings after steam reforming of Norpar13 with 350 ppm sulfur at 800 °C for 55 h. Reforming conditions: 1 g of catalyst, S/C =3.
Figure E-8. Sulfur K-edge XANES spectra of the Rh (2 wt%) and Ni (10 wt%) catalysts supported on CeO$_2$(20 wt%)-Al$_2$O$_3$ after steam reforming of diesel fuel with 15 ppm sulfur at 800 °C for 150 h. Reforming conditions: 1 g of catalyst, S/C = 3.
Appendix F

Additional carbon K-edge XANES spectra

Figure F-1. Carbon K-edge XANES spectrum of the copper tape used for sample preparation together with the spectrum of the Rh catalyst tested in the steam reforming reaction at 800 °C for 55 hours. It can be seen that the spectra of carbon tap is completely different from that from the used Rh catalyst.
Figure F-2. Carbon K-edge XANES spectra of the used pure CeO$_2$(20wt%)-Al$_2$O$_3$ support after steam reforming of Norpar13 with 350 ppm sulfur at 550 and 800 °C for 55 h. Reforming conditions: 1 g of catalyst, S/C =3.
Figure F-3. Carbon K-edge XANES spectra of different carbon standards.
Figure F-4. Carbon K-edge XANES spectra of the Rh (2 wt%) and Ni (10 wt%) catalysts supported on CeO$_2$(20wt%)-Al$_2$O$_3$ after steam reforming of diesel fuel with 15 ppm sulfur at 800 °C for 150 h. Reforming conditions: 1 g of catalyst, S/C = 3.
Appendix G

Al$_2$O$_3$-supported Ni catalysts modified by Co, Fe, and K

![Graph showing TPR profiles of Ni/Al, Ni-Fe/Al, and Ni-Co/Al catalysts.](image)

**Figure G-1.** TPR profiles of Ni/Al, Ni-Fe/Al, and Ni-Co/Al catalysts.
Figure G-2. Steam reforming of diesel fuel with 15 ppm sulfur over Ni/Al, Ni-Fe/Al, Ni-Fe-K/Al, and Ni-Co/Al catalysts. Reforming conditions: 1 g of catalyst, S/C = 3, T = 800 °C.
Figure G-3. The sulfur and carbon contents in used Ni/Al, Ni-Fe/Al, Ni-Fe-K/Al, and Ni-Co/Al catalysts after steam reforming of diesel fuel with 15 ppm sulfur. Reforming conditions: 1 g of catalyst, S/C = 3, T = 800 °C.
Figure G-4. Carbon K-edge XANES spectra of the used Ni/Al, Ni-Fe/Al, Ni-Fe-K/Al, and Ni-Co/Al catalysts after steam reforming of diesel fuel with 15 ppm sulfur. Reforming conditions: 1 g of catalyst, S/C = 3, T = 800 °C.
Figure G-5. Sulfur K-edge XANES spectra of the used Ni/Al, Ni-Fe/Al, Ni-Fe-K/Al, and Ni-Co/Al catalysts after steam reforming of diesel fuel with 15 ppm sulfur. Reforming conditions: 1 g of catalyst, S/C =3, T = 800 °C.
Appendix H

Characterization of mono- and bi-metallic Rh and Ni catalysts supported on Al$_2$O$_3$ and CeO$_2$-Al$_2$O$_3$ for hydrocarbon reforming

Abstract

To clarify the effects of Rh and CeO$_2$ addition on the structural and surface properties of Al$_2$O$_3$-supported Ni reforming catalyst, a series of catalysts (Ni/Al$_2$O$_3$, Rh/Al$_2$O$_3$, Rh-Ni/Al$_2$O$_3$, Ni/CeO$_2$-Al$_2$O$_3$, Rh/CeO$_2$-Al$_2$O$_3$, and Rh-Ni/CeO$_2$-Al$_2$O$_3$) was thoroughly characterized in this study. It was demonstrated by TPR, XRD, and XPS that addition of Rh and CeO$_2$ promoted the Ni reduction. The XRD results showed that the Ni crystallites became smaller in the presence of Rh. STEM investigation on Rh-Ni/Al$_2$O$_3$ provided visual evidence of intimate Rh-Ni interaction, which was corroborated by EXAFS verifying the Rh-Ni alloy formation in the bimetallic catalysts. The hetero-atomic metal-metal interaction is proposed to account for the promotion effects of Rh on the Ni catalyst. XPS indicated that the Rh and CeO$_2$ addition suppressed the Ni surface concentration drop probably because (I) the presence of Rh hindered Ni agglomeration, (II) the CeO$_2$ addition retarded Ni diffusion into the Al$_2$O$_3$ bulk.
1. Introduction

Hydrogen (H$_2$) is not only a critical feedstock for numerous industrial processes (e.g., chemical syndissertation and petroleum refining), but also an efficient and ultra-clean fuel for generating electric power in fuel cells [1-3, 5, 8]. So far, hydrocarbon steam reforming (C$_x$H$_y$ + H$_2$O $\rightarrow$ H$_2$ + CO) over Al$_2$O$_3$-supported Ni catalysts is the most important and economical process for large-scale H$_2$ production [3, 5, 6]. One of issues associated with the Ni catalysts is that they are prone to deactivate due to carbon deposition and sulfur poisoning [5, 38, 44, 46, 74, 186]. Consequently, how to improve their resistance to the catalyst deactivation has become a hotspot in the field of catalytic fuel processing [5, 9, 19, 20, 33, 38, 44, 65, 75, 77, 134, 163, 187, 188].

It has been well known that addition of a promoter (e.g., Au [81, 84], Sn [63, 65, 66, 70, 71], B [67-69], Re [21, 53, 189], W [21], Sr [52], etc.) to the Ni catalysts can improve their stability during hydrocarbon reforming. Besenbacher et al. [81] developed a bimetallic Au-Ni alloy catalyst, which showed much higher carbon resistance than Ni alone catalyst in butane steam reforming. Their DFT calculations revealed that the presence of Au notably increased the barrier for hydrocarbon dissociation and suppressed the carbon adsorption on Ni surfaces [81]. The retardation effect of Au on the carbon accumulation over Ni was further confirmed by Chin et al., who comparatively studied the carbon deposition on MgAl$_2$O$_4$-supported Ni catalysts without and with Au modification for steam reforming of methane [84]. Sn is another well-known promoter that has been theoretically and experimentally demonstrated to be effective in reducing the carbon deposition on Ni catalysts [63, 65, 66, 70, 71]. Nikolla et al. have shown that the Sn modification made carbon oxidation preferred versus forming C-C bonds on Ni.
Wang et al.’s studies [21, 53] showed that a Re-Ni catalyst exhibited promising sulfur tolerance in steam reforming of liquid hydrocarbons, and addition of W further enhanced its performance in oxidative steam reforming of sulfur-containing gasoline.

Although being effective in improving the Ni catalyst stability, the aforementioned promoters are mostly inert to hydrocarbon reforming reactions, implying their modification may deteriorate the catalytic behaviors of Ni catalysts. To circumvent this obstacle, considerable attention has been paid to the Ni catalysts promoted with highly reactive noble metals such as Rh, Pt, and Ru because their addition is generally beneficial for hydrocarbon reforming over Ni-based catalysts [9, 10, 18, 97, 187, 190-192]. Of various noble-metal-modified Ni catalysts, bimetallic Rh-Ni has been shown to be a promising formulation [9, 10, 97, 187, 193-196]. Kugai et al [97] developed a novel Rh-Ni/CeO$_2$ catalyst with exceptional activity, selectivity, and stability for ethanol steam reforming. Lakhapatri and Abraham evaluated the catalytic behaviors of Al$_2$O$_3$-supported Rh-Ni catalysts in steam reforming of sulfur-doped n-hexadecane, and clearly demonstrated the better stability of the bimetallic system compared with monometallic Ni in the sulfur-containing reaction [18].

Apart from the Rh addition, CeO$_2$ modification of Al$_2$O$_3$ support is also an effective way to enhance the Ni catalyst performance [77-79, 134, 188, 197]. Wang and Lu [77] investigated the role of CeO$_2$ in Ni/CeO$_2$-Al$_2$O$_3$ catalysts for CO$_2$ dry reforming of CH$_4$, and found out that CeO$_2$ enhanced the catalyst activity and stability due largely to the less carbon deposition in the presence of CeO$_2$. Likewise, Natesakhawat et al. [79, 134, 188] reported that the CeO$_2$ addition promoted the carbon gasification (C + O → CO) on Ni
catalysts in propane steam reforming. According to literature [77-79], the positive effect of CeO$_2$ on carbon gasification can be associated with its outstanding redox property, which increases the active oxygen species (e.g., O and OH) on reforming catalysts for efficient carbon gasification.

Our previous studies have demonstrated the superior carbon resistance and sulfur tolerance of the bimetallic Rh-Ni/CeO$_2$-Al$_2$O$_3$ catalyst in hydrocarbon steam reforming [9, 10, 187]. For example, Strohm et al. reported that this catalyst allowed for successful low-temperature (510 °C) steam reforming of a JP-8 jet fuel containing 22 ppm sulfur for 72 h with > 95% conversion, while the monometallic ones very rapidly deactivated by sulfur with time on stream [9]. Though great efforts have been devoted to exploring the hydrocarbon reforming behaviors of the Rh-Ni/CeO$_2$-Al$_2$O$_3$ catalyst, its physico-chemical properties are not systemically studied yet. In order to clarify the effects of Rh and CeO$_2$ addition on the structural and surface properties of Al$_2$O$_3$-supported Ni catalyst, the present study investigates a series of catalysts (Ni/Al$_2$O$_3$, Rh/Al$_2$O$_3$, Rh-Ni/Al$_2$O$_3$, Ni/CeO$_2$-Al$_2$O$_3$, Rh/CeO$_2$-Al$_2$O$_3$, and Rh-Ni/CeO$_2$-Al$_2$O$_3$) using various characterization techniques including temperature-programmed reduction (TPR), H$_2$-chemisorption, X-ray diffraction (XRD), scanning transmission electron microscopy (STEM), extended X-ray absorption fine structure (EXAFS), and X-ray photoelectron spectroscopy (XPS). Moreover, we discuss the feasible correlations between the structural and surface properties of the Rh-Ni/CeO$_2$-Al$_2$O$_3$ catalyst and its exceptional catalytic performance in hydrocarbon reforming reactions based on the results shown in this contribution and previous work.
2. Experimental

2.1. Catalyst preparation

High-purity reagent-grade Ce(NO$_3$)$_3$, Rh(NO$_3$)$_3$, and Ni(NO$_3$)$_2$ salts were purchased from Aldrich and used as received. γ-Al$_2$O$_3$ (Sasol PURALOX TH 100/150) was used as the alumina support (Al$_2$O$_3$). 20 wt% CeO$_2$ modified Al$_2$O$_3$ (CeO$_2$-Al$_2$O$_3$) was fabricated by wet impregnation of Ce(NO$_3$)$_3$ aqueous solution onto the Al$_2$O$_3$ support, followed by calcination at 550 °C for 6 h. The monometallic catalysts were prepared via wet impregnation of Rh(NO$_3$)$_3$ or Ni(NO$_3$)$_2$ onto the Al$_2$O$_3$ support or the CeO$_2$-Al$_2$O$_3$ support at 2 and 10 wt% for Rh and Ni, respectively. The bimetallic Rh-Ni catalysts were synthesized via wet co-impregnation of Rh(NO$_3$)$_3$ and Ni(NO$_3$)$_2$ onto the Al$_2$O$_3$ support or the CeO$_2$-Al$_2$O$_3$ support at the metal loading of 2 and 10 wt% for Rh and Ni, respectively. The as-prepared catalysts were then dried at around 100 °C overnight, followed by calcination at 550 °C for 6 h. The catalysts prepared in this work were 10wt%Ni/Al$_2$O$_3$, 2wt%Rh/Al$_2$O$_3$, 10wt%Ni/20wt%CeO$_2$-Al$_2$O$_3$, 2wt%Rh/20wt%CeO$_2$-Al$_2$O$_3$, 2wt%Rh-10wt%Ni/Al$_2$O$_3$, and 2wt%Rh-10wt%Ni/20wt%CeO$_2$-Al$_2$O$_3$, which are denoted as Ni/Al$_2$O$_3$, Rh/Al$_2$O$_3$, Ni/CeO$_2$-Al$_2$O$_3$, Rh/CeO$_2$-Al$_2$O$_3$, Rh-Ni/Al$_2$O$_3$, and Rh-Ni/CeO$_2$-Al$_2$O$_3$, respectively.

2.2. Catalyst characterization

N$_2$ adsorption-desorption was carried out at liquid-nitrogen temperature with a Quartchrome Autosorb-1 analyzer to examine the BET (Brunauer-Emmett-Teller method)
surface area \( (S_{BET}) \) of the fresh catalysts. Each sample was degassed by heating at 200 °C under vacuum prior to the measurement. \( \text{H}_2 \)-TPR of fresh catalysts was conducted on a Micromeritics TPR/TPD AutoChem 2910 with 5\%H\_2/Ar at a temperature ramp of 5 °C/min. Metal dispersion was measured through \( \text{H}_2 \) pulse chemisorption using the same device. The monometallic Rh and Ni catalysts were reduced by \( \text{H}_2 \) at 280 and 500 °C, respectively, and then cooled down to 50 °C in Ar. Subsequently, 24\%H\_2/Ar was pulsed for measuring the dispersion of Rh and Ni. A “sequential \( \text{H}_2 \) pulse chemisorption” method has been developed to separately determine the dispersion of Rh and Ni in the bimetallic Rh-Ni catalysts \[9, 97\]. The RhO\_x species in the bimetallic catalysts were reduced in \( \text{H}_2 \) at 280 °C, followed by cooling down to 50 °C under Ar. Then 24\%H\_2/Ar was pulsed for the measurement of Rh dispersion. Immediately after that, the sample was heated up to 500 °C in the presence of \( \text{H}_2 \) to reduce the NiO species. Then after cooling to 50 °C under Ar, 24\%H\_2/Ar was pulsed again to measure the dispersion of Ni metal by deducting the contribution of Rh metal. It was shown that at 280 °C in \( \text{H}_2 \), only RhO\_x would be reduced with little reduction of NiO \[9, 97\]. The metal dispersion was calculated by assuming the chemisorption stoichiometry of one hydrogen atom per surface metal atom.

In situ XRD experiments were performed on a Philips X’Pert Pro vertical \( \theta/\theta \) goniometer located at High Temperature Materials Laboratory in Oak Ridge National Laboratory. The instrument employs Cu Ka radiation \( (\lambda = 0.154 \text{ nm}) \) operated at 40 mA and 45 kV, and has an Anton Paar XRK 900 high-temperature furnace with a rotating sample stage (up to 900 °C), in which in situ \( \text{H}_2 \) reduction treatments were conducted. The XRD patterns were obtained every 100 °C in 4\%H\_2/N\_2 from room temperature (RT).
to 800 °C (retained 1 h at each temperature except RT). All the XRD patterns were
analyzed using MDI JADE 8.0 software and the standard JCPDS files. The crystallite
sizes of NiO, Ni, Al2O3 and CeO2 were calculated using the NiO (200), Ni (200), Al2O3
(440), and CeO2 (111) peaks by Scherrer equation, \(D = \frac{0.85\lambda}{\beta\cos\theta}\), where \(D\) is the
crystallite size, \(\lambda\) is the wavelength of the radiation, \(\beta\) is the full-width at half maximum
(FWHM) of the diffraction peak (in rad.) and \(\theta\) is the half of the diffraction angle.

The STEM images shown in this work were recorded in a JEOL 2200FS-AC
aberration-corrected STEM-TEM instrument located at High Temperature Materials
Laboratory in Oak Ridge National Laboratory. A CEOS GmbH (Heidelberg, Germany)
aberration corrector was installed on the illumination lens system. The field emission
electron gun was operated at an accelerating voltage of 200 kV. The instrument provides
a nominal probe diameter of 0.7 Å. The catalyst samples were loaded into a specially
designed heating chip, and reduced (4%H2/Ar, 550 °C, 10 min) in an airlock reaction
system that is directly connected to the STEM-TEM analytical chamber. Thus, the
reduced samples can be transferred into the analytical chamber without air exposure.

X-ray absorption measurements were conducted on the 10BM beamline of the
Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon
Source, Argonne National Laboratory. The beam was detuned to 50% of the maximum
intensity to minimize the presence of harmonics. Measurements were made in step scan
mode at 0.2 sec per point in transmission mode with the ionization chambers optimized
for the maximum current with linear response (~10^10 photons detected/s) using a mixture
of N2 and He in the incident X-ray detector and a mixture of ca. 50%Ar/N2 in the
transmission X-ray detector. A Ni foil spectrum was acquired simultaneously with each
measurement for energy calibration. Catalyst samples were pressed into a cylindrical holder and treated in a continuous-flow EXAFS reactor cell (18 in. long, 0.75 in diameter) fitted at both ends with polyimide windows and valves to isolate the reactor from the atmosphere. The reduction temperature was set at 550 and 700 ºC for Rh and Ni edge (4%H₂/He and 1 h for both), respectively. All the spectra were obtained at room temperature. For each spectrum, the Fourier transforms of k²-weighted EXAFS oscillations were obtained using a Hanning-type window in the interval k = 2-14.9¹. EXAFS results were fitted using Artemis with FEFF8 [100]. EXAFS spectra of Ni foil, NiO, Rh foil, Rh₂O₃ were recorded at room temperature as the references for the EXAFS fitting.

XPS measurements on the unreduced and reduced catalysts were performed on a Physical Electronics Quantum 2000 Scanning ESCA microprobe located at Environmental Molecular Sciences Laboratory in the Pacific Northwest National Laboratory. The fresh catalysts were loaded into a quartz reactor and reduced in 10%H₂/He at 550 ºC for 1 h before cooling down to room temperature. The quartz reactor is connected to the XPS analytical chamber such that the reduced samples can be transferred into the chamber without air exposure. The XPS instrument uses a focused monochromatic Al Kα X-ray (1486.6 eV) source for excitation and a spherical section analyzer. Electrons of 1 eV, 20 µA, and low-energy Ar⁺ ions were used to avoid the charging on the catalysts during XPS analysis. All the binding energies were referenced using Al 2p (74.7 eV).
3. Results

3.1. Catalytic performances in hydrocarbon reforming

Table H-1 briefly summarizes the catalytic performances of mono- and bi-metallic Ni and Rh catalysts supported on Al\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} in steam reforming of sulfur-containing liquid hydrocarbons, as reported in previous studies [9, 10, 187]. The catalytic activities of all these catalysts decreased with time on stream primarily due to sulfur poisoning. However, the bimetallic catalysts exhibited much longer time period than the monometallic counterparts for fuel conversion higher than 90% (TOS\textsubscript{90%}). We observed that the Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} and Rh/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalysts very rapidly deactivated at the beginning, and even did not show a stable time period for complete fuel conversion in steam reforming of Norpar13 doped with 350 ppmw sulfur at 550 °C [9, 10, 187]. After 30 h on stream for this reaction, the sulfur content in the used Rh-Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalyst was 4.7 mg/g\textsubscript{cat}, which is significantly higher than that of Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} (0.4 mg/g\textsubscript{cat}) and Rh/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} (2.4 mg/g\textsubscript{cat}). This fact indicated that the bimetallic catalyst is able to accommodate more sulfur than the monometallic ones, suggestive of the higher sulfur tolerance of the former. Moreover, comparing the catalysts without and with Rh and CeO\textsubscript{2} modification shows that their addition suppressed the carbon deposition. The data in Table H-1 clearly indicated the superior sulfur tolerance and carbon resistance of the bimetallic Rh-Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalyst in steam reforming of sulfur-containing hydrocarbons.
3.2. Physical and redox properties

The textural properties and metal dispersion data of the materials studied in this work are summarized in Table H-2. The Al₂O₃ support has a surface area of 144 m²/g and a pore volume of 0.81 cm³/g. With the loading of Ni and CeO₂, both the surface area and pore volume obviously dropped (123 m²/g and 0.61 cm³/g for Ni/Al₂O₃, 121 m²/g and 0.63 cm³/g for CeO₂-Al₂O₃, and 109 m²/g and 0.54 cm³/g for Ni/CeO₂-Al₂O₃) because their loading covered the surfaces of the Al₂O₃ support. In contrast, the Rh addition much less affected the textural property (148 m²/g and 0.77 cm³/g for Rh/Al₂O₃, 126 m²/g and 0.63 cm³/g for Rh-Ni/Al₂O₃, and 102 m²/g and 0.49 cm³/g for Rh-Ni/CeO₂-Al₂O₃) due to the pretty low Rh loading. The measured Ni metal dispersion for Ni/Al₂O₃ is about 1.9%, and significantly increased with the Rh addition (Rh-Ni/Al₂O₃: 7.3%, Rh-Ni/CeO₂-Al₂O₃: 8.2%). Compared with Rh, the CeO₂ addition less impacted the Ni metal dispersion (Ni/CeO₂-Al₂O₃: 2.7%).

Figure H-1 exhibits the TPR profiles of all the catalysts studied in this work. The observed H₂ consumption between 550 and 850 °C in the case of Ni/Al₂O₃ can be assigned to Ni reduction. Previous studies have assigned the Ni reduction at temperatures above 700 °C for Al₂O₃-supported Ni catalysts to the formation of NiAl₂O₄ spinel structure [144, 198]. It seems that the TPR result of Ni/Al₂O₃ allows us to rationalize the generation of NiAl₂O₄ in this catalyst. On the contrary, the reduction of Rh/Al₂O₃ started from much lower temperature (ca. 100 °C) and extended up to 600 °C. The Rh-Ni/Al₂O₃ catalyst exhibited an intensive peak between 400 and 600 °C dominantly resulting from the Ni reduction, as reported by our previous work [9, 10]. The addition of CeO₂ into the Ni/Al₂O₃ and Rh/Al₂O₃ catalysts changed their reduction profiles. It can be seen that (I)
small bump appeared at temperatures between 200 and 400 °C for Ni/CeO$_2$-Al$_2$O$_3$ due very likely to the reduction of Ni species associated with CeO$_2$, and (II) a very sharp peak associated with Rh reduction can be seen at 100 °C for Rh/CeO$_2$-Al$_2$O$_3$ [9, 10]. Furthermore, the Ni reduction peak of Rh-Ni/Al$_2$O$_3$ was further shifted to the low-temperature direction with the addition of CeO$_2$. These above-mentioned TPR results imply that the presence of Rh made the Ni reduction easier, and the CeO$_2$ addition facilitated the reduction of both metals.

3.3. Structural characterization

3.3.1. XRD

Figure H-2 shows the XRD patterns of Ni/Al$_2$O$_3$, Rh-Ni/Al$_2$O$_3$, Ni/CeO$_2$-Al$_2$O$_3$, and Rh-Ni/CeO$_2$-Al$_2$O$_3$ as a function of H$_2$ reduction temperatures from room temperature (RT) up to 800 °C. Based on the XRD pattern of the Al$_2$O$_3$ support, the peaks at 37.1, 39.4, 45.8, and 66.7° observed in the aforementioned catalysts can be assigned to (311), (222), (400), and (440) lattice planes of γ-Al$_2$O$_3$, respectively. It can be seen that the positions and intensities of these Al$_2$O$_3$ peaks were essentially unchanged with elevating the reduction temperature. Moreover, the calculated crystalline sizes of the Al$_2$O$_3$ support keep constant around 7 nm in the entire reduction temperature range (Table H-3). Taking these facts into account, we can deduce that the Al$_2$O$_3$ support used in this study is stable in a reducing environment up to 800 °C. It should be mentioned that there are no phases related to the presence of Rh (Rh$_2$O$_3$: 20 = 34.9, 48.7, and 53.3°, and metallic Rh: 20 = 41.0, 47.7, and 69.8°) can be identified in the bimetallic catalysts, which may be due to
the low Rh loading at relatively high metal dispersion [10]. As a result, the Rh crystallites may be too small to be seen by XRD. It is very difficult to confirm the formation of NiAl$_2$O$_4$ spinel structure ($2\theta = 37.0, 44.9, 65.5^\circ$) from XRD because the diffraction peaks of $\gamma$-Al$_2$O$_3$ and NiAl$_2$O$_4$ significantly overlap each other. Furthermore, it is only feasible to form NiAl$_2$O$_4$ at the interface of Ni and Al$_2$O$_3$ for Al$_2$O$_3$-supported Ni catalysts. This will generate a small amount of NiAl$_2$O$_4$ crystallites such that their presence is hardly detected by XRD. In fact, studies regarding Al$_2$O$_3$-supported Ni catalysts have claimed that no crystalline phases related to NiAl$_2$O$_4$ could be detected from XRD [144, 198].

As to the Ni/Al$_2$O$_3$ catalyst, strong diffraction peaks of NiO (200) and (220) can be seen at 43.3 and 62.9° up to 400 °C. Afterwards, two weak peaks associated with metallic Ni (111) and (200) appeared at 44.2 and 51.5°, indicative of the phase transformation from NiO to metallic Ni. This finding is consistent with our TPR result demonstrating that the reduction of Ni/Al$_2$O$_3$ began at 400 °C. With further increasing the temperature, the peak intensities of metallic Ni crystallites continuously increased due to their growth during H$_2$ reduction treatment. Though the XRD patterns of Rh-Ni/Al$_2$O$_3$ are similar to those of Ni/Al$_2$O$_3$, the peak intensities of NiO and metallic Ni for the former are obviously lower than those for the latter under the same reduction temperature. This distinction suggests that the Rh addition promoted the Ni metal dispersion, which is also supported by the H$_2$-chemisorption result (Table H-1) and the calculated Ni crystalline sizes based on the XRD patterns (Table H-3). For example, upon H$_2$ reduction at 800 °C, the Ni crystalline size in Rh-Ni/Al$_2$O$_3$ is ca. 4.5 nm, whereas that for Ni/Al$_2$O$_3$ is ca. 8.2 nm.
Apart from those observed in Ni/Al₂O₃ and Rh-Ni/Al₂O₃, Ni/CeO₂-Al₂O₃ and Rh-Ni/CeO₂-Al₂O₃ exhibited more peaks at 33.2, 47.5, and 56.4° at room temperature. Compared with pure CeO₂, these peaks belong to the CeO₂ lattice plane of (200), (220), and (311), respectively. It is worthwhile to point out that all the CeO₂-related peaks shifted to the low-angle direction with increasing the reduction temperature. These variations should be a result of the CeO₂ structure changes (e.g., thermal CeO₂ lattice expansion) caused by the high-temperature reduction treatment [199], rather than by the metal loading and by the interaction between CeO₂ and Al₂O₃ as we observe the same trend in the XRD patterns of the CeO₂ and CeO₂-Al₂O₃ supports. In contrast to the significantly increased crystalline size of pure CeO₂ at high reduction temperature (ca. 69 nm at 800 °C), those in the CeO₂-Al₂O₃ support and CeO₂-Al₂O₃-supported catalysts remained rather stable at ca. 9 nm up to 800 °C (Table H-3).

In order to obtain the information regarding Ni reduction from the in situ XRD experiments, the normalized peak intensities of NiO (200) at 43.3° from RT to 500 °C for Ni/Al₂O₃, Rh-Ni/Al₂O₃, Ni/CeO₂-Al₂O₃, and Rh-Ni/CeO₂-Al₂O₃ are presented in Figure H-3. It can be seen that the NiO (200) peak intensity kept constant up to 200 °C for Ni/Al₂O₃, implying little Ni reduction at this temperature. Afterwards, the peak progressively decreased and disappeared at 500 °C. Compared with Ni/Al₂O₃, the peak intensity for Rh-Ni/Al₂O₃ and Ni/CeO₂-Al₂O₃ dropped faster at reduction temperatures higher than 200 °C. These observations are evidence that the addition of Rh and CeO₂ facilitated the Ni reduction, in consistence with our TPR result. It seems that Rh is more effective in improving Ni reduction than CeO₂, justified by the faster drop of peak intensity for Rh-Ni/Al₂O₃ than that for Ni/CeO₂-Al₂O₃. Among the four catalysts, Rh-
Ni/CeO$_2$-Al$_2$O$_3$ showed the fastest peak intensity drop, revealing the most effective Ni reduction in this catalyst due to the presence of both Rh and CeO$_2$.

3.3.2. STEM

Dark-field STEM images of unreduced and reduced Ni/Al$_2$O$_3$ and Rh-Ni/Al$_2$O$_3$ are presented in Figure H-4. Since the contrast of STEM images strongly depends on the atomic numbers of the materials studied, it is feasible to distinguish metals from supports for supported metal catalysts. This is because metals are usually heavier (higher atomic numbers) than supports, thus making the former brighter than the latter in STEM images. As shown in Figure H-4a, a bright spot in area A can be clearly recognized in the unreduced Ni/Al$_2$O$_3$ catalyst, corresponding to the (101) plane of NiO by lattice fringe analysis (Figure H-4b). It is very interesting to note that this Ni particle disappeared after H$_2$ reduction (Figure H-4c). Figures H-4d-g display another set of STEM images of unreduced and reduced Ni/Al$_2$O$_3$. In Figure H-4d multiple bright spots in area B were visible before reduction, and the lattice fringe analysis (Figure H-4e) on one of them (area C) indicated that they correspond to NiO. After H$_2$ reduction the Ni particle in area C became larger and brighter (Figure H-4f), whereas several particles around it vanished. The reduction in Ni/Al$_2$O$_3$ is confirmed by the lattice fringe analysis on the Ni particle in area C (Figure H-4g). These STEM images demonstrate that the Ni particles in Ni/Al$_2$O$_3$ are not stable upon H$_2$ reduction, and tend to migrate and agglomerate to form larger ones.

Figure H-5 displays the STEM images of unreduced and reduced Rh-Ni/Al$_2$O$_3$ as well as the EDX elemental mapping of the reduced catalyst. Unlike the unreduced Ni/Al$_2$O$_3$ catalyst, no very clear Ni particles can be detected in the unreduced Rh-
Ni/Al$_2$O$_3$ catalyst (Figure H-5a). This distinction implies that the Rh addition facilitated the Ni metal dispersion, agreeing well with our result of H$_2$-chemisorption and XRD. After H$_2$ reduction a number of bright spots appeared (Figure H-5b), which are Rh and Ni particles as evidenced by the EDX elemental mapping (Figure H-5c). Meanwhile, significant overlaps of the EDX signals of Rh and Ni in areas of E, D, and F strongly support the intimate Rh-Ni interaction in Rh-Ni/Al$_2$O$_3$. As presented in Figures H-5d and H-e, the particle “1” is metallic Ni, while the particles “2” and “3” are metallic Rh based on the EDX elemental mapping and lattice fringe analyses. Apparently, the two Rh particles closely interacted with the Ni particle, providing visual evidence regarding the intimate hetero-atomic metal-metal interaction in the bimetallic catalyst.

3.3.3. X-ray absorption

Figure H-6a plots the Rh K-edge XANES spectra of the reduced Rh/Al$_2$O$_3$, Rh-Ni/Al$_2$O$_3$, Rh/CeO$_2$-Al$_2$O$_3$ and Rh-Ni/CeO$_2$-Al$_2$O$_3$ catalysts along with Rh foil and Rh$_2$O$_3$ in photon energy from 23180 to 23300 eV. In this range, Rh foil exhibited an absorption peak between 23220 and 23240 eV and a relative stronger one between 23240 and 23670, whereas Rh$_2$O$_3$ only showed a broad peak from 23220 to 23260 eV. The XANES spectrum of the reduced Rh/Al$_2$O$_3$ catalyst is very close to that of Rh foil, reflecting the significant Rh reduction in Rh/Al$_2$O$_3$ at 550 °C. The Rh XANES spectrum of Rh-Ni/Al$_2$O$_3$ is dramatically different from that of Rh/Al$_2$O$_3$, whereas those of Rh/Al$_2$O$_3$ and Rh/CeO$_2$-Al$_2$O$_3$ are comparable (the same also applicable to Rh-Ni/Al$_2$O$_3$ and Rh-Ni/CeO$_2$-Al$_2$O$_3$). Accordingly, it can be deduced that the Rh-Ni interaction substantially changed the Rh metal structure, whereas the CeO$_2$ addition did not.
The Fourier transform Rh K-edge EXAFS of Rh foil, Rh₂O₃, and the reduced Rh/Al₂O₃, Rh-Ni/Al₂O₃, Rh/CeO₂-Al₂O₃, and Rh-Ni/CeO₂-Al₂O₃ catalysts are shown in Figure H-6b. The Rh-Rh and Rh-O bonds appeared at 2.39 and 1.48 Å (uncorrected for phase shift) for Rh foil and Rh₂O₃, respectively. As to the Rh/Al₂O₃ and Rh/CeO₂-Al₂O₃ catalysts, they both showed a major peak at the same position as Rh foil but with a much lower intensity. Since the EXAFS peak intensity for supported metal catalysts is proportional to metal particle size, the pretty weak Rh peaks for Rh/Al₂O₃ and Rh/CeO₂-Al₂O₃ allow us to infer that the Rh particles in these two catalysts are small [200-202]. The EXAFS fitting shows that the coordination number (CN) for Rh-Rh bond in the reduced Rh/Al₂O₃ and Rh/CeO₂-Al₂O₃ catalyst is between 5 and 6, suggestive of about 2 nm of Rh particles in these two catalysts. Such well-dispersed Rh particles on the Al₂O₃ and CeO₂-Al₂O₃ supports can be explained by the intimate interaction between Rh and Al₂O₃, which may effectively confine the growth of Rh crystallites [105-108, 111]. In fact, many studies have been performed to understand the mechanism of the strong Rh-Al₂O₃ interaction. So far, various hypotheses have been proposed, including (I) the generation of Rh-Al₂O₃ spinel structure [111], (II) covering Rh by a layer of Al₂O₃ [107], and (III) the formation of non-stoichiometric rhodium oxides (e.g., RhOₓ) that are capable of strongly interacting with Al₂O₃ [108].

It is interesting to note that the Rh EXAFS peaks evidently shifted to the short-distance direction as the two metals were combined. This fact illustrates that the Rh metal structure in the bimetallic catalysts (Rh-Ni/Al₂O₃ and Rh-Ni/CeO₂-Al₂O₃) was changed compared with the monometallic ones (Rh/Al₂O₃ and Rh/CeO₂-Al₂O₃), which should be correlated with the intimate Rh-Ni interaction. The Rh EXAFS peaks of Rh/Al₂O₃ and
Rh/CeO$_2$-Al$_2$O$_3$ are very similar to each other (the same applicable to Rh-Ni/Al$_2$O$_3$ and Rh-Ni/CeO$_2$-Al$_2$O$_3$), further confirming the negligible influence of CeO$_2$ on the Rh metal structure. As listed in Table H-4, the EXAFS fitting at Rh edge suggests that a Rh atom has about 6 Ni neighbors on average for both Rh-Ni/Al$_2$O$_3$ and Rh-Ni/CeO$_2$-Al$_2$O$_3$ (Table H-4). The observation of Rh-Ni bond at Rh edge provides strong evidence regarding the Rh-Ni alloy formation in the bimetallic catalysts, which is in accordance with our STEM results indicating the intimate Rh-Ni interaction in Rh-Ni/Al$_2$O$_3$. Furthermore, the fitting results (Tables H-4 and H-5) also suggest that the CeO$_2$ addition little affected the Rh and Ni metal structures in the monometallic catalysts as well as the hetero-atomic metal-metal interaction in the bimetallic ones.

Figure H-7a shows the Ni K-edge XANES spectra of the reduced Ni/Al$_2$O$_3$, Rh-Ni/Al$_2$O$_3$, Ni/CeO$_2$-Al$_2$O$_3$, and Rh-Ni/CeO$_2$-Al$_2$O$_3$ catalysts along with Ni foil and NiO in photon energy from 8325 to 8380 eV. It is apparent that NiO presented strong absorption between 8340 and 8360 eV, while that of Ni foil was much weaker in the same energy range but with a pre-edge between 8330 and 8340 eV. The Ni XANES spectra of all the reduced Ni-containing catalysts are between those of Ni foil and NiO due to the incomplete Ni reduction at 700 °C.

The Fourier transform Ni K-edge EXAFS of Ni foil, NiO, and the reduced Ni/Al$_2$O$_3$, Rh-Ni/Al$_2$O$_3$, Ni/CeO$_2$-Al$_2$O$_3$, and Rh-Ni/CeO$_2$-Al$_2$O$_3$ catalysts are shown in Figure H-7b. The Ni-Ni and Ni-O bonds occurred at 2.21 and 1.58 Å (uncorrected phase shift) for Ni foil and NiO, respectively. All the reduced catalysts exhibited peaks very similar to Ni foil except their intensities are lower. It is obvious that the Ni peak intensity of Rh-Ni/Al$_2$O$_3$ is lower than that of Ni/Al$_2$O$_3$ because of the smaller Ni particle size in the
presence of Rh. Fitting results show that only Ni-Ni and Ni-O contributions can be detected from the Ni EXAFS data (Table H-5). It should be noted that the CN of Ni-O for Ni/Al$_2$O$_3$ is ca. 1.6, which is larger than those of Rh-Ni/Al$_2$O$_3$ (ca. 0.9), Ni/CeO$_2$-Al$_2$O$_3$ (ca. 0.7), and Rh-Ni/CeO$_2$-Al$_2$O$_3$ (ca. 0.6). This fact further supports the promotion effect of Rh and CeO$_2$ addition on Ni reduction. There is no evidence supporting the Rh-Ni alloy formation at Ni edge, which is most likely due to the high molar ratio of Ni/Rh (roughly 9:1) in the bimetallic catalysts such that the contribution of Rh-Ni bonds may be very weak compared with those of Ni-Ni and Ni-O. The same situation has been encountered in a recent study from our group about CeO$_2$-supported Cu-Pd bimetallic catalyst (Cu: 20-30 wt%, Pd: 0.5-1 wt%) [203]. The EXAFS analysis showed no sign of the interaction between the two metals at Cu edge, while clear evidence for the alloy formation was obtained at Pd edge.

3.4. Surface properties

XPS studies were performed to determine the effects of Rh and CeO$_2$ addition on the Ni catalyst surface properties. The Ni 2p XPS spectra of the unreduced and reduced Ni/Al$_2$O$_3$, Rh-Ni/Al$_2$O$_3$, Ni/CeO$_2$-Al$_2$O$_3$, and Rh-Ni/CeO$_2$-Al$_2$O$_3$ catalysts are presented in Figure H-8. These unreduced catalysts showed a Ni 2p XPS peak at 856.3 eV together with a satellite peak at 862.5 eV, corresponding to the binding energy (BE) of Ni$^{2+}$ species on the Al$_2$O$_3$ support [9]. With H$_2$ reduction, in addition to the Ni$^{2+}$ peaks, a new peak appeared at 853.1 eV as a result of the formation of metallic Ni. Quantitative analyses (Table H-6) based on the Ni 2p XPS results indicate that the Ni surface reduction degree increases in an order of Ni/Al$_2$O$_3$ (36.1%) < Rh-Ni/Al$_2$O$_3$ (43.4%) ≈
Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} (44.7%) < Rh-Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} (53.3%). These XPS-related facts corroborate our speculation from TPR, XRD, and EXAFS that the addition of Rh and CeO\textsubscript{2} enhanced the Ni reduction. In addition, it can be seen that the Ni surface concentrations for all the Ni-containing catalysts dropped upon the reduction treatment. This phenomenon may be explained by the Ni sintering induced by H\textsubscript{2} reduction, leading to less exposed Ni surfaces. Meanwhile, it is possibly caused by the diffusion of Ni the Al\textsubscript{2}O\textsubscript{3} bulk, which is a well-known phenomenon for Al\textsubscript{2}O\textsubscript{3}-supported Ni catalysts [190, 204]. Nonetheless, the percentage of Ni surface concentration drop was lowered with the addition of Rh and CeO\textsubscript{2} (Ni/Al\textsubscript{2}O\textsubscript{3}: 40.1%, Rh-Ni/Al\textsubscript{2}O\textsubscript{3}: 22.0%, Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}: 30.5%, and Rh-Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}: 9.9%). Our results of XRD and STEM have clearly pointed out that the Rh addition retarded the growth of Ni crystallites and improved their dispersion. This may account for why the Rh addition slowed down the Ni surface concentration drop. As to CeO\textsubscript{2} its presence may weaken the Ni-Al\textsubscript{2}O\textsubscript{3} interaction, thus hindering the Ni diffusion into the Al\textsubscript{2}O\textsubscript{3} bulk.

For the Rh/Al\textsubscript{2}O\textsubscript{3}, Rh-Ni/Al\textsubscript{2}O\textsubscript{3}, Rh/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}, and Rh-Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} catalysts before H\textsubscript{2} reduction, the Rh 3d XPS peak appeared at 309.8 eV with a satellite at 314.8 eV (Figure H-9), indicative of the presence of Rh\textsuperscript{3+} in these unreduced catalysts [9]. Upon H\textsubscript{2} reduction, the BE values of Rh 3d obviously downshifted to 307.9 eV with a satellite at 312.7 eV due to the reduction of Rh in these catalysts. Comparison of the XPS data summarized in Table H-7 demonstrates that the BE values of the Rh and Ni in the bimetallic catalysts are almost the same as those in the monometallic ones. It seems to indicate that there is no charge transfer between the two metals in the bimetallic catalysts.
4. Discussion

4.1. Effects of the Rh addition

4.1.1. Promotion effects on the physical properties of Ni catalyst

One of major issues associated with Al₂O₃-supported Ni catalysts is the difficulty in Ni reduction due to the intimate Ni-Al₂O₃ interaction [77, 144, 198]. Thus, high-temperature H₂ treatment is generally necessary for their significant reduction, which unfortunately gives rise to rapid growth of Ni crystallites [42, 205, 206]. Our results of TPR and XPS have pointed out that the Rh addition is effective in enhancing the Ni reduction. Therefore, the H₂ reduction treatment for the bimetallic Rh-Ni catalysts can be carried out at relatively lower temperatures to alleviate the issue of Ni crystallite growth. The promotion effect of Rh on the Ni reduction can be largely attributed to the superior hydrogen spillover capability of Rh [10, 190]. During H₂ reduction, Rh atoms may serve as H₂ dissociation sites, followed by transferring atomic H species onto adjacent Ni particles to facilitate their reduction. The intimate Rh-Ni interaction in the bimetallic catalysts may greatly benefit this process because of the shortened hydrogen spillover distance between the two metals.

The growth of metal particles, so-called sintering, is a challenge for supported metal catalysts as it negatively affects their catalytic capabilities due to the loss of active surface sites [42, 74]. Based on a number of studies [205-208], two mechanisms, i.e., particle migration/coalescence and Ostwald ripening, have been proposed to explain the metal sintering phenomenon. In the process of particle migration/coalescence, metal
particles migrate over supports, followed by their coalescence with other metal particles to form larger ones. Ostwald ripening (i.e., atom migration or vapor transport) is such a process in which metal atoms emitted from metal particles migrate over supports or via gas phase, and are eventually captured by other metal particles. Many studies have demonstrated that particle migration/coalescence is the main route for metal sintering at temperatures lower than 700 °C, while Ostwald ripening becomes dominant at higher temperatures [206]. Accordingly, the vanished Ni particles observed in the STEM images of the reduced Ni/Al₂O₃ catalyst (Figure H-4) should be primarily induced by particle migration/coalescence rather than by Ostwald ripening as the H₂ reduction temperature (550 °C) in the STEM study was not sufficiently high. Compared with Ni/Al₂O₃, the smaller Ni particles in Rh-Ni/Al₂O₃ may be because of the Rh species closely interacting with the Ni particles, which can serve as “spacers” to prevent the growth of the latter via particle migration/coalescence. Moreover, even if the Ni particles grow via Ostwald ripening to some extent, the emitted Ni atoms perhaps preferred to combine with the surrounding Rh species to form Rh-Ni alloy prior to being captured by other Ni particles. It is very likely that the intimate Rh-Ni interaction played a critical role in suppressing the growth of Ni crystallites in the bimetallic catalysts.

4.1.2. Improved catalytic reforming activity and stability

Generally, supported metal catalysts with smaller particle sizes are more catalytically reactive largely because of more exposed metal surfaces. In the meantime,
smaller metal particles are known to have more steps and kinks that are highly active reaction sites [75, 209, 210]. However, supported Ni catalysts tend to undergo severe metal sintering and grow into large particles, as demonstrated by XRD (Figure H-2) and STEM (Figure H-4). As a result, their catalytic activities often decrease with time on stream in hydrocarbon reforming reactions. We strongly believe that the retardation effect of Rh on the growth of Ni crystallites is a critical contribution to the enhanced reforming activities of bimetallic Rh-Ni catalysts.

It is also feasible that the smaller Ni particles make the bimetallic catalysts more sulfur-tolerant and carbon-resistant. It has been reported that, for Ni catalysts at 500 °C, sulfur coverage (θ) = 0.5 corresponds to the partial pressure H₂S in H₂ as low as 1.6 × 10⁻¹² [2, 42]. This is to say, Ni metals will quantitatively withhold sulfur until their saturation in reforming of sulfur-containing fuels. This fact can be partially responsible for the high sensitivity of Ni catalysts to sulfur poisoning. The smaller Ni particles in the bimetallic Rh-Ni catalysts mean that more exposed Ni surfaces are available for sulfur accommodation, which can contribute to their better sulfur tolerance. With regard to the carbon formation on Ni catalysts, a number of studies have proven that it is a structure-sensitive process because the carbon deposition is pronouncedly affected by Ni particle size [209, 211, 212]. Rostrup-Nielsen [212] established a relationship between Ni particle size (Dₙ) and the formation energy of graphitic carbon (ΔGₕ), i.e., ΔGₕ is proportional to 1/Dₙ. It is therefore clear that, the smaller the Ni particle, the more significant the ΔGₕ is. As a consequence, the carbon formation on Ni catalysts becomes thermodynamically unfavorable with the decrease of their particle sizes.
Previous in situ TEM work has disclosed that carbon accumulation on Ni particles prefer to occur on their step-edge sites, which has also been corroborated by DFT calculations [76]. It was demonstrated that carbon atoms bind with step-edge sites more strongly than close-packed facets [76]. In order to prohibit the carbon deposition, various additives such as K, Au, and Sn have been applied to modify Ni catalysts [65, 70, 81, 84, 213, 214]. The effectiveness of these promoters principally derives from their preferential blocking of the step-edge sites of Ni such that carbon accumulation on these sites becomes unfavorable [75]. Our STEM and EXAFS results have demonstrated the intimate Rh-Ni interaction in the bimetallic catalysts. Moreover, there is a general trend that noble metals form surface alloy with Ni in noble-metal-modified Ni catalysts [76, 215]. Hence, it is reasonable to expect to see the following scenario in our bimetallic Rh-Ni catalysts: Rh atoms and/or clusters preferentially occupy the step-edge sites on Ni surfaces to interrupt the carbon nucleation and growth.

4.1.3. Potential changes of metal electronic structures

With respect to various bimetallic catalysts, it is common to observe charge redistribution around the bonded metals induced by the hetero-atomic metal-metal interaction [54, 55, 122, 216-219]. This is believed to be a crucial reason why bimetallic catalysts are better than monometallic ones for a wide range of catalytic processes. However, our XPS results show that the BE values of Rh and Ni for the bimetallic catalysts are very close to those for the monometallic counterparts (Table H-7). Seemingly, the Rh-Ni interaction did not alter the electronic structures of the two metals, which may not be true based on a number of recent studies concerning $d$-band theory [71,
Nikolla et al.’s study about supported Sn-Ni catalysts has illustrated that the Sn-Ni alloy formation generated new electronic states above and below the Fermi level of Ni, but the total number of $d$-band charges (i.e., holes and electrons) in the alloy was constant [71]. This is to say, the Sn addition broadened the Ni $d$-band without giving rise to charge transfer between the two metals [71]. Similarly, we may anticipate the same in our bimetallic systems: in spite of no XPS-measurable charge transfer between Rh and Ni, their $d$-band structures may be changed due to the intimate Rh-Ni interaction. This hypodissertation can be supported by recent theoretical and experimental studies on the electronic structure of bimetallic Rh-Ni nanowires [216, 222].

The effect of hetero-atomic metal-metal interaction on the sulfur tolerance of bimetallic catalysts has been extensively investigated in the last decades [47, 223]. Many studies have shown that bimetallic bonding (e.g., Sn-Pt [218, 219] and Pd-Rh [54]) can lower the chemical reactivity of metals towards sulfur. For example, Rodriguez et al. reported that a Sn-Pt catalyst is more significantly inert to various sulfur compounds (e.g., $\text{SO}_2$, $\text{H}_2\text{S}$, and thiophene) in comparison with the monometallic counterparts [55, 218]. Their high-resolution photoemission results revealed that the intimate Sn-Pt interaction reduced the electron donor ability of the two metals to sulfur. A very recent DFT study [224] regarding sulfur poisoning of mono- and bi-metallic Rh and Ni surfaces found out that sulfur adsorption becomes difficult with combining the two metals together. In order to explore the mechanism regarding the improved sulfur tolerance of the bimetallic Rh-Ni catalysts, the CO dissociation rates over the mono- and bi-metallic Rh and Ni surfaces were compared in this study as well. It was shown that the CO dissociation on the bimetallic Rh-Ni surface was less destabilized by a sulfur adatom compared with the
monometallic ones. These DFT calculations about the sulfur adsorption and CO
dissociation on the mono- and bi-metallic Rh and Ni surfaces may be related with the
potential changes of electronic structures of the two metals due to their intimate
interaction at an atomic level.

4.2. Effects of the CeO$_2$ addition

4.2.1. Enhanced Ni reduction

The EXAFS result suggests that the CeO$_2$ addition did not remarkably alter the
metal structures in the monometallic Ni and Rh catalysts as well as the Rh-Ni interaction
in the bimetallic catalysts. The major physical change induced by CeO$_2$ is that its
presence facilitated the Ni reduction as revealed by TPR, EXAFS, and XPS. This can be
partially attributed to the fact that the reduction of Ni on CeO$_2$ is much easier than that on
Al$_2$O$_3$. In Kugai et al.’s study [97], the reduction of Ni/CeO$_2$ was found to take place at
temperatures below 450 °C, which is notably lower than that for Al$_2$O$_3$-supported Ni
catalysts. Besides, it is plausible that covering the Al$_2$O$_3$ support by CeO$_2$ may weaken
the Ni-Al$_2$O$_3$ interaction, thus giving rise to easier Ni reduction.

4.2.2. Beneficial effects on hydrocarbon reforming

With regard to the enhanced catalytic reforming performances of CeO$_2$-modified Ni
reforming catalysts, it can be first attributed to the promotion effect of CeO$_2$ on Ni
reduction. Second, CeO$_2$ itself is an active component towards catalytic hydrocarbon
reforming, as demonstrated by recent studies [225-228]. It was claimed that high-surface-
area CeO$_2$ is able to catalyze various reforming reactions such as steam reforming of ethanol [225, 227], dry reforming of methane [226], and autothermal reforming of liquefied petroleum gas [228]. Third, the CeO$_2$ addition can lower hydrocarbon activation energy on reforming catalysts. For example, Yan et al’s work [10] regarding propane steam reforming has demonstrated that the activation energy of propane was lowered from ca. 68 kJ/mol for Rh/Al$_2$O$_3$ to ca. 50 kJ/mol for Rh/CeO$_2$-Al$_2$O$_3$.

The CeO$_2$ addition can enhance the stability of the bimetallic Rh-Ni catalyst in hydrocarbon reforming. A well-known fact is that CeO$_2$ has superior oxygen storage capability and strong surface oxygen mobility [77-79]. As a result, CeO$_2$ can release its surface oxygen species (CeO$_2$ → CeO$_{2-x}$) to facilitate the carbon removal from reforming catalysts. Thus-generated CeO$_{2-x}$ can then react to steam with its oxidation back to CeO$_2$. Obviously, there exists a redox cycle between CeO$_2$ and CeO$_{2-x}$, which can enhance the steam adsorption and activation on reforming catalysts, and thereby suppress the carbon deposition on CeO$_2$-modified catalysts.

Apart from its beneficial impact on carbon gasification, the CeO$_2$ addition may enhance the catalyst resistance to sulfur poisoning as well. Laosiripojana et al. [229] demonstrated that adding an appropriate amount of H$_2$S increased the catalytic activity of CeO$_2$ in steam reforming of methane. This fact was attributed to the reaction between CeO$_2$ and H$_2$S leading to the formation of Ce(SO$_4$)$_2$, which is able to promote the oxygen storage capacity, the lattice oxygen mobility, and eventually the reforming activity of CeO$_2$ [229]. In our previous studies, we did observe the formation of sulfate on the used Rh-Ni/CeO$_2$-Al$_2$O$_3$ catalyst after steam reforming of sulfur-containing liquid hydrocarbons [112, 187]. It is plausible that the sulfate species in this used catalyst
reacted with the CeO$_2$ in the CeO$_2$-Al$_2$O$_3$ support to generate Ce(SO$_4$)$_2$. This may not only protect the Rh and Ni metals from sulfur poisoning, but also enhance its catalytic performance in reforming of sulfur-containing hydrocarbons.

It has been well known that a major issue for the applications of CeO$_2$ in fuel processing is its poor thermal stability [78]. Therefore, CeO$_2$ alone generally possesses very low surface area under high-temperature conditions. This is deleterious for catalytic reactions because low-surface-area CeO$_2$ is much less reactive and as a support does not favor high metal dispersion. Our XRD results indicated that loading of CeO$_2$ onto the Al$_2$O$_3$ support is effective in stabilizing the former, which may be due to the strong interaction between CeO$_2$ and Al$_2$O$_3$. Previous studies have demonstrated that CeO$_2$ is able to react with Al$_2$O$_3$ to form a stable compound like CeAl$_2$O$_5$ [230], which should have a pronounced impact on inhibiting the agglomeration of CeO$_2$ particles.

5. Conclusions

The effects of Rh and CeO$_2$ addition on the structural and surface properties of the Al$_2$O$_3$-supported Ni reforming catalyst were investigated using various characterization techniques. As revealed by TPR, XRD, and XPS, the Rh addition facilitated the Ni reduction, which may be largely interpreted by hydrogen spillover from Rh to Ni. The XRD results further indicated that the presence of Rh effectively suppressed the growth of Ni crystallites. It was found by STEM that the Ni particles on Al$_2$O$_3$ were unstable, and tended to migrate and agglomerate to form larger ones upon H$_2$ reduction of the Ni/Al$_2$O$_3$ catalyst. The STEM images of the reduced Rh-Ni/Al$_2$O$_3$ catalyst provided visual evidence regarding the intimate Rh-Ni interaction. Moreover, EXAFS
demonstrated the Rh-Ni alloy formation in the bimetallic catalysts at Rh edge. The hetero-atomic metal-metal interaction is believed to play a key role in promoting the Ni reduction and reducing the Ni crystalline size for the bimetallic catalysts. This may be because that (I) intimate Rh-Ni interaction shortened the hydrogen spillover distance between the two metals, and (II) the Rh species closely interacting with the Ni particles served as “spacers” to prevent the growth of the latter.

In addition to the promotion effect of CeO$_2$ on reduction of Rh and Ni, there is no evidence indicating that its addition significantly affected the structures of the two metals in the monometallic catalysts as well as their interaction in the bimetallic ones. The promotion effect of CeO$_2$ on the catalytic reforming performance of the bimetallic Rh-Ni catalyst may largely originate from its superior redox property. Loading CeO$_2$ onto the Al$_2$O$_3$ support dramatically stabilized the former. As a result, the crystalline size of CeO$_2$ maintained at ca. 9 nm even upon high-temperature (800 °C) reduction, while that of pure CeO$_2$ increased to ca. 69 nm after the same treatment.

XPS studies indicated that the addition of Rh and CeO$_2$ retarded the Ni surface concentration drop as compared with Ni/Al$_2$O$_3$ upon H$_2$ reduction. This may be attributed to the followings: (I) the presence of Rh hindered Ni particle agglomeration, thus allowing for more exposed metal surfaces, and (II) the CeO$_2$ addition weakened the Ni-Al$_2$O$_3$ interaction so as to retard Ni diffusion into the Al$_2$O$_3$ bulk.
### Table H-1. Catalytic performances of mono- and bi-metallic Ni and Rh catalysts in steam reforming of sulfur-containing liquid hydrocarbon

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Sulfur conc. of Norpar13(^b) (ppmw)</th>
<th>Reaction Temp (°C)</th>
<th>TOS(_{\text{total}}) (h)</th>
<th>TOS(_{90%}) (h)</th>
<th>Carbon (g/g cat·h)*10(^3)</th>
<th>Sulfur (mg/g cat)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh-Ni/CeAl</td>
<td>100</td>
<td>510</td>
<td>32</td>
<td>~ 30</td>
<td>10</td>
<td>NA(^e)</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>550</td>
<td>30</td>
<td>~ 7</td>
<td>6</td>
<td>4.7</td>
</tr>
<tr>
<td>Ni/CeAl</td>
<td>104</td>
<td>510</td>
<td>5</td>
<td>ND(^g)</td>
<td>298</td>
<td>NA(^e)</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>550</td>
<td>30</td>
<td>ND(^f)</td>
<td>10</td>
<td>0.4</td>
</tr>
<tr>
<td>Rh/CeAl</td>
<td>15</td>
<td>510</td>
<td>57</td>
<td>~ 40</td>
<td>0.5</td>
<td>NA(^e)</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>510</td>
<td>10</td>
<td>~ 6</td>
<td>3</td>
<td>NA(^e)</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>550</td>
<td>30</td>
<td>ND(^f)</td>
<td>6</td>
<td>2.4</td>
</tr>
<tr>
<td>Rh/Al</td>
<td>15</td>
<td>510</td>
<td>10</td>
<td>NA(^e)</td>
<td>4</td>
<td>NA(^e)</td>
</tr>
</tbody>
</table>

\(^a\) The reaction data were obtained from previous studies [9, 187]. Reaction conditions were as follows: volumetric flow rate for steam and Norpar13 was 4.08 and 1.38 mL/h, respectively, for a steam-to-carbon molar ratio (S/C) of 3:1 and feed weight hourly space velocity (WHSV) of 5.1 h\(^{-1}\). The metal loading for Rh and Ni is 2 and 10 wt%, respectively.

\(^b\) Norpar13 is a liquid hydrocarbon fuel from Exxon Mobile, comprising only normal paraffins with an average carbon number of 13.

\(^c\) Total time on stream (TOS\(_{\text{total}}\)).

\(^d\) TOS for fuel conversion higher than 90% (TOS\(_{90\%}\)).

\(^e\) Not available.

\(^f\) Not detectable.

\(^g\) Carbon deposition was significant, which may lead to severe carbon deactivation.
Table H-2. Basic physical properties of the materials studied

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
<th>Pore vol. (cm$^3$/g)</th>
<th>Metal loading (wt%)</th>
<th>Metal dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>144</td>
<td>0.81</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>CeO$_2$-Al$_2$O$_3$</td>
<td>121</td>
<td>0.63</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Ni/Al$_2$O$_3$</td>
<td>123</td>
<td>0.61</td>
<td>10(Ni)</td>
<td>1.9</td>
</tr>
<tr>
<td>Rh/Al$_2$O$_3$</td>
<td>148</td>
<td>0.77</td>
<td>2(Rh)</td>
<td>45.3</td>
</tr>
<tr>
<td>Ni/CeO$_2$-Al$_2$O$_3$</td>
<td>109</td>
<td>0.54</td>
<td>10(Ni)</td>
<td>2.7</td>
</tr>
<tr>
<td>Rh/CeO$_2$-Al$_2$O$_3$</td>
<td>116</td>
<td>0.57</td>
<td>2(Rh)</td>
<td>49.3</td>
</tr>
<tr>
<td>Rh-Ni/Al$_2$O$_3$</td>
<td>126</td>
<td>0.63</td>
<td>2(Rh)/10(Ni)</td>
<td>30.9(Rh)/7.3(Ni)</td>
</tr>
<tr>
<td>Rh-Ni/CeO$_2$-Al$_2$O$_3$</td>
<td>102</td>
<td>0.49</td>
<td>2(Rh)/10(Ni)</td>
<td>32.5(Rh)/8.2(Ni)</td>
</tr>
</tbody>
</table>
Table H-3. Crystalline sizes of NiO, Ni, Al$_2$O$_3$, and CeO$_2$ in the unreduced and reduced catalysts calculated based on the XRD results

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reduction Temp (ºC)</th>
<th>Crystalline size (nm)</th>
<th>NiO</th>
<th>Ni</th>
<th>Al$_2$O$_3$</th>
<th>CeO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Al$_2$O$_3$</td>
<td>RT</td>
<td></td>
<td>7.8 ± 0.6</td>
<td>-----</td>
<td>6.9 ± 0.2</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td></td>
<td>-----</td>
<td>7.2 ± 0.7</td>
<td>6.8 ± 0.2</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td></td>
<td>-----</td>
<td>8.2 ± 0.5</td>
<td>7.0 ± 0.2</td>
<td>-----</td>
</tr>
<tr>
<td>Ni/CeO$_2$-Al$_2$O$_3$</td>
<td>RT</td>
<td></td>
<td>8.5 ± 0.9</td>
<td>-----</td>
<td>6.7 ± 0.3</td>
<td>8.8 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td></td>
<td>-----</td>
<td>7.6 ± 0.9</td>
<td>6.6 ± 0.4</td>
<td>9.1 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td></td>
<td>-----</td>
<td>8.9 ± 0.6</td>
<td>6.9 ± 0.3</td>
<td>9.2 ± 0.2</td>
</tr>
<tr>
<td>Rh-Ni/Al$_2$O$_3$</td>
<td>RT</td>
<td></td>
<td>-----</td>
<td>-----</td>
<td>6.6 ± 0.3</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td></td>
<td>-----</td>
<td>3.9 ± 1.3</td>
<td>6.9 ± 0.5</td>
<td>-----</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td></td>
<td>-----</td>
<td>4.5 ± 0.5</td>
<td>7.2 ± 0.5</td>
<td>-----</td>
</tr>
<tr>
<td>Rh-Ni/CeO$_2$-Al$_2$O$_3$</td>
<td>RT</td>
<td></td>
<td>-----</td>
<td>-----</td>
<td>6.8 ± 0.2</td>
<td>8.8 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td></td>
<td>-----</td>
<td>4.1 ± 0.3</td>
<td>7.0 ± 0.4</td>
<td>8.9 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td></td>
<td>-----</td>
<td>5.7 ± 0.4</td>
<td>7.1 ± 0.5</td>
<td>9.1 ± 0.2</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>RT</td>
<td></td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>10.2 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td></td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>11.1 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td></td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>69.0 ± 3.0</td>
</tr>
<tr>
<td>CeO$_2$-Al$_2$O$_3$</td>
<td>RT</td>
<td></td>
<td>-----</td>
<td>-----</td>
<td>6.9 ± 0.3</td>
<td>8.6 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td></td>
<td>-----</td>
<td>-----</td>
<td>7.2 ± 0.5</td>
<td>8.7 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>800</td>
<td></td>
<td>-----</td>
<td>-----</td>
<td>7.3 ± 0.5</td>
<td>8.8 ± 0.2</td>
</tr>
</tbody>
</table>
### Table H-4. Fitting results of Rh K-edge EXAFS of reduced Rh-containing catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scatter</th>
<th>CN</th>
<th>R (Å)</th>
<th>DWF $(10^3)$</th>
<th>$E_o$ (eV)</th>
<th>$R_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh/Al₂O₃</td>
<td>Rh-O</td>
<td>0.6</td>
<td>1.99</td>
<td>± 0.3</td>
<td>± 0.032</td>
<td>± 8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>± 0.004</td>
<td>± 0.004</td>
<td>± 0.5</td>
</tr>
<tr>
<td>Rh-Rh</td>
<td>5.4</td>
<td>2.66</td>
<td>8</td>
<td>-7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh/Al₂O₃</td>
<td>Rh-O</td>
<td>0.7</td>
<td>1.97</td>
<td>± 0.5</td>
<td>± 0.04</td>
<td>± 14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>± 0.003</td>
<td>± 0.003</td>
<td>± 0.4</td>
</tr>
<tr>
<td>Rh-Rh</td>
<td>6.0</td>
<td>2.67</td>
<td>7</td>
<td>-7.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh/Ni/Al₂O₃</td>
<td>Rh-Ni</td>
<td>5.9</td>
<td>2.52</td>
<td>± 0.5</td>
<td>± 0.005</td>
<td>± 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>± 0.005</td>
<td>± 0.004</td>
<td>± 0.9</td>
</tr>
<tr>
<td>Rh-Rh</td>
<td>2.9</td>
<td>2.65</td>
<td>6</td>
<td>-9.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh/Ni/Al₂O₃</td>
<td>Rh-Ni</td>
<td>5.8</td>
<td>2.52</td>
<td>± 0.5</td>
<td>± 0.005</td>
<td>± 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>± 0.004</td>
<td>± 0.004</td>
<td>± 0.9</td>
</tr>
<tr>
<td>Rh-Rh</td>
<td>3.0</td>
<td>2.65</td>
<td>9</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rh/Al₂O₃</td>
<td>Rh-O</td>
<td>6</td>
<td>2.01</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Rh foil</td>
<td>Rh-Rh</td>
<td>12</td>
<td>2.69</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
</tbody>
</table>

*CN, R, and DWF are the coordination number, bond distance, and the Debye–Waller factor, respectively. k range is from 2 to 14.9 Å⁻¹, and $k^2$-weighting is applied.*
Table H-5. Fitting results of Ni K-edge EXAFS of reduced Ni-containing catalysts $^a$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scatter</th>
<th>CN</th>
<th>R</th>
<th>DWF ($10^3$)</th>
<th>$E_o$ (eV)</th>
<th>$R_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni/Al$_2$O$_3$</td>
<td>Ni-O</td>
<td>1.6</td>
<td>2.02</td>
<td>± 0.5</td>
<td>± 0.02</td>
<td>± 6</td>
</tr>
<tr>
<td></td>
<td>Ni-Ni</td>
<td>7.8</td>
<td>2.46</td>
<td>± 0.6</td>
<td>± 0.004</td>
<td>± 0.6</td>
</tr>
<tr>
<td>Ni/CeO$_2$-Al$_2$O$_3$</td>
<td>Ni-O</td>
<td>0.7</td>
<td>2.01</td>
<td>± 0.4</td>
<td>± 0.03</td>
<td>± 5.2</td>
</tr>
<tr>
<td></td>
<td>Ni-Ni</td>
<td>8.1</td>
<td>2.47</td>
<td>± 0.5</td>
<td>± 0.004</td>
<td>± 0.5</td>
</tr>
<tr>
<td>Rh-Ni/Al$_2$O$_3$</td>
<td>Ni-O</td>
<td>0.9</td>
<td>2.00</td>
<td>± 0.3</td>
<td>± 0.025</td>
<td>± 8</td>
</tr>
<tr>
<td></td>
<td>Ni-Ni</td>
<td>7.2</td>
<td>2.46</td>
<td>± 0.4</td>
<td>± 0.003</td>
<td>± 0.4</td>
</tr>
<tr>
<td>Rh-Ni/CeO$_2$-Al$_2$O$_3$</td>
<td>Ni-O</td>
<td>0.6</td>
<td>1.98</td>
<td>± 0.4</td>
<td>± 0.04</td>
<td>± 1.1</td>
</tr>
<tr>
<td></td>
<td>Ni-Ni</td>
<td>7.2</td>
<td>2.47</td>
<td>± 0.5</td>
<td>± 0.004</td>
<td>± 0.5</td>
</tr>
<tr>
<td>Ni foil</td>
<td>Ni-Ni</td>
<td>12</td>
<td>2.48</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>NiO</td>
<td>Ni-O</td>
<td>6</td>
<td>2.02</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
</tbody>
</table>

$^a$ CN, R, and DWF are the coordination number, bond distance, and the Debye–Waller factor, respectively. $k$ range is from 2 to 14.9 Å$^{-1}$, and $k^2$-weighting is applied.
Table H-6. Surface concentrations of unreduced and reduced catalysts derived from the XPS measurements

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Treatment</th>
<th>Surface composition (atom%)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Ni surface conc. drop (atom%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ni</td>
<td>Rh</td>
</tr>
<tr>
<td>Ni/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Unreduced</td>
<td>3.12</td>
<td>38.00</td>
</tr>
<tr>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;/550 °C</td>
<td>1.87</td>
<td>41.66</td>
</tr>
<tr>
<td>Ni/CeO&lt;sub&gt;2&lt;/sub&gt;-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Unreduced</td>
<td>3.60</td>
<td>36.26</td>
</tr>
<tr>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;/550 °C</td>
<td>2.50</td>
<td>39.48</td>
</tr>
<tr>
<td>Rh/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Unreduced</td>
<td></td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;/550 °C</td>
<td></td>
<td>0.40</td>
</tr>
<tr>
<td>Rh/CeO&lt;sub&gt;2&lt;/sub&gt;-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Unreduced</td>
<td></td>
<td>0.58</td>
</tr>
<tr>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;/550 °C</td>
<td></td>
<td>0.61</td>
</tr>
<tr>
<td>Rh-Ni/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Unreduced</td>
<td>2.99</td>
<td>38.36</td>
</tr>
<tr>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;/550 °C</td>
<td>2.33</td>
<td>41.10</td>
</tr>
<tr>
<td>Rh-Ni/CeO&lt;sub&gt;2&lt;/sub&gt;-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Unreduced</td>
<td>3.73</td>
<td>36.62</td>
</tr>
<tr>
<td></td>
<td>H&lt;sub&gt;2&lt;/sub&gt;/550 °C</td>
<td>3.36</td>
<td>40.32</td>
</tr>
</tbody>
</table>

<sup>a</sup> Values in parentheses are the element surface concentrations in wt%
Table H-7. Binding energy of unreduced and reduced catalysts and the degrees of Ni reduction derived from XPS measurements

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Treatment</th>
<th>Binding energy (eV)</th>
<th>Ni reduction degree (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>Rh: 74.7</td>
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<td>H₂/550 °C</td>
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* Values in parentheses are the full width at half maximum (FWHM)
Figure H-1. TPR profiles of 10wt%Ni/Al$_2$O$_3$, 2wt%Rh/Al$_2$O$_3$, 2wt%Rh-10wt%Ni/Al$_2$O$_3$, 10wt%Ni/CeO$_2$-Al$_2$O$_3$, 2wt%Rh/CeO$_2$-Al$_2$O$_3$, and 2wt%-10wt%Ni/CeO$_2$-Al$_2$O$_3$. 
Figure H-2. In situ XRD patterns of 10wt%Ni/Al₂O₃, 2wt%-10wt%Ni/Al₂O₃, 10wt%Ni/CeO₂-Al₂O₃, and 2wt%Rh-10wt%Ni/CeO₂-Al₂O₃, during H₂ reduction (4% H₂/N₂) from room temperature (RT) to 800 ºC.
Figure H-3. Normalized peak intensities of NiO (200) at 43.3° for 10wt%Ni/Al₂O₃, 2wt%Rh-10wt%Ni/Al₂O₃, 10wt%Ni/CeO₂-Al₂O₃, and 2wt%Rh-10wt%Ni/CeO₂-Al₂O₃ based on the in situ XRD experiments shown in Figure 2. For each catalyst, the peak intensities of NiO (200) at temperatures higher than RT were normalized to the corresponding one at RT.
Figure H-4. Dark-field STEM (scanning transmission electron microscopy) images of unreduced and reduced (4%H₂/Ar, 550 °C, 10 min) 10wt%Ni/Al₂O₃. Figures a-c and figures d-g represent two different catalyst areas.
Figure H-5. Dark-field STEM (scanning transmission electron microscopy) images of unreduced and reduced (4%H$_2$/Ar, 550 ºC, 10 min) 2wt%Rh-10wt%Ni/Al$_2$O$_3$. 
Figure H-6. (a) Rh K-edge XANES and (b) Fourier transform Rh EXAFS ($k^2$, $\Delta k = 2-14.9$ Å$^{-1}$) of reduced (4%H$_2$/He, 550 °C, 1 h) 2wt%Rh/Al$_2$O$_3$, 2wt%Rh-10wt%Ni/Al$_2$O$_3$, 2wt%Rh/CeO$_2$-Al$_2$O$_3$, and 2wt%Rh-10wt%Ni/CeO$_2$-Al$_2$O$_3$. Rh foil and Rh$_2$O$_3$ are included as references.
Figure H-7. (a) Ni K-edge XANES and (b) Fourier transform Ni EXAFS ($k^2$, $\Delta k = 2-14.9$ Å$^{-1}$) of reduced (4%H$_2$/He, 700 °C, 1 h) 10wt%Ni/Al$_2$O$_3$, 2wt%Rh-10wt%Ni/Al$_2$O$_3$, 10wt%Ni/CeO$_2$-Al$_2$O$_3$, and 2wt%Rh-10wt%Ni/CeO$_2$-Al$_2$O$_3$. Ni foil and NiO are included as references.
Figure H-8. Ni 2p XPS spectra of unreduced and reduced (10%H\textsubscript{2}/He, 550 °C, 1 h) 10wt%Ni/Al\textsubscript{2}O\textsubscript{3}, 2wt%Rh-10wt%Ni/Al\textsubscript{2}O\textsubscript{3}, 10wt%Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}, and 2wt%Rh-10wt%Ni/CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}.
Figure H-9. Rh 3d XPS spectra of unreduced and reduced (10%H₂/He, 550 °C, 1 h) 2wt%Rh/Al₂O₃, 2wt%Rh-10wt%Ni/Al₂O₃, 2wt%Rh/CeO₂-Al₂O₃, and 2wt%Rh-10wt%Ni/CeO₂-Al₂O₃.
References


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