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Bimetallic Rh–Ni/BN catalyst for methane reforming with CO_2

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ABSTRACT

The dry reforming of methane (CH_4) with carbon dioxide (CO_2) was carried out using bimetal (Rh–Ni)-loaded boron nitride (BN) and γ-Al_2O_3 catalysts. The incipient wetness method was used to load different ratios of Rh/Ni on BN and γ-Al_2O_3 supports. The metal particles were too small to be observed in the XRD indicating highly dispersed Rh–Ni particles on the supports. XPS results showed that, after H_2 reduction at 500 °C, Rh became metallic element while most Ni remained in its oxidized state. The addition of Rh increased the activity of dry reforming as well as the stability of the catalysts. In general, the conversions of CH_4 with CO_2 on Rh–Ni/BN catalysts were higher than those on Rh–Ni/γ-Al_2O_3 catalysts. The optimum ratio of Rh/Ni loading on BN was 0.01. The ratio of H_2 and CO as the products was near 0.7. The maximum conversions of CH_4 and CO_2 reached 72% and 81%, respectively, at 700 °C, while only slight deactivation was observed after 6 h of reaction time. Boron nitride has many unique properties, such as inertness and negligible metal-support interference, as compared with traditional oxide supports. Metal particles can migrate freely and easily to form Rh–Ni clusters on the BN surface. This may be the origin of the activity enhancement in dry reforming.

1. Introduction

Carbon dioxide is one of the major greenhouse gases that lead to global warming. Hydrogen is one of the best alternative energies. The reforming of CH_4 with CO_2 (also called dry reforming) provides an effective way to solve both problems, that is, CO_2 remediation and H_2 production. In this process, valuable syngas, H_2 and CO, can be obtained based on Eq. (1). Since this reaction is strongly endothermic, high temperature is quite favorable for the reaction. Despite this fact, high temperature may also have detrimental effect on the catalyst as well as the reaction because coke formation may occur during CH_4 cracking (Eq. (2)) and CO disproportionation (Eq. (3)) [1]. Furthermore, H_2 can also be consumed by CO_2 to form water and generate excess CO as shown in Eq. (4). Metal sintering is considered to be one of the major causes of catalyst deactivation in dry reforming because the reaction is usually carried out above 700 °C.

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad (1)$$

$$CH_4 \rightarrow 2H_2 + C \quad (2)$$

$$2CO \rightarrow CO_2 + C \quad (3)$$

$$H_2 + CO_2 \rightarrow H_2O + CO \quad (4)$$

Inui et al. performed CH_4 reforming with CO_2 to generate H_2 on Ni based catalysts at 700 °C and indicated that the precious metals, Rh and Pt, may enhance the reaction rate markedly. This synergistic effect is ascribed to H_2 spillover on the surface of the precious metals [2]. Loading of transition metals, such as Ru and Pd, also strongly improves the activity and stability of Ni based catalysts for CH_4 reforming with CO_2 [3]. The improved activity is attributed to the formation of Ni–Ru cluster with increasing Ni dispersion that causes the formation of reactive intermediate carbonaceous species. One difficulty of dry reforming is to achieve high CH_4 conversion and H_2 selectivity simultaneously. Traditionally, Ni catalyst is used in CH_4 reforming with CO_2 at temperature of above 700 °C [4]. Coke formation can be significantly reduced by Rh addition, which increases the stability of the catalysts. Jozwiak et al. reported that SiO_2 supported monometallic Ni, Rh and bimetallic Ni–Rh catalysts are comparably good catalysts for CH_4 reforming with CO_2 and Rh-rich catalysts are resistant to deactivation and carbon formation, resulting in high CH_4 conversion and H_2 selectivity [5–7].

Materials traditionally used as supports are insulating oxides such as SiO_2, γ-Al_2O_3, V_2O_5, TiO_2 and various zeolites. These oxides possess large surface area, numerous acidic/basic sites, and metal-support interaction that offer particular catalytic activity for many reactions. Metal oxides have also been thoroughly studied and employed in the chemical industry for decades. On the other hand, non-oxide materials, unlike metal oxides, possess many unique properties, such as high thermal conductivity, acid–base resistance, hydrophobicity and possibly negligible metal-support interaction. Boron nitride has been used as catalyst support recently [8,9]. The

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graphite-like hexagonal BN is the most stable BN isomer under ambient conditions [10]. In general, BN is inert for catalytic reaction. In a supported metal system such as Pt/BN, BN has been shown to have negligible interaction with Pt in the catalytic oxidation [8]. The migration of Pt particles occurred easily on the crystalline face of BN due to the weaker adhesion between the crystalline face and Pt [8,9]. Such effect may lead to the formation of bimetallic clusters. Our previous study indicated that Pt–Sn alloy on BN support significantly enhanced the oxidative dehydrogenation of propane with less coking [11]. The migration of a particular metal species to the surface will affect catalytic properties, such as adsorption, oxidation and reduction. The bimetallic clusters are favorable for dry reforming to reduce coking. Therefore, for the first time, CH_4 reforming with CO_2 is selected to explore the enhanced activity and selectivity toward H_2 generation by the bimetallic clusters on the unique BN support.

2. Experimental

2.1. Catalysts preparation

Hexagonal-BN was obtained from the High Performance Materials Inc. (Taiwan). It was crystallized at roughly 800 °C during synthesis, a temperature lower than the typical 1000 °C. Gamma alumina (γ-Al_2O_3), a commonly used oxide support, was obtained from Merck (USA) and used for comparison. Precursor salt, $Ni(NO_3)_2{\cdot}6H_2O$, with 20.18 wt% nickel (Ni) and pure $RhCl_3$ with 48.7 wt% rhodium (Rh) were purchased from Alfa Aesar (USA). Methanol was chosen as the diluting solvent for improved soaking of the hydrophobic BN support. The supported Rh–Ni catalysts were prepared by the co-incipient wetness method. The quantity of methanol required to completely fill the support's pore volume was predetermined. Calculated amounts of Rh and Ni precursor salts were dissolved in methanol to obtain the desired metal loading. After the co-incipient wetness process, catalysts were air-dried at room temperature for 48 h. These are referred to as fresh catalysts. The Rh loading was varied from 0.1 to 1 wt% and the Ni loading was varied from 1.0 to 10.0 wt%. The nomenclature of catalyst with X wt% Rh and Y wt% Ni on BN support was assigned as RhXNiY/BN. In addition, 1 wt% Rh/BN, 10 wt% Ni/BN and the counterparts in Rh–Ni/γ-Al_2O_3 were also prepared for comparison. The detailed incipient wetness procedure is described in literature [12].

2.2. Characterization

The specific surface area of the support was determined from N_2 adsorption measured by Micromeritics ASAP 2010. The particle sizes and distributions of BN and γ-Al_2O_3 were measured by laser-light scattering. γ-Al_2O_3 was suspended and dispersed ultrasonically in water for 3 min. BN was dispersed in ethanol due to its hydrophobicity. Coulter LS 230 was used to measure the scattering of incident light at the 90° position, thereafter the particle size was calculated using the Fraunhofer equation. Hydrogen chemisorption was measured by Micromeritics Autochem II. Fresh catalyst was reduced in 10% H_2/Ar flow at 500 °C for 1 h then cooled down to 50 °C under He purge before H_2 pulse chemisorption. Each pulse contained 0.05 ml of 10% H_2/Ar and the time between pulses was 3 min. The value of H_2 chemisorption was taken to determine Rh+Ni dispersion by assuming H:metal = 1.

A transmission electron microscope (TEM, Hitachi H-7100) was employed to observe the shape of BN and the appearance of metal particles dispersed on the support. The crystalline phases of catalysts were identified by X-ray diffraction (XRD). The XRD equipment, type M03XHF22 from the Material Analysis and Characterization Company, was operated at 40 kV, with a X-ray of 1.54056 Å in wavelength from a Cu target, and a scanning speed of 0.5°/min. X-ray photoelectron spectroscopy (XPS) was conducted on a spectrometer of VG Microtech MT500. The measured binding energy was referenced to carbon (1 s) at 285.6 eV.

2.3. Methane reforming with CO_2

Fresh catalyst (0.06 g) was charged in the middle of a straight-tube quartz reactor with a 10-mm ID. The catalyst was reduced for 1 h at 500 °C using pure hydrogen (99.999%) in the reactor. Subsequently, the temperature was increased to the reaction temperature under Ar purge before switching to the reactant mixture. In some cases, the fresh catalyst was calcined in air at 300 °C followed by the H_2 reduction as mentioned above. The reactant mixture was composed of pure CH_4 and CO_2. The CH_4/CO_2 mixture, with molar ratio maintained at one, was passed through the reactor at a total flow rate of 55 ml/min (WHSV = 60 l/(g-cat h)) under atmospheric pressure. The concentration of CH_4 and CO_2 in the reactant mixture was accurately adjusted by tuning the corresponding flow meter. The concentration was further confirmed by an on-line GC (Agilent GC6890) before reaction. The reaction temperatures were maintained at 600, 700 and 800 °C in a tubular furnace. A thermocouple was placed in the center of the catalyst bed to record the reaction temperature and to control the furnace. The reformate was analyzed by the on-line GC equipped with a 30 m Supelco Carboxen 1006 Plot capillary column using FID and TCD detectors in series.

The conversions of CH_4 and CO_2 as well as the yields of H_2 and CO were calculated using Eqs. (5)–(8) [13]. In order to estimate the amount of coke formed, the overall carbon balance was calculated based on the difference of input and output total hydrocarbons.

$$\mathrm{CH_4\ conversion\ (\%)} = \frac{\text{moles of } CH_4 \text{ converted}}{\text{moles of } CH_4 \text{ in feed}} \times 100 \quad (5)$$

$$\mathrm{CO_2\ conversion\ (\%)} = \frac{\text{moles of } CO_2 \text{ converted}}{\text{moles of } CO_2 \text{ in feed}} \times 100 \quad (6)$$

$$\mathrm{CO\ yield\ (\%)} = \frac{\text{moles of CO produced}}{\text{moles of } CH_4 \text{ in feed} + \text{moles of } CO_2 \text{ in feed}} \times 100 \quad (7)$$

$$\mathrm{H_2\ yield\ (\%)} = \frac{\text{moles of } H_2 \text{ produced}}{2 \text{ moles of } CH_4 \text{ in feed}} \times 100 \quad (8)$$

3. Results

3.1. Characteristics of catalysts

The specific surface areas of BN and γ-Al_2O_3 are 47.2 and 112.2 m^2/g, respectively. The mean particle size of BN and γ-Al_2O_3 were calculated to be 3.7 and 77.4 μm, respectively, from the measurement of laser-light scattering. Table 1 summarizes the results of H_2 chemisorption and metal dispersion of all catalysts. Since the chemisorption of Rh and Ni cannot be distinguished, all surface metals (M_{sur}), including Rh and Ni, are counted together. The metal dispersion, M_{sur}/M_{bulk}, is estimated from H_{ad}/M_{bulk} ratio assuming chemisorption stoichiometry H/M = 1 for both monometallic and bimetallic catalysts [5]. In general, the amount of H_2 chemisorbed on γ-Al_2O_3 catalyst is higher than that on BN catalyst, implying higher metal dispersion on γ-Al_2O_3 due to the nature of support. For the monometallic catalyst, the metal dispersion of Rh is much higher than that of Ni on γ-Al_2O_3 and BN supports. As compared with Ni catalyst, the amount of H_2 chemisorbed on Rh–Ni catalyst increased upon Rh addition. This suggests that the chemisorption of H_2 on Rh–Ni catalyst is attributed mostly to Rh because of the incomplete reduction of Ni by H_2 at 500 °C (see XPS in Fig. 5). Leclercq et al. reported that Ni could not be completely reduced at

Table 1
H_2 chemisorption and metal dispersion and particle size.

Catalyst	Hydrogen atom (ml/g)	Metal dispersion (%)
Ni10/BN	0.382	0.9
Rh0.1Ni10/BN	0.808	1.9
Rh0.1Ni1/BN	0.044	1.0
Rh1Ni1/BN	0.106	1.6
Rh1/BN	0.092	3.9
Ni10/γ-Al_2O_3	1.194	2.9
Rh0.1Ni10/γ-Al_2O_3	1.582	3.8
Rh0.1Ni1/γ-Al_2O_3	0.524	11.9
Rh1Ni1/γ-Al_2O_3	0.216	3.3
Rh1/γ-Al_2O_3	0.556	23.4

Reduced at 500 °C in H_2 before chemisorption, metal dispersion = hydrogen atom/loaded (Ni atom + Rh atom).

450 °C on Ni–Rh bimetallic catalysts and Ni hardly adsorbed hydrogen. In addition, they found the Ni surface enrichment on the Ni–Rh catalysts [14]. That is, Ni–Rh clusters could partially cover by Ni, which suppressed the H_2 chemisorption resulting in low metal dispersion in Table 1. In general, the dispersion of Rh and Ni metals on BN is lower than that on γ-Al_2O_3 because metals are easily migrated and sintered to form large metal particles on slippery BN surface during H_2 reduction.

Fig. 1 shows the XRD patterns of BN, Rh1/BN, Ni10/BN and series of RhNi/BN catalysts which were H_2 reduced at 500 °C. The diffraction pattern of Rh1/BN is similar to that of pure BN. The highest diffraction peak of Rh is at 41.1° which overlapped with that of BN. The diffraction peak of Rh at 47.8° can be barely observed on Rh1/BN. The major diffraction peaks of Ni at 44.5° and 51.8° can only be identified for high Ni loading catalysts, Ni10/BN and Rh0.1Ni10/BN. No diffraction peaks of Rh and Ni can be found in Rh1Ni1/BN and Rh0.1Ni1/BN implying that metal particles are very small. Fig. 2 shows the XRD patterns of γ-Al_2O_3, Rh1/γ-Al_2O_3, Ni10/γ-Al_2O_3 and series of Rh–Ni/γ-Al_2O_3 catalysts, which were H_2 reduced at 500 °C. They appear to be the same as the background diffraction pattern of γ-Al_2O_3 alone. Even the high Ni loading catalysts, Ni10/γ-Al_2O_3 and Rh0.1Ni10/γ-Al_2O_3, do not display the major Ni diffraction peaks located at 44.5° and 51.8°. The metal particles are too small to be observed from the XRD patterns, revealing highly dispersed Ni and Rh–Ni metal particles on the γ-Al_2O_3 support. Based on the results of H_2 chemisorption and XRD, these catalysts exhibit a wide distribution in metal particle size.

Fig. 3 shows the TEM images of Ni10/BN and Rh0.1Ni10/BN. Most metal particles with sizes <10 nm can be observed in Fig. 3(a), which indicates that most of the Ni particles are located on the edges

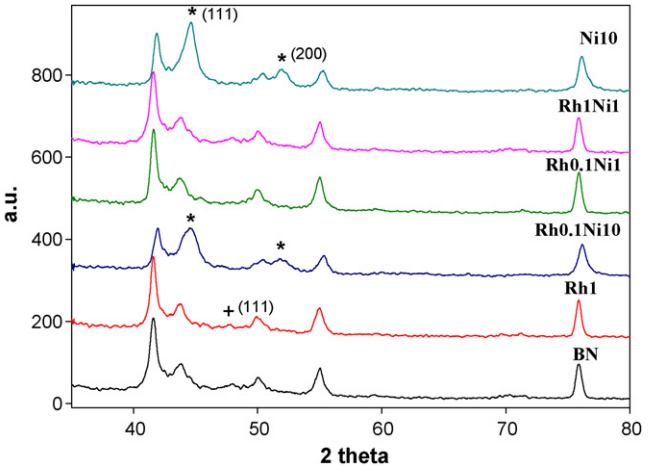

Fig. 1. XRD of BN, Rh1/BN, Ni10/BN and series of RhNi/BN, H_2 reduced at 500 °C for 1 h Ni(*) and Rh(+).

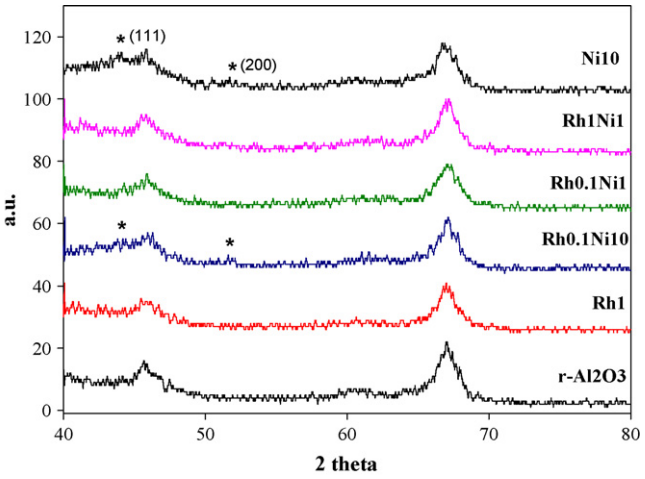

Fig. 2. XRD of γ-Al_2O_3, Rh/γ-Al_2O_3, Ni/γ-Al_2O_3 and RhNi/γ-Al_2O_3, H_2 reduced at 500 °C for 1 h Ni(*).

of BN particles. The metal particles <10 nm are also observed on Rh0.1Ni10/BN as shown in Fig. 3(b). However, Rh, Ni or Rh–Ni cluster cannot be distinguished from each other on the BN support.

The chemical status of Rh and Ni on the fresh and H_2 reduced Rh1Ni1/BN catalysts were investigated by XPS and shown in Figs. 4 and 5, respectively. As shown in Fig. 4, the binding energy of Rh $3d_{5/2}$ in H_2 reduced Rh1Ni1/BN is detected at 308.6 eV indicating metal Rh^0, whereas that in fresh Rh1Ni1/BN is located near 310.2 eV suggesting Rh^{3+} state as in the precursor $RhCl_3$ [15]. As shown in Fig. 5, the binding energy of Ni $3p_{1/2}$ in fresh Rh1Ni1/BN is at 873.0 eV indicating Ni^{2+} state as in the precursor $Ni(NO_3)_2$. After H_2 reduction at 500 °C, the binding energy of Ni $3p_{1/2}$ on Rh1Ni1/BN is slightly shifted to 872.5 eV indicating most of Ni remains as Ni^{2+} state on BN support [15]. Similar results are also found in the XPS of Rh–Ni/γ-Al_2O_3 (not shown). Thus after H_2 reduction at 500 °C, the surface Rh is mostly reduced but large portion of Ni^{2+} still remains oxidized. Based on the semi-quantitative XPS analysis, the molar ratio of Ni/Rh after H_2 reduction is twice as much as that before H_2 reduction, suggesting Rh^0 could be partially covered by Ni^{2+} on Rh–Ni/BN catalyst.

3.2. Methane reforming with CO_2

Various pretreatment procedures were investigated based on CH_4 conversions and H_2 yields of the catalysts performed in the temperature range between 600 and 800 °C. Catalysts were either calcined in air at 300, 400 and 500 °C, or reduced with hydrogen at temperature ranging from 300 to 500 °C. In summary of experimental results, the conversion of CH_4 and CO_2 increased from 20% to 80% and 25% to 92%, respectively, as the temperature was varied from 600 to 800 °C, while H_2 yield changed from less than 5% up to 65% depending on the reaction conditions. Although CH_4 conversion of higher than 80% can be reached at 800 °C, CO_2 conversion was decreased due to coke formation according to Eq. (3). Meanwhile, H_2 yield was significantly reduced to 35% because hydrogen is oxidized by CO_2 to produce water (Eq. (4)). In conclusion, the optimal temperature of calcination and H_2 reduction is found to be at 300 and 500 °C, respectively. The highest H_2 yield is found to be at reaction temperature of 700 °C, which gives a H_2/CO ratio of near 0.7. Accordingly, a reaction temperature of 700 °C was selected for the detailed study of the catalysts.

Table 2 summarizes the overall performances, including CH_4 conversion, H_2 and CO yields, of catalysts initially (0 h) and at 6-h period under reaction temperature of 700 °C. The stability of catalysts is defined as the percentage change of 6-h and initial

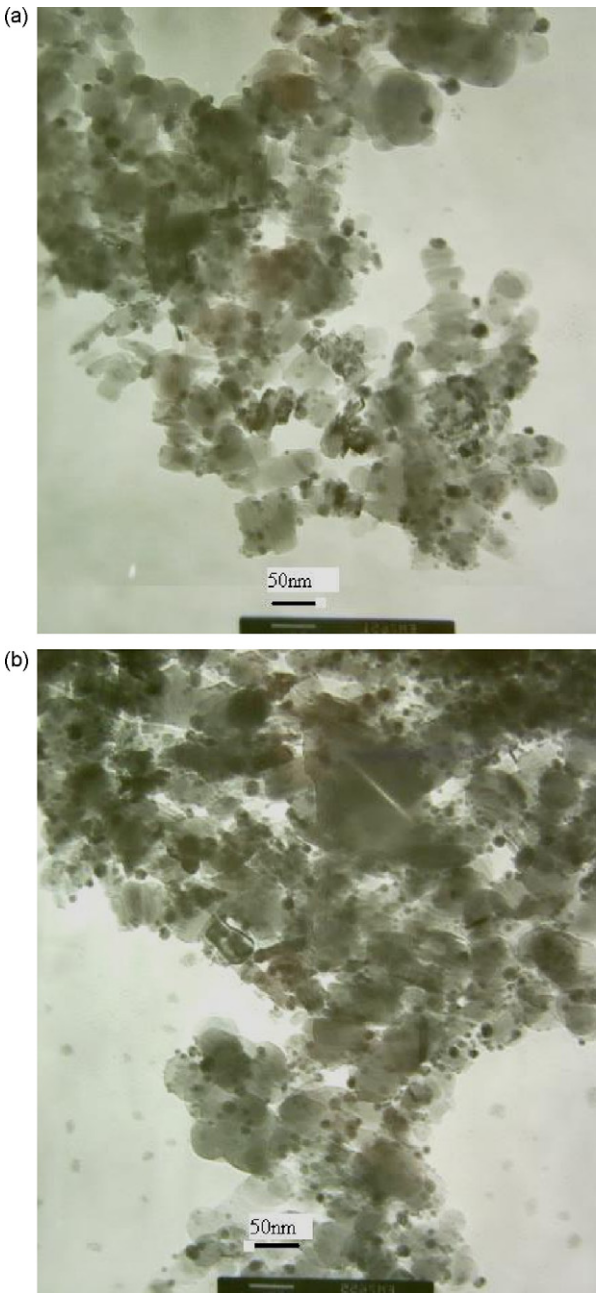

Fig. 3. TEM of (a) Ni10/BN and (b) Rh0.1Ni10/BN.

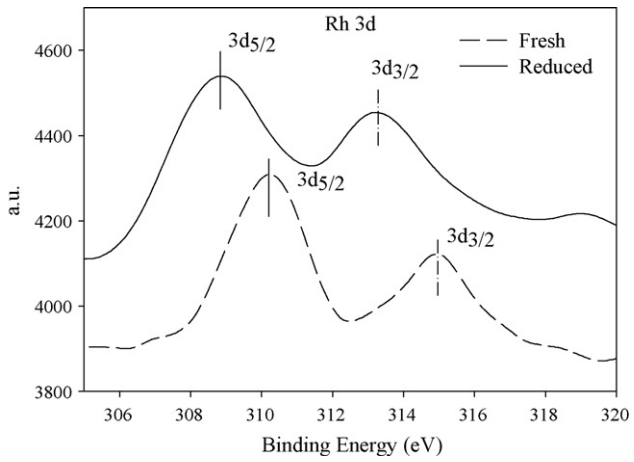

Fig. 4. XPS of Rh 3d on Rh1Ni1/BN.

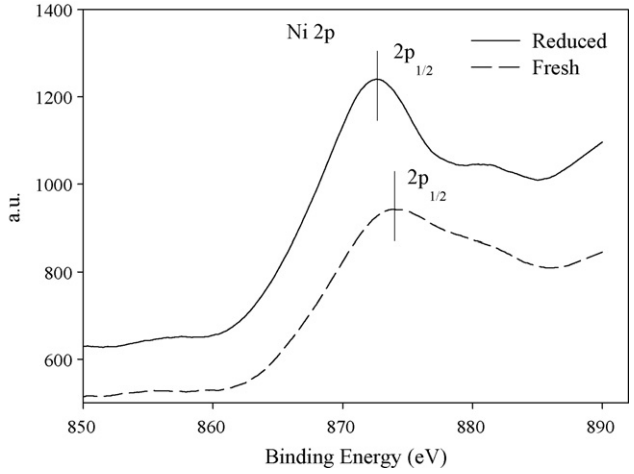

Fig. 5. XPS of Ni 2p on Rh1Ni1/BN.

methane conversions [6]. The number of stability implies the activity variation of catalysts in dry reforming. These catalysts were H_2 reduced at 500 °C prior to reaction. It is noted that Rh/BN and Rh/γ-Al_2O_3 give the lowest CH_4 conversion as expected because Rh is not a reforming catalyst. The CH_4 conversion of Ni10/BN and Ni10/γ-Al_2O_3 are almost the same (~50%) initially. However, deactivation of Ni10/BN is more significant than that of Ni10/γ-Al_2O_3. The CH_4 conversion is either increased or decreased with Rh addition on bimetallic Rh–Ni catalysts. For Rh–Ni/γ-Al_2O_3, a negative effect on CH_4 conversion is found. The CH_4 conversion decreases with

Table 2
Summary of CH_4 reforming with CO_2 on Rh–Ni catalysts at 700 °C.

Catalyst[a] (%)	CH_4 conversion (%)		CO_2 conversion (%)		H_2 yield (%)		CO yield (%)		Stability[b] (%)
	0 h	6 h	0 h	6 h	0 h	6 h	0 h	6 h	
Rh1/BN	27.6	9.5	32.0	9.2	17.9	4.2	31.6	5.3	−65.6
Rh1Ni1/BN	42.1	42.4	65.3	50.9	38.9	26.9	76.7	51.4	0.7
Rh0.1Ni1/BN	36.9	32.0	61.2	49.2	53.9	32.1	74.3	57.9	−13.3
Rh0.1Ni10/BN	70.4	49.6	81.0	62.4	60.2	55.5	78.4	71.0	−29.5
Ni10/BN	50.6	29.7	60.7	44.1	40.3	12.2	52.2	37.0	−41.3
Rh1/γ-Al_2O_3	2.5	0.9	7.6	0.5	8.7	0.6	16.0	1.1	−64.0
Rh1Ni1/γ-Al_2O_3	45.0	36.1	60.3	48.2	38.9	31.8	72.0	58.8	−19.8
Rh0.1Ni1/γ-Al_2O_3	27.6	2.3	39.6	4.2	53.2	8.6	51.7	9.4	−91.7
Rh0.1Ni10/γ-Al_2O_3	47.9	44.1	66.0	61.1	42.3	36.1	76.3	68.7	−7.9
Ni10/γ-Al_2O_3	51.8	47.0	70.0	62.0	42.3	30.5	76.9	65.8	−9.3

[a] Catalysts were H_2 reduced at 500 °C for 1 h before reaction.
[b] Defined as (6-h conv. of CH_4 − initial conv. of CH_4)/initial conv. of CH_4 × 100%.

Table 3
Summary of CH_4 reforming with CO_2 on calcined Rh–Ni catalysts at 700 °C.

Catalyst[a] (%)	CH_4 conversion (%)		CO_2 conversion (%)		H_2 yield (%)		CO yield (%)		Stability[b] (%)
	0 h	6 h	0 h	6 h	0 h	6 h	0 h	6 h	
Rh1/BN	11.5	2.2	22.8	6.6	27.8	5.8	37.2	9.9	−80.9
Rh1Ni1/BN	42.8	38.3	63.6	59.0	64.0	40.4	78.0	71.6	−10.5
Rh0.1Ni1/BN	65.0	42.2	68.2	51.9	59.4	48.2	68.8	52.6	−35.1
Rh0.1Ni10/BN	72.4	68.9	88.3	86.0	62.2	61.1	88.1	81.4	−4.8
Ni10/BN	55.9	29.7	56.4	28.5	42.4	40.7	55.0	31.8	−46.9
Rh1/γ−Al_2O_3	0.1	0.6	0.9	1.4	1.0	0.0	3.8	0.7	500.0
Rh1Ni1/γ-Al_2O_3	44.4	33.0	58.3	42.7	38.6	26.1	69.5	51.2	−25.7
Rh0.1Ni1/γ-Al_2O_3	21.5	4.2	26.6	7.6	13.8	2.4	18.5	2.8	−80.5
Rh0.1Ni10/γ-Al_2O_3	53.6	55.2	74.0	78.0	66.0	51.1	76.0	85.4	3.0
Ni10/γ-Al_2O_3	46.5	42.9	61.8	57.4	57.7	29.2	76.3	70.1	−7.7

[a] Catalysts were calcined at 300 °C for 2 h followed by H_2 reduction at 500 °C for 1 h.
[b] Defined as (6-h conv. of CH_4 − initial conv. of CH_4)/initial conv. of CH_4 × 100%.

various Rh/Ni ratios. However, it is substantially increased to 70.4% on Rh0.1Ni10/BN while other Rh–Ni/BN catalysts show less CH_4 conversion than that of Ni10/BN. Furthermore, H_2 and CO yields of Rh0.1Ni10/BN are also the highest among all catalysts. As compared with monometallic Ni/BN catalyst, both CH_4 conversion and H_2 yield of Rh0.1Ni10/BN are significantly improved concurrently.

Table 3 summarizes the overall performances of catalysts performed under the same condition as described earlier in Table 2 with the exception of the pretreatment procedure. A calcination step was applied to the catalysts in air at 300 °C prior to H_2 reduction at 500 °C. It appears that the initial CH_4 conversions of bimetallic Rh–Ni catalysts in Table 3 are higher than those in Table 2, except Rh0.1Ni1/γ-Al_2O_3. Similarly, H_2 yields in Table 3 are also higher than those in Table 2, with the exception of Rh0.1Ni1/γ-Al_2O_3. The performance of Rh-containing monometallic catalyst is the worst among other monometallic catalysts shown in Tables 2 and 3. The performances of Ni10/BN and Ni10/γ-Al_2O_3 are worse than those of Rh–Ni/BN and Rh–Ni/γ-Al_2O_3, respectively. To sum up the results listed in Tables 2 and 3, the calcination pretreatment procedure of fresh catalyst at 300 °C followed by H_2 reduction at 500 °C can improve both the activity and stability of bimetallic Rh–Ni catalysts.

The stability of a catalyst is the percentage change of CH_4 conversions during dry reforming in 6 h. As shown in Tables 2 and 3, bimetallic catalysts are more stable than monometallic Ni catalysts on BN support. The major cause of deactivation in catalyst is due to coke formation. The degree of coking can be deduced from the rate of carbon deposition, which is estimated by the carbon balance. Table 4 lists the carbon balances of all catalysts during 6-h reforming. A negative carbon balance means that carbon is deposited on the catalyst. The coking is more severe initially because CH_4 is decomposed rapidly by some highly active sites on the fresh catalyst (Eq. (2)). Less coking is found on Rh–Ni catalysts as compared with Ni catalysts. After 6 h of reaction, the coke formation on Rh–Ni/BN catalysts is slightly less than that on Rh–Ni/γ-Al_2O_3 catalysts.

Table 4
Carbon balances for CH_4 reforming with CO_2 on various catalysts at 700 °C.

Catalyst	Initial (0 h) (%)[a]	Final (6 h) (%)[a]
Rh1/BN	−5.32	−3.57
Rh1Ni1/BN	−9.83	−4.53
Rh0.1Ni1/BN	−9.32	−5.44
Rh0.1Ni10/BN	−13.74	−5.87
Ni10/BN	−15.50	−7.03
Rh1/γ-Al_2O_3	−2.44	−3.14
Rh1Ni1/γ-Al_2O_3	−8.13	−5.45
Rh0.1Ni1/γ-Al_2O_3	−13.31	−5.74
Rh0.1Ni10/γ-Al_2O_3	−14.01	−8.33
Ni10/γ-Al_2O_3	−16.11	−9.12

[a] (moles of carbon output − moles of carbon input)/(moles of carbon input) × 100%.

Fig. 6 shows the dependency of CH_4 conversion on reaction time for Rh1, Ni10 and Rh–Ni/BN catalysts performed at 700 °C. The pretreatment of the catalysts is the same as that described for Table 3. It is obvious that the conversions are gradually decreased during the 6-h reaction period. Among the catalysts

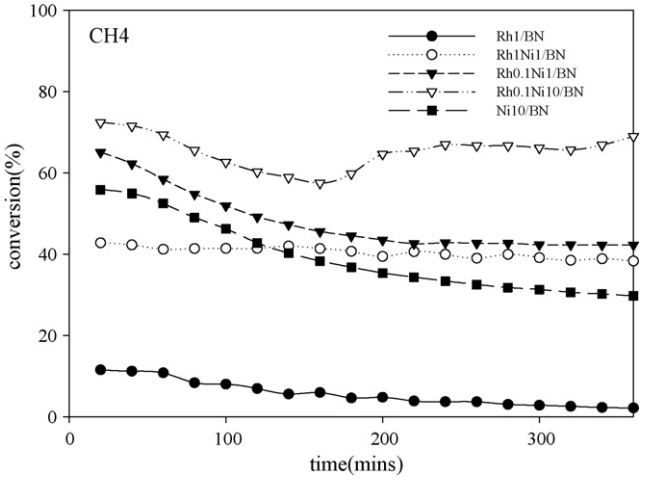

Fig. 6. CH_4 conversions of dry reforming on Ni and Ni–Rh catalysts at 700 °C. (Catalysts were calcined in air at 300 °C, then H_2 reduced at 500 °C, weight = 0.06 g, pressure = 1 atm, total flow rate = 55 ml/min, CH_4/CO_2 = 1/1.)

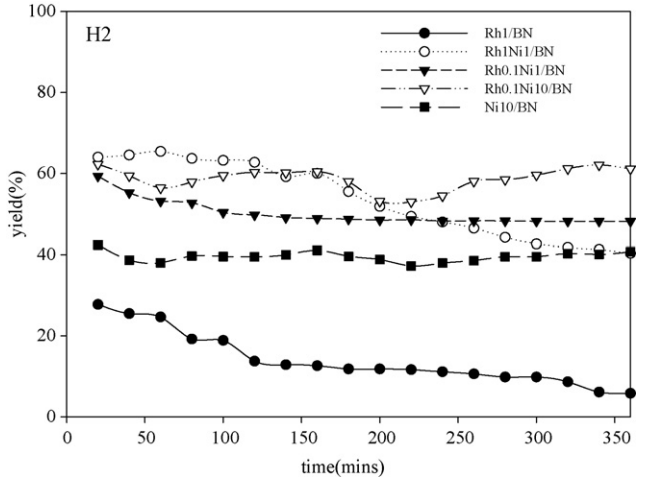

Fig. 7. H_2 yields of dry reforming on Ni and Ni–Rh catalysts at 700 °C. (Catalysts were calcined in air at 300 °C, then H_2 reduced at 500 °C, weight = 0.06 g, pressure = 1 atm, total flow rate = 55 ml/min, CH_4/CO_2 = 1/1.)

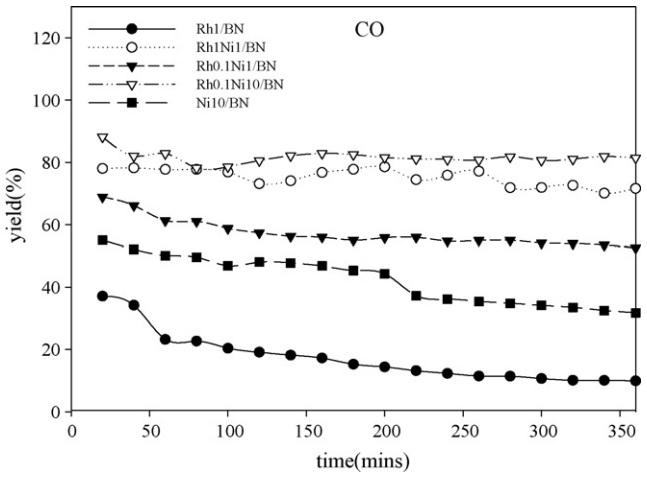

Fig. 8. CO yields of dry reforming on Ni and Ni–Rh catalysts at 700 °C. (Catalysts were calcined in air at 300°C, then H_2 reduced at 500 °C, weight = 0.06 g, pressure = 1 atm, total flow rate = 55 ml/min, CH_4/CO_2 = 1/1.)

tested, Rh0.1Ni10/BN gives the highest CH_4 conversion and H_2 yield, which is also higher than its counterpart, Rh0.1Ni1/γ-Al_2O_3 (not shown). The plots of H_2 and CO yields versus time for catalysts (Rh1/BN, Ni10/BN and Rh–Ni/BN) performed at 700 °C are shown in Figs. 7 and 8, respectively. Clearly, the H_2 and CO yields of monometallic Rh1/BN and Ni10/BN catalysts are lower than those of bimetallic Rh–Ni/BN catalysts. Compared with various Rh and Ni loadings on Rh–Ni/BN catalysts, Rh0.1Ni10/BN gives the highest H_2 and CO yields. The H_2 and CO yields reach 62% and 88% initially, followed by a slight decrease to 61% and 81%, respectively, with some fluctuations.

The effects of catalyst regeneration on the catalytic performance in terms of CH_4 conversion for Rh0.1Ni10/BN and Rh0.1Ni10/γ-Al_2O_3 are illustrated in Fig. 9. In the regeneration process, the catalysts were calcined again at 300 °C to remove carbon deposit after the first 6-h run. Despite the fact that the conversions of CH_4 in the second run have declined for both catalysts, the activity of Rh0.1Ni10/BN still outperformed that of Rh0.1Ni10/γ-Al_2O_3. Moreover, the degree of deactivation for Rh0.1Ni10/BN is less than that for Rh0.1Ni10/γ-Al_2O_3, indicating that the regeneration process under air is more effective for BN support.

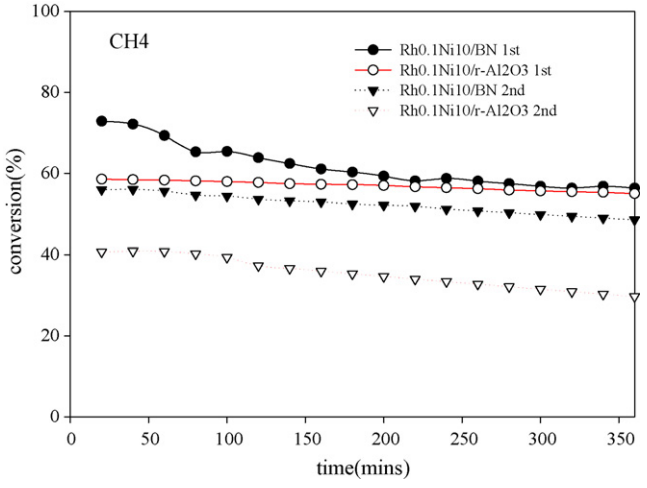

Fig. 9. CH_4 conversions of dry reforming in the regeneration test on Rh0.1Ni1/BN and Rh0.1Ni1/γ-Al_2O_3 at 700 °C. (Catalysts were calcined in air at 300 °C, then H_2 reduced at 500 °C; after first run, catalysts were calcined again in air at 300 °C for 2 h in the reactor, weight = 0.06 g, pressure = 1 atm, total flow rate = 55 ml/min, CH_4/CO_2 = 1/1.)

4. Discussion

Rhodium plays a major role in the reduction of coke and the enhancement of H_2 yield. Hydrogen spillover on Rh is believed to suppress coke formation from CO (Eq. (3)) as well as the hydrogenation of CO_2 (Eq. (4)) [2]. The synergistic effect of bimetallic catalyst can increase CH_4 conversion as well as H_2 yield in dry reforming, which is evidenced by the performance of both Rh–Ni/BN and Rh–Ni/γ-Al_2O_3 catalysts. The stability of bimetallic Rh–Ni catalyst was improved due to less coke formation as compared with that of monometallic Ni catalyst [5].

Besides the Rh effect, support can also be an important factor affecting the activity in CH_4 dry reforming. By and large, the stabilities of Rh–Ni/BN catalysts are close to those of Rh–Ni/γ-Al_2O_3 catalysts as shown in Tables 2 and 3. However, CH_4 conversions and H_2 yields are substantially enhanced on Rh–Ni/BN catalysts as compared with Rh–Ni/γ-Al_2O_3 catalysts, even though the metal dispersion on BN is less than that on γ-Al_2O_3 (Table 1). Boron nitride provides an inert and slippery surface that facilitates the formation of Rh–Ni cluster during H_2 reduction at 500 °C due to the unrestrained migration of metals. On the other hand, γ-Al_2O_3 usually constrains the mobility of Rh and Ni during H_2 reduction owing to the metal-support affinity, thus separating Rh and Ni particles. For this reason, Rh–Ni clusters are much easily formed on BN surface. The Rh–Ni cluster on BN surface is composed of Rh^0 particle partially covered with Ni^{2+} (Table 1, Figs. 4 and 5). Therefore, Ni^{2+} on BN may become more active in CH_4 activation than that on γ-Al_2O_3, which is suggested to be the origin of the activity enhancement in CH_4 dry reforming. In addition, the neutral BN surface is favorable to CH_4 dry reforming. Our previous study indicated that acidic site on BN is much less than that on γ-Al_2O_3 [9]. Coke formation is less severe on the BN surface resulting in higher activity as compared with γ-Al_2O_3 for long-term reaction.

5. Conclusion

This study has presented favorable findings for the dry reforming of CH_4 with CO_2 into H_2 and CO by employing BN-supported Rh–Ni catalysts. Compared with the traditional γ-Al_2O_3 support, BN exhibits a unique property of minimum metal-support interference thus facilitates the formation of Rh–Ni clusters during H_2 reduction. The yield of H_2 is improved without sacrificing the conversion of CH_4. Coke formation is slightly reduced on BN due to the lack of acidic sites. Therefore, BN offers a promising support for dry reforming catalyst.

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References

[1] J.R. Rostrupnielsen, J.H.B. Hansen, J. Catal. 144 (1993) 38–49.
[2] T. Inui, K. Saigo, Y. Fujii, K. Fujioka, Catal. Today 26 (1995) 295–302.
[3] C. Crisafulli, S. Scire, R. Maggiore, S. Minico, S. Galvagno, Catal. Lett. 59 (1999) 21–26.
[4] X.E. Verykios, Int. J. Hydrogen Energy 28 (2003) 1045–1063.
[5] W.K. Jozwiak, M. Nowosielska, J. Rynkowski, Appl. Catal. A: Gen. 280 (2005) 233–244.
[6] Z. Hou, P. Chen, H. Fang, X. Zheng, T. Yashima, Int. J. Hydrogen Energy 31 (2006) 555–561.
[7] Z.Y. Hou, T. Yashima, Catal. Lett. 89 (2003) 193–197.
[8] C.-A. Lin, J.C.S. Wu, J.-W. Pan, C.-T. Yeh, J. Catal. 210 (2002) 39–45.
[9] J.C.S. Wu, Y.C. Fan, C.A. Lin, Ind. Eng. Chem. Res. 42 (2003) 3225–3229.
[10] S. Alkoy, C. Toy, T. Gonul, A. Tekin, J. Eur. Ceram. Soc. 17 (1997) 1415–1422.

[11] J.C.S. Wu, S.-J. Lin, Chem. Eng. J. 140 (2008) 391–397.
[12] J.C.S. Wu, Z.-A. Lin, J.-W. Pan, M.-H. Rei, Appl. Catal. A: Gen. 219 (2001) 117–124.
[13] N. Sahli, C. Petit, A.C. Roger, A. Kiennemann, S. Libs, M.M. Bettahar, Catal. Today 113 (2006) 187–193.
[14] G. Leclercq, S. Pietrzyk, L. Gengembre, L. Leclercq, Appl. Catal. 27 (1986) 299–312.
[15] J.F. Moulder, J. Chastain, R.C. King, Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data, Physical Electronics, Eden Prairie, MN, 1995.