

## Rh-Ni and Rh-Co Catalysts for Autothermal Reforming of Gasoline

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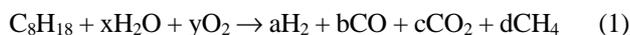
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Rh doped Ni and Co catalysts, Rh-M/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> (0.2 wt % of Rh; M = Ni or Co, 20 wt %) were synthesized to produce hydrogen via autothermal reforming (ATR) of commercial gasoline at 700 °C under the conditions of a S/C ratio of 2.0, an O/C ratio of 0.84, and a gas hourly space velocity (GHSV) of 20,000 h<sup>-1</sup>. The Rh-Ni/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> catalyst (**1**) exhibited excellent activities, with H<sub>2</sub> and (H<sub>2</sub>+CO) yields of 2.04 and 2.58 mol/mol C, respectively. In addition, this catalyst proved to be highly stable over 100 h without catalyst deactivation, as evidenced by energy dispersive spectroscopy (EDX) and elemental analyses. Compared to **1**, Rh-Co/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> catalyst (**2**) exhibited relatively low stability, and its activity decreased after 57 h. In line with this observation, elemental analyses confirmed that nearly no carbon species were formed at **1** while carbon deposits (10 wt %) were found at **2** following the reaction, which suggests that carbon coking is the main process for catalyst deactivation.

**Key Words** : Autothermal reforming, Bimetallic catalyst, CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Gasoline, Carbon coking

### Introduction

Fuel cells have attracted significant attention as promising alternatives to currently employed power systems.<sup>1-3</sup> In general, direct use of hydrogen for a fuel cell is desirable for on-site applications, but due to the insufficient infrastructure for hydrogen production and/or distribution, the cost of hydrogen is rather expensive to date. In this context, considerable efforts have been made to develop industrially viable technology for hydrogen production particularly using various liquid fuels since utilization of liquid hydrocarbons such as gasoline and diesel would provide an opportunity to employ the existing infrastructure without significant investment.<sup>4</sup>



Autothermal reforming (ATR) process (Eq. 1) has been recognized as an economically feasible process for hydrogen production from carbon-based fuels.<sup>5,6</sup> Ni-based catalysts have widely employed to catalyze ATR reactions,<sup>7-9</sup> but they have proved to be vulnerable to deactivation by carbon coking and/or sulfur poisoning during reforming. In contrast, noble metals have shown to be highly tolerable against carbon coking as well as sulfur poisoning.<sup>10,11</sup> For example, Rh and Ru based catalysts were previously reported to exhibit activities towards the ATR process of sulfur-containing fuels.<sup>12</sup> Moreover, we previously reported Rh-based catalysts supported onto various metal oxides including Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, and CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub> for ATR reactions using iso-octane and commercial gasoline, and among them, Rh/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>

(0.5 wt % Rh, 20 wt % CeO<sub>2</sub>) particularly showed excellent activity and stability towards the reforming of commercial gasoline.<sup>13</sup> Likewise, bimetallic catalysts with noble metals have also been studied for a number of reforming reactions.<sup>14,15</sup> For instance, a Pt-Pd based catalyst was shown to have superior performance over monometallic counterparts for the autothermal reforming of synthetic diesel.<sup>16</sup>

We report here on synthesis of Rh-M/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (M = Ni and Co, 20 wt %; CeO<sub>2</sub>, 20 wt %) materials containing only 0.2 wt % of Rh. Their catalytic activities towards ATR reactions were determined using commercial gasoline. The bimetallic Rh-Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> material (**1**) showed excellent performance than Rh/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (Rh, 0.5 wt %; CeO<sub>2</sub>, 20 wt %) with high stability over 100 h, whereas the Rh-Co/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (**2**) catalyst exhibited initially comparable activity to **1** but showed decreased durability. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and elemental analyses were further employed to understand the observed high stability of **1**.

### Experimental

**Preparation of Catalysts.** The mixed oxide based support, CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub>, was prepared according to the literature method.<sup>13</sup> To prepare Rh-Ni/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> (**1**) and Rh-Co/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> (**2**), RhCl<sub>3</sub>·xH<sub>2</sub>O (Alfa Aesar, 99.99%), Ni(NO<sub>3</sub>)<sub>2</sub> (Sigma Aldrich), and Co(NO<sub>3</sub>)<sub>2</sub> (Sigma Aldrich) were employed as metal precursors. In a typical incipient impregnation method, desired amounts of the metal precursors, RhCl<sub>3</sub>·xH<sub>2</sub>O and either Ni(NO<sub>3</sub>)<sub>2</sub> or Co(NO<sub>3</sub>)<sub>2</sub> were dissolved in distilled water, followed by transferring this solution dropwise into the synthesized

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CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> support. The heterogeneous mixture was vigorously stirred at room temperature, following by drying overnight at 120 °C. The resulting powders were then calcined at 800 °C for 3 h. Unless noted otherwise, as-synthesized heterogeneous catalysts contained 20 wt % of either Ni or Co content as well as 0.2 wt % of Rh content with respect to the CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> support.

**Characterization of the Rh-M/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> catalysts (M = Ni and Co).** Scanning electron microscope (SEM) images were obtained using a FEI XL-30 FEG operating at 15 kV. A small angle X-ray diffractometer (D/MAX-2500) was employed to obtain the powder X-ray diffraction (XRD) patterns of the as-prepared catalysts, using Cu K $\alpha$  radiation with an acceleration voltage of 40 kV as well as 2 $\theta$  scanning range of 5-80°. Hydrogen-temperature programmed reduction (H<sub>2</sub>-TPR) profiles were carried out using a BELCAT-M (BEL, Japan, Inc) instrumentation. For the H<sub>2</sub>-TPR analyses, samples (0.03 g) were treated with a heating rate of 10 °C min<sup>-1</sup> from 50 °C to 800 °C under the flow of 5% H<sub>2</sub>/Ar. To remove moisture and adsorbed gases, a desired sample was pre-treated with He gas at 500 °C for 30 min, prior to the H<sub>2</sub>-TPR analyses.

**Catalytic Reforming of Gasoline.** The ATR reactions of gasoline were carried out, based on the previously reported procedure.<sup>13</sup> In a typical experiment, either **1** or **2** was located at a fixed-bed reactor with a continuous-flow quartz tube. The desired catalyst (0.135-0.165 g) was pre-treated using a 30% H<sub>2</sub>/N<sub>2</sub> gas with a heating rate of 5 °C min<sup>-1</sup> from 23 °C to 700 °C before a reaction. Reforming of a commercial gasoline using a S/C ratio of 2.0, an O/C ratio of 0.84, and a gas hourly space velocity (GHSV) of 20,000 h<sup>-1</sup> were then monitored as a function of time.<sup>12,17,18</sup> The commercial gasoline contains sulfur (< 10 ppm), Pb (0.013 g/L), aromatic compounds (21 vol %), and olefin (19 vol %). A syringe pump (Havard Apparatus, Inc) was employed to supply gasoline, and a mass flow controller (MFC, MKP-TSC100) was utilized to transport N<sub>2</sub>, H<sub>2</sub>, and air. Gases produced during reforming were passed through a chiller maintained at 5 °C to condense water vapor, followed by analyses using an on-line gas chromatograph (HP 7890N) equipped with a thermal conductivity detector (carboxen packed column, Supelco, Inc) and a flame ionization detector (HP-PLOT/U, Agilent technologies). Nickel wire mesh was employed in the evaporator to facilitate heat transfer and gas-vapor mixing. The fuel conversion, H<sub>2</sub> yield, and (H<sub>2</sub> + CO) yield are defined as follows (Eqs. 2-4):

Fuel conversion (%) =

$$\frac{\text{total moles of carbon components in reformat}}{8 \times \text{total moles of fuel employed}} \times 100 \quad (2)$$

H<sub>2</sub> Yield (mol/mol) =

$$\frac{\text{total moles of H}_2 \text{ produced}}{8 \times \text{total moles of fuel reacted}} \quad (3)$$

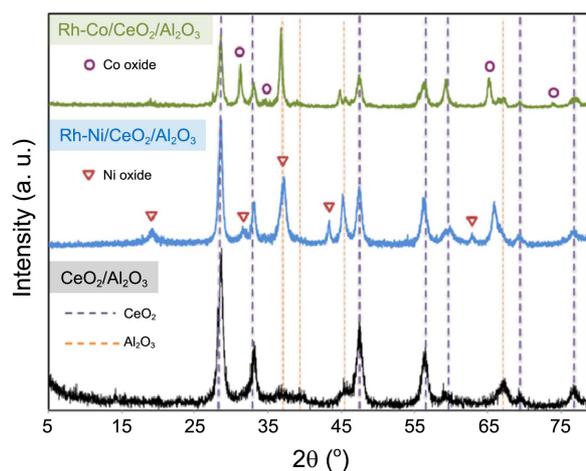
(H<sub>2</sub> + CO) yield (mol/mol) =

$$\frac{\text{total moles of (H}_2 + \text{CO) produced}}{8 \times \text{total moles of fuel reacted}} \quad (4)$$

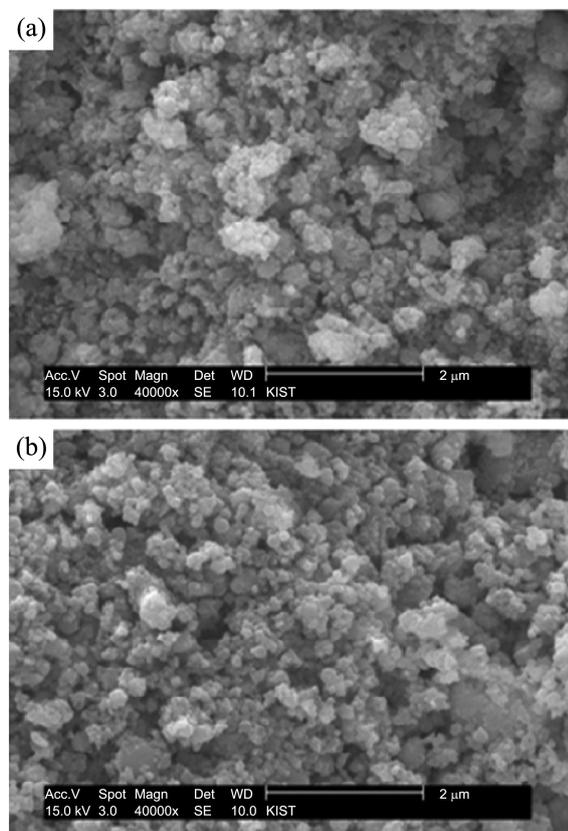
## Results and Discussion

### Characterizations of the Rh-Ni and Rh-Co Catalysts.

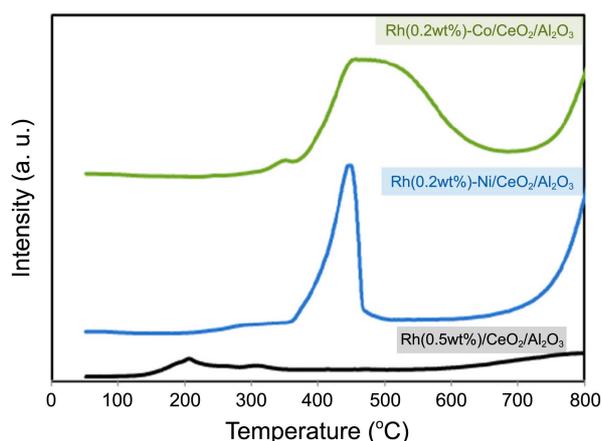
The XRD patterns of the as-prepared Rh-Ni/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> (**1**) and Rh-Co/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> (**2**) catalysts are shown in Figure 1. The XRD spectrum of CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> (Figure 1, black) was nearly unchanged following the deposition of Ni or Co metal onto the support, except for the peaks corresponding to nickel oxides or cobalt oxide (Figure 1, blue or green). These results suggest that desired non-



**Figure 1.** XRD patterns of the as-synthesized Rh-M catalysts supported on CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub>.

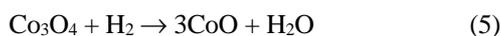


**Figure 2.** SEM images of the fresh Rh-M/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> catalysts: (a) M = Ni and (b) M = Co.



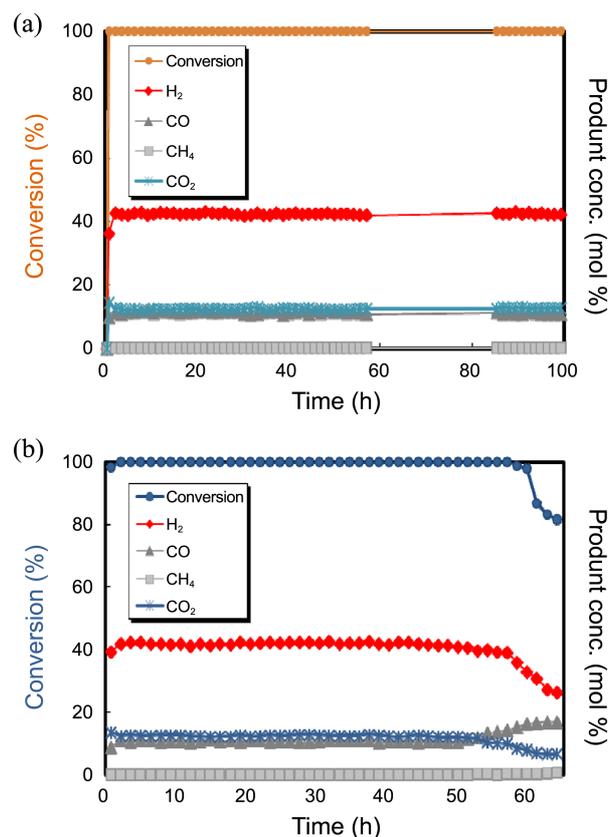
**Figure 3.** TPR profiles of the Rh-M/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> catalysts (M = no metal, black; M = Ni, blue; M = Co, green).

noble metals, Ni and Co, were positioned at the surface of the CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> support. In all cases, however, peaks attributed to Rh(0) were not found in the XRD patterns presumably due to the high dispersion and low loading of rhodium (0.2 wt %).<sup>19</sup> The catalysts, **1** and **2**, appear to possess relatively rough surface with particle sizes in a range of 150-700 nm, as evidenced by SEM (Figure 2).



To understand reduction properties of the as-prepared catalysts, temperature programmed reduction (TPR) studies were further conducted, and the resulting TPR profiles are shown in Figure 3. Upon reduction of Rh/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub>, a small peak centered at 200 °C was found, which is attributed to the reduction of rhodium oxide.<sup>20,21</sup> The reduction peak centered at *ca.* 310 °C could be caused by the formation of rhodium species strongly interacting at defect sites of the support.<sup>20,22</sup> The observed small intensity for rhodium oxide resulted from the limited quantity of Rh. In contrast, **1** showed sharp peaks with a maximum centered at 440 °C, likely attributable to the reduction of NiO (Figure 3, blue). In the TPR with **2**, a broad peak ranging from 350 °C and 650 °C was observed. The small peak centered at 350 °C appears to result from the reduction of Co<sub>3</sub>O<sub>4</sub> to CoO (Eq. 5) while the broad signal found at higher temperatures (> 450 °C) could originate from the reduction of CoO to Co (Eq. 6), as depicted in Figure 3 (green).<sup>23</sup> However, the reduction peak for Co<sub>3</sub>O<sub>4</sub> could be overlapped with that of CoO in the broad signal appeared between 350 °C and 650 °C. No peaks responsible for the reduction of rhodium oxide species were found in the reduction profiles with **1** and **2**, which is due to the low loading of rhodium (0.2 wt %) and/or the formation of Rh-M (M = Ni or Co) alloy.

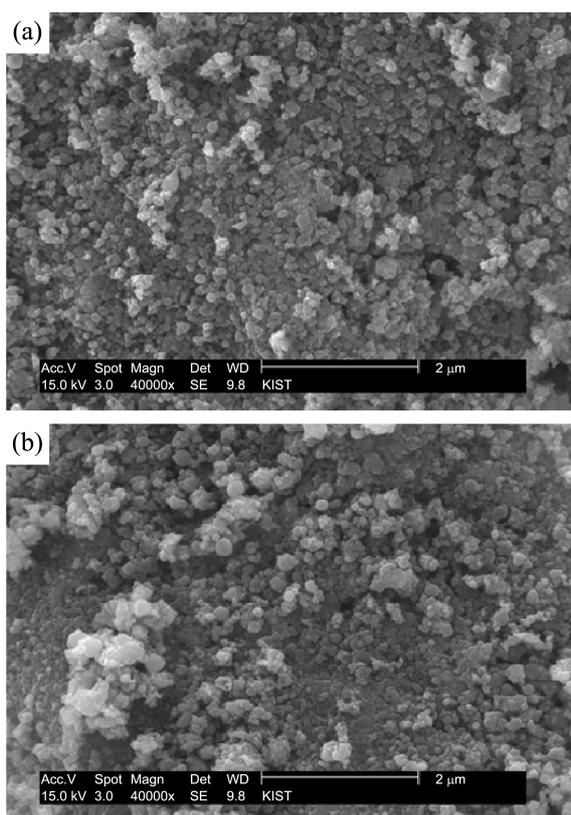
**Catalytic Hydrogen Production from Gasoline.** To examine the catalytic activities of the as-synthesized catalysts, **1** and **2** were tested for ATR reactions using commercial gasoline at 700 °C. The catalyst **1** showed excellent catalytic activity and stability for 100 h with an average conversion of



**Figure 4.** Catalytic activities of the Rh-M/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> catalysts: (a) M = Ni and (b) M = Co.

nearly 100% (Figure 4(a)), and the H<sub>2</sub> and (H<sub>2</sub> + CO) yields were determined as 2.04 mol/mol C and 2.58 mol/mol C, respectively. The obtained H<sub>2</sub> and (H<sub>2</sub> + CO) yields with **1** were found to be higher than those with previously reported Rh(0.5 wt %)/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub>.<sup>13</sup> In addition, the ratio of H<sub>2</sub>/CO is unchanged during the reforming reaction. Notably, upon dehydrogenation of gasoline, nearly no CH<sub>4</sub> was formed. Likewise, **2** initially exhibited superior activity with H<sub>2</sub> and (H<sub>2</sub> + CO) yields of 2.01 and 2.53 mol/mol C, respectively. However, the conversion with **2** decreased continuously after 57 h to ultimately give < 30 mol % of H<sub>2</sub> (Figure 4(b)). Consistent with this result, the conversion reached close to 80%.

Morphological changes of **1** and **2** after the ATR reactions were monitored by scanning electron microscope (SEM). As depicted in Figure 5, no significant changes were observed at the surface of **1**. Moreover, no filamentous carbon species were found in the catalytic material. Consistent with this result, EDS analyses confirmed the formation of no carbon and/or sulfur species at the surface of **1**. Similarly, no significant changes were observed following the ATR reaction in the presence of **2**. Since carbon and/or sulfur species could exist inside the spent-catalysts, elemental analyses were further conducted to accurately quantify the amounts of residual carbon and/or sulfur deposits after the ATR reactions. Carbon species existed at **1** were found to be less than 0.3 wt %, whereas those presented in **2** were determined to



**Figure 5.** SEM images of the used Rh-M/CeO<sub>2</sub>(20 wt %)-Al<sub>2</sub>O<sub>3</sub> catalysts (a, M = Ni; b, M = Co) after the reforming reactions.

be 10 wt %. Notably, no sulfur containing products were formed on both **1** and **2**. The absence of sulfur following the reforming reactions over **1** and **2** is consistent with a previous result for ATR reactions of iso-octane containing sulfur (100 ppm) over Ni/Fe/MgO/Al<sub>2</sub>O<sub>3</sub><sup>24</sup> that afforded increased rates of carbon formation as the sulfur content in iso-octane increased. Note that carbon coking would induce catalyst deactivation. In addition, Ferrandon *et al.*<sup>25</sup> demonstrated that a Rh(2 wt %)/La-Al<sub>2</sub>O<sub>3</sub> catalyst produced hydrogen via ATR of gasoline containing sulfur (34 ppm), and this catalyst showed decreased activity due to the deactivation process induced by carbon coking. Moreover, the existence of sulfur also increased rate of carbon formation.<sup>25</sup> The decreased activity of **2** after 50 h may thus originate from carbon coking, which could indirectly be influenced by sulfur species.

### Conclusion

ATR reactions of commercial gasoline were performed at 700 °C in the presence of Rh-based catalysts, **1** and **2**. The Rh-Ni bimetallic catalyst, **1** proved to be excellent for the autothermal reforming of gasoline with high stability. The H<sub>2</sub> and (H<sub>2</sub> + CO) yields were determined as 2.04 mol/mol C and 2.58 mol/mol C, respectively, which are better than those with the monometallic Rh/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> material containing 0.5 wt % of Rh (H<sub>2</sub> yield, 1.83 mol/mol C; (H<sub>2</sub> + CO) yield, 2.34 mol/mol C). In addition, **1** showed high stability

during the reforming reactions over 100 h. In contrast to **1**, **2** turned out to be less stable and its activity decreased after 50 h. The SEM, EDS, and elemental analyses indicated that **1** produced nearly no carbon and sulfur containing species following reforming while **2** formed 10 wt % of carbon under the same conditions. Thus, carbon coking is a primary catalyst deactivation process for the ATR reactions. The as-developed Rh-Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst (**1**) could potentially be applied to the direct reforming of gasoline with high stability.

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