Small amounts of Rh-promoted Ni catalysts for methane reforming with CO_2

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Small amounts of Rh-promoted Ni/α-Al_2O_3 catalysts possessed higher activity than pure Ni/α-Al_2O_3, Rh/α-Al_2O_3 catalysts and exhibited excellent coke resistance ability in methane reforming with CO_2. XRD, H_2-TPR, CO_2-TPD and coking reaction (via CH_4 temperature-programmed decomposition) indicated that Rh improved the dispersion of Ni, retarded the sintering of Ni and increased the activation of CO_2 and CH_4 on the surface of catalyst.

KEY WORDS: methane; dry reforming; Ni; Rh.

1. Introduction

Methane reforming with CO_2 attracted more attention in the past twenty years for its lower H_2/CO ratio in product gas and the utilization of the two greenhouse gases (equation (1)) [1,2].

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \qquad (\Delta H = 259.85\,\mathrm{kJ/mol}, 800\,^\circ C) \qquad (1)$$

At the same time, the high endothermicity of reaction (1) makes it attractive as a choice of media in energy transmission system [3,4].

Ni is popularly used as the catalyst for reaction (1) in earlier papers for its high activity and low price, but Ni deactivates easily because of coke deposition and/or metal sintering. Mechanism investigations indicated that CH_4 decomposes easily to carbon and hydrogen on Ni particles, and carbon would accumulate on the surface of catalyst if the gasification (of the intermediate carbons) step were slow. Many promoters on Ni catalyst are reported in order to eliminate the coke deposition [2,5,6]. Among them, alkaline and alkaline earth metals are helpful to the adsorption, surface enrichment of CO_2, and then increase the gasification of intermediate carbons. But the reforming activity of Ni is depressed by the addition of those alkaline promoters [7–9]. Noble metals (Rh, Ru, and Pt) are less sensitive to carbon deposition in this reforming process [1,10,11], while the application of noble metal catalysts is difficult because of the high price and limited resources. From the viewpoint of industrial application, the promotion of Ni by a small amount of noble metal is more practical [12–14].

According to the fundamental studies of supported bimetallic catalysts, the second element sometimes enhances the activity, selectivity, and stability of the parent monometallic catalysts [15,16]. In this research, different amounts of Rh was added to Ni/α-Al_2O_3 catalyst and these promoted catalysts were characterized by X-ray diffraction (XRD), temperature-programmed reduction with H_2 (H_2-TPR), CO_2 temperature-programmed desorption (CO_2-TPD) and coking reaction via CH_4 temperature-programmed decomposition. The excellent performance of Rh-promoted Ni catalyst in CH_4 reforming with CO_2 was discussed on the basis of characterization results.

2. Experimental

2.1. *Catalysts and reforming reaction*

Catalysts used in this paper were prepared by co-impregnation method. $Rh(NO_3)_2$ and $Ni(NO_3)_2 \cdot 6H_2O$ were purchased from Wako Pure Chemicals (Japan) and directly used without further treatment. α-Al_2O_3 was kindly supplied by the Basic Research Center of Sumitomo Chemical Co., Japan. The loading amount of Ni was 10 wt% of α-Al_2O_3 and the added amount of Rh was defined as the mol ratio between Rh and Ni. A pure Rh/α-Al_2O_3 (5 wt%) was also prepared by impregnation method and tested as a reference catalyst. Each catalyst (50 mg) was reduced in H_2 at 800 °C in a quartz reactor (6 mm inner diameter) for 1 h. Reforming reaction was carried out in a stoichiometric ratio (1:1) of CH_4 (99.99%) and CO_2 (99.99%) without dilution. The conversions of CH_4 and CO_2 were calculated on the

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basis of the reforming reaction (equation (1)) and trans-water-shift reaction (equation (2)):

$$CO_2 + H_2 \rightarrow CO + H_2O$$

$$(\Delta H = 33.91\,\mathrm{kJ/mol}, 800\,^{\circ}\mathrm{C}) \qquad (2)$$

Each used catalyst was analyzed by TG-DTA (Riguku TAS200, Japan) from 25 to 700 °C in order to detect the amount of coke formed during the 4-h on stream.

2.2. Characterizations

X-ray diffraction was carried out in a RINT2000 system (Rigaku, Japan). Anode Cu Kα (40 kV, 40 mA) was used as the X-ray source. The mean size of nickel crystallites was calculated from the broadening of the Ni (111) peak, according to the Scherrer–Warren equation [17].

Temperature-programmed reduction with H_2 (H_2-TPR), CO_2 temperature-programmed desorption (CO_2-TPD) and coking reaction via CH_4 temperature-programmed decomposition were performed using a TPD51 auto-adsorption system (Belsorp, Japan). The effluent gas was analyzed by on-line quadruple mass analyzer system and the MS signals of different mass numbers were recorded as functions of temperature. In H_2-TPR analysis, samples (100 mg) were pretreated in He at 500 °C for 30 min, cooling to 100 °C and then a reducing gas mixture (5% H_2 in He) was introduced at 50 mL/min. The experimental temperature was raised to 950 °C at 15 °C/ min. In CO_2-TPD, samples (100 mg) were first reduced under the same condition as the reforming reaction, cooled to room temperature, exposed to 10% CO_2/He for 20 min, purged in He for 30 min and then the desorption temperature was increased linearly to 850 °C at 20 °C/ min. In coking reaction, samples (100 mg) were reduced under the same condition as the reforming reaction, cooled to room temperature and shifted to 10% of CH_4 (He in balance). The test temperature was increased linearly to 900 °C at 10 °C/ min.

3. Results and discussions

3.1. Activity of small amounts Rh-promoted Ni/α-Al_2O_3 catalysts

Figure 1 shows the activity of Rh-promoted Ni/α-Al_2O_3 catalyst for methane reforming with CO_2. Pure Ni/α-Al_2O_3 catalyst exhibited a high reforming activity (the conversion of CH_4 and CO_2 were 71.5% and 77.1%, respectively) and high coke-formation rate (24.0 mg-coke/g-cat · h). No coke deposition was detected on pure Rh/α-Al_2O_3 catalyst, but the reforming activity was low (the conversion of CH_4 and CO_2 were 56.9% and 63.8%, respectively). On the other hand, the detected reforming activity increased slightly on small amounts of Rh-promoted Ni/α-Al_2O_3 catalysts, while it should be emphasized that the coke-formation rate decreased continuously to zero. It can be concluded that Rh and Ni exhibited synergetic effects in the promoted Ni/α-Al_2O_3 catalysts and possessed higher activity and lower coke deposition.

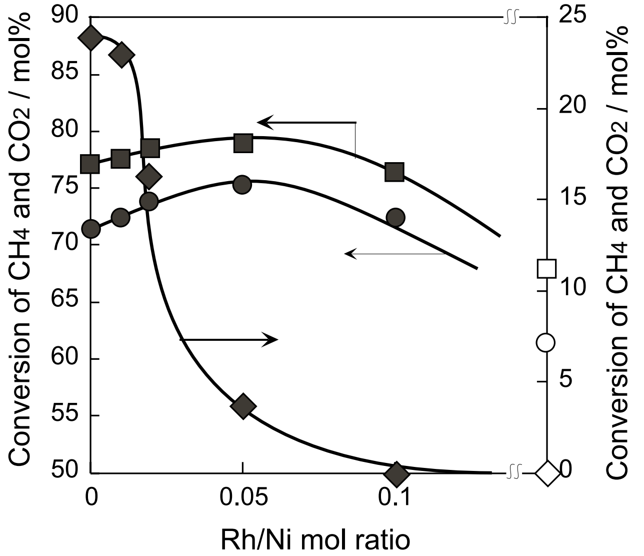

Figure 1. Activity of small amounts of Rh-promoted Ni/α-Al_2O_3 catalysts and Rh/α-Al_2O_3. (■, □) conversion of CO_2, (●, ○) conversion of CH_4 and (◆, ◇) coke-formation rate (mg-coke/g-cat · h). Open symbols are the activity of 5 wt% Rh/α-Al_2O_3. Reaction conditions: 800 °C, 1.0 atm, catalyst 50 mg, CH_4 25 mL/min (STP), CO_2 25 mL/min (STP) and 4 h on stream.

3.2. X-ray diffraction

Table 1 summarizes the XRD analysis results of the fresh, reduced and used catalysts. Besides α-Al_2O_3, only NiO was detected in fresh Ni/α-Al_2O_3 and Rh-promoted Ni/α-Al_2O_3 catalysts; NiO was reduced to metallic Ni after pretreatment in H_2. In pure Ni/α-Al_2O_3 catalyst, Ni existed in big particles and the sintering of Ni happened during the reforming reaction (as the detected Ni particles increased from 54.3 nm to 72.5 nm), while the detected Ni particle size of Rh-promoted Ni/α-Al_2O_3 catalysts in both reduced and used samples decreased continuously with the added amount of Rh. These results indicated that Rh would improve the dispersion of Ni and might retard the sintering of Ni during the reaction.

3.3. H_2-TPR

The reducibility of the pure Ni/α-Al_2O_3, Rh/α-Al_2O_3 catalysts and small amounts Rh-promoted Ni/α-Al_2O_3 catalysts were detected by 5% H_2 (He in balance) and shown in figure 2. Pure Ni/α-Al_2O_3 catalyst was reduced

Table 1
XRD analysis results of Rh-promoted Ni/α-Al_2O_3 catalysts

Catalysts	Crystalline phases[a]		Ni crystallize size (nm)[b]	
	Fresh	Reduced[c]	Reduced[c]	Used[d]
Ni/α-Al_2O_3	α-Al_2O_3 (+++), NiO (++)	α-Al_2O_3 (+++), Ni (++)	54.3	72.5
$Rh_{0.01}$Ni/α-Al_2O_3	α-Al_2O_3 (+++), NiO (++)	α-Al_2O_3 (+++), Ni (++)	43.8	48.3
$Rh_{0.02}$Ni/α-Al_2O_3	α-Al_2O_3 (+++), NiO (++)	α-Al_2O_3 (+++), Ni (++)	41.6	47.1
$Rh_{0.05}$Ni/α-Al_2O_3	α-Al_2O_3 (+++), NiO (++)	α-Al_2O_3 (+++), Ni (++)	36.4	36.6
$Rh_{0.1}$Ni/α-Al_2O_3	α-Al_2O_3 (+++), NiO (++)	α-Al_2O_3 (+++), Ni (++)	33.6	34.2
Rh/α-Al_2O_3	α-Al_2O_3 (+++), Rh_2O_3 (+), Rh_3O_4 (+)	α-Al_2O_3 (+++), Rh (+)	—	—

[a] Analysis conditions: 10–85°, at 1.5°/min, step 0.02°; (+) weak intensity; (++) medium intensity; (+++) strong intensity.
[b] Analysis conditions: 43–46°, at 0.1°/min, step 0.02°.
[c] Samples were reduced in H_2, 800 °C, 1 h.
[d] 240 min on stream.

mainly at 624 °C and pure Rh/α-Al_2O_3 catalyst was reduced at 198 °C with a shoulder peak at 215 °C. In Rh-promoted Ni/α-Al_2O_3 samples, mainly one reduction peak was detected and the reduction peak shifted continuously to lower temperature with the amount of Rh added. In $Rh_{0.1}$Ni/α-Al_2O_3, a small peak at 260 °C was detected. According to the published data [7,18–20] and the XRD analysis results, the peak at 624 °C was assigned as the reduction of NiO contacted with the support. The two peaks of Rh/α-Al_2O_3 were assigned as the reduction of mixed Rh_2O_3 and Rh_3O_4. In Rh-promoted Ni/α-Al_2O_3 catalysts, the decrease of reduction temperature was assigned as the highly dispersed Ni species. The small reduction peak at 260 °C in $Rh_{0.1}$Ni/α-Al_2O_3 inferred the strong interaction between Rh and Ni. These results confirmed that Rh increased the dispersion of Ni. The strong interaction between Rh and Ni might retard the sintering of Ni.

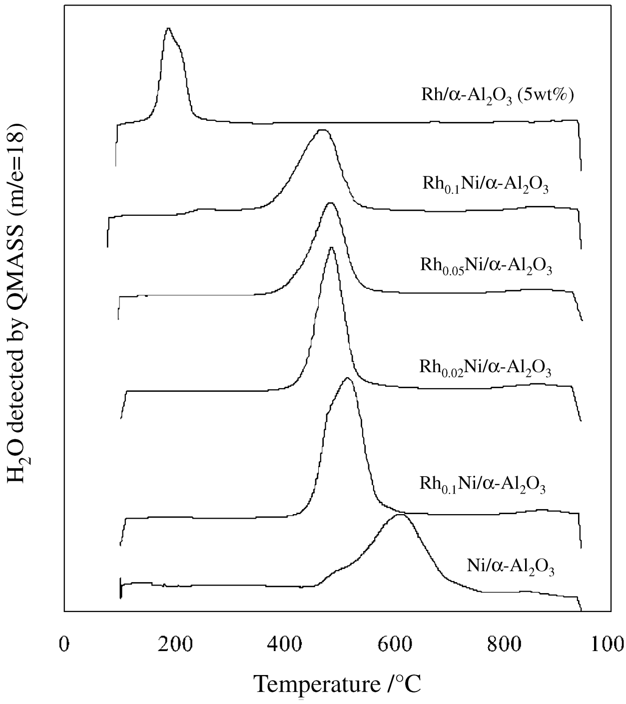

Figure 2. H_2-TPR profile of small amounts of Rh-promoted Ni/α-Al_2O_3 catalysts. Analysis conditions: catalyst 100 mg, 5% H_2 (He in balance, 50 mL/min) and 15 °C/ min.

3.4. CO_2-TPD

Figure 3 shows the CO_2-TPD analysis results of Ni/α-Al_2O_3, $Rh_{0.1}$Ni/α-Al_2O_3 and Rh/α-Al_2O_3, catalysts. It can be found that mainly one desorption peak of CO_2 below 500 °C was detected on the surface of pure Ni/α-Al_2O_3 catalyst, while another peak at 590 °C was detected on the surface of pure Rh/α-Al_2O_3 and $Rh_{0.1}$Ni/α-Al_2O_3 catalysts and the overall amount of CO_2 in effluent was higher than pure Ni/α-Al_2O_3 catalyst. It was confirmed that the detected CO_2 species above 500°C in effluent are from the desorption of dissociated adsorbed CO_2 (in the form of CO + O) [21]. This kind of adsorbed CO_2 species is stable and has

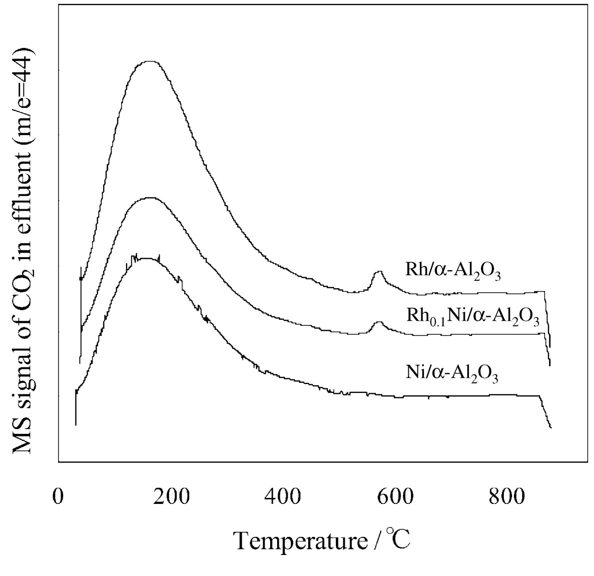

Figure 3. CO_2-TPD profile of Ni/α-Al_2O_3, $Rh_{0.1}$Ni/α-Al_2O_3 and Rh/α-Al_2O_3. Analysis conditions: catalyst 100 mg and 20 °C/ min.

enough lifetime in the reaction condition (800 °C) to react with the intermediate carbons formed from CH_4 dehydrogenation. These results indicated that Rh might improve the activation and dissociation of CO_2, which would supply enough oxygen species for the gasification of intermediate carbons.

3.5. *Coking reaction*

Coking reaction via CH_4 temperature-programmed decomposition of Ni/α-Al_2O_3, $Rh_{0.1}$Ni/α-Al_2O_3, and Rh/α-Al_2O_3 catalysts were carried out and the produced H_2 in effluent are summarized in figure 4. On pure Ni/α-Al_2O_3 catalyst, a small amount of H_2 was detected since 335 °C (owing to the chemical adsorption of CH_4), and a large amount of H_2 was produced after 425 °C (from the decomposition of CH_4). On pure Rh/α-Al_2O_3 catalyst, the chemical adsorption of CH_4 took place at 300 °C, while the decomposition of CH_4 took place at the same temperature as Ni/α-Al_2O_3 and only a small amount of H_2 was produced. But on the surface of $Rh_{0.1}$Ni/α-Al_2O_3, the chemical adsorption of CH_4 took place at 300 °C and the produced amount of H_2 was higher than both pure Ni/α-Al_2O_3 and Rh/α-Al_2O_3 catalysts. The increase of the reforming activity on $Rh_{0.1}$Ni/α-Al_2O_3 might be due to its higher activity of CH_4 decomposition. From the analysis results in XRD and H_2-TPR, the higher decomposition activity of the promoted sample would be caused by the highly dispersed Ni particles.

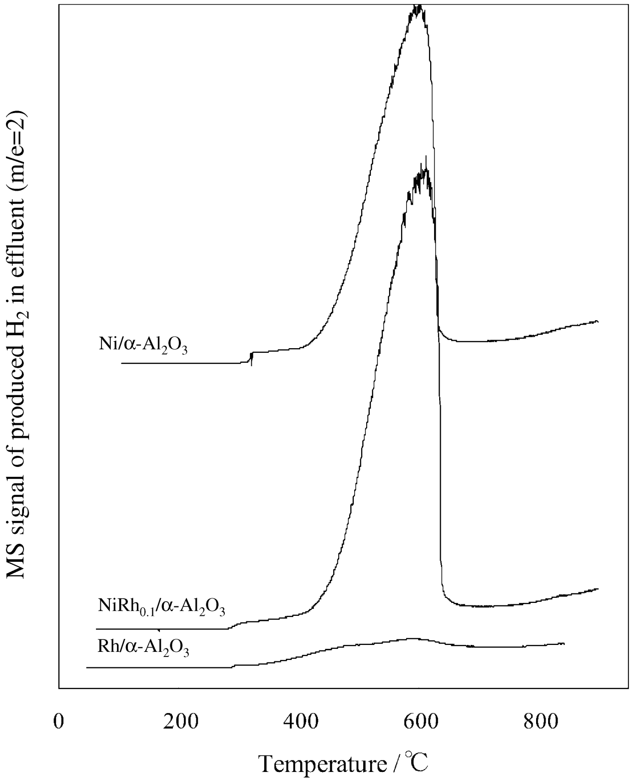

Figure 4. H_2 produced via CH_4 temperature-programmed decomposition on Ni/α-Al_2O_3, $Rh_{0.1}$Ni/α-Al_2O_3, and Rh/α-Al_2O_3. Analysis conditions: catalyst 100 mg and 10 °C/ min.

4. Conclusions

In methane reforming with CO_2, pure Ni/α-Al_2O_3 catalyst possesses a high activity, but it deactivates easily because of the coke deposition and/or metal sintering. Though pure Rh/α-Al_2O_3 has excellent coke resistance ability, its activity is low. Small amount of Rh-promoted Ni/α-Al_2O_3 combine the advantages of both Ni and Rh, and exhibit excellent performance for its higher activity and lower coke-formation rate. XRD and H_2-TPR characterization indicate that Rh improved the dispersion of Ni and the strong interaction between Rh and Ni retarded the sintering of Ni. CO_2-TPD confirms that small amounts of Rh-promoted Ni/α-Al_2O_3 catalysts (and pure Rh/α-Al_2O_3) possess excellent activation ability of CO_2 and the activated CO_2 can supply enough surface oxygen for the gasification of carbon. The low activity of pure Rh/α-Al_2O_3 catalyst is due to its poor activity for CH_4 decomposition.

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