

Elucidation of the Influence of Ni-Co Catalytic Properties on Dry Methane Reforming Performance

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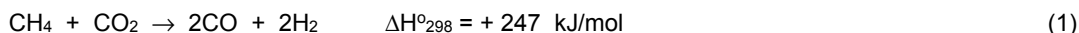
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Carbon deposition is a major problem of dry methane reforming (DMR) over Ni-based catalyst. Recently, Ni-Co bimetallic catalyst has shown the improvement of carbon resistance of Ni-based catalyst. The objective of this work is to study the influence of properties of Ni-Co catalysts on its DMR performance, as well as the influence of Ni-Co alloy formation in Ni-Co catalyst. In this work, Al-Mg mixed oxide (Al-Mg-O) was prepared by sol-gel method. Catalyst samples; 10 wt% Ni/Al-Mg-O (Ni/MA), 10 wt% Co/Al-Mg-O (Co/MA) and 5 wt% Ni-5 wt% Co/Al-Mg-O (Ni-Co/MA), were prepared by incipient wetness impregnation method. All catalysts were characterized by H₂-TPR, H₂-TPD and TPH. The results indicate that Ni-Co/MA provides excellent reducibility with strong metal support interaction (SMSI) as compared with monometallic catalysts. The bimetallic catalyst also exhibits better metal dispersion. Ni-Co/MA shows highest performance of CO₂ adsorption. TPH profiles of spent catalysts from CH₄-decomposition and CO₂-decomposition reveal that Ni-Co/MA can suppress coking from both decomposition reactions, whereas TPH profiles of Ni/MA and Co/MA show the hydrogenation of carbon deposition from CH₄-decomposition and CO₂-decomposition. DMR tests over catalyst samples were carried out at 620 °C under atmospheric pressure with the flow of CH₄:CO₂:N₂ mixture after the reduction at 620 °C for 12 h. The H₂/CO ratio of DMR over Ni-Co/MA is 0.94 which is close to stoichiometry ratio (unity) without the occurrence of carbon deposition. This result can be attributed to the high CO₂ adsorption performance with excellent carbon resistance. The effect of Ni-Co alloy formation of Ni-Co/MA on DMR was investigated when Ni-Co/MA was reduced at higher temperature (800 °C). It was found that increasing in the degree of alloy formation between Ni-Co improves the selectivity of the catalyst which shows H₂/CO ratio of almost unity.

1. Introduction

It is important to develop alternative high quality liquid fuels to replace fossil fuels because of the oil crisis. Gas to liquid (GTL) is a process to convert natural gas into liquid fuel product. This process begins with a reforming of natural gas in order to produce syngas (CO + H₂) which is a reactant of the following Fischer-Tropsch synthesis (FTS). In FTS, syngas is polymerized on solid catalysts to yield a wide range of synthetic hydrocarbon. Because CH₄ is the major component of natural gas, the natural gas reforming is the conversion of CH₄ to syngas. Among various reforming techniques, dry methane reforming (DMR) that is expressed in Eq.(1) has lowest operating cost and helps to decrease CO₂, an abundant greenhouse gas, in atmosphere (Ross 2005). The conventional catalyst for DMR is Ni-based catalysts. However, the deactivation of Ni-based catalysts due to the carbon formation and loss of active site has to be suppressed. Three pathways to prevent these deactivation problems include (i) improving redox properties and oxygen mobility by the use of different metal oxide support (ii) increasing the basicity of catalyst by the addition of alkali metal promoter (iii)

generating a special structure or electronic effect by the alloy formation of bimetallic catalysts (Djinovic et al., 2012)



The work focuses on the influence of the Ni-Co catalyst properties on catalytic performance with an attempt to resist carbon deposition for DMR. The influence of alloy formation on DMR performance of Ni-Co catalyst is also discussed.

2. Experimental

2.1 Catalyst preparation

Catalyst samples in this work consist of 10 wt% Ni/Al-Mg mixed oxide (Ni/MA), 10 wt% Co/Al-Mg mixed oxide (Co/MA) and 5 wt% Ni- 5 wt% Co/Al-Mg mixed oxide (Ni-Co/MA). Al-Mg mixed oxide support (MA) was firstly prepared by sol-gel method. The resulting material was dried at 45 °C for 24 h and calcined at 800 °C for 6 h. The metal supported catalysts were prepared by incipient wetness impregnation method. Appropriate amount of aqueous solution of nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) or cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) or mixed metal nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dropped onto MA support. After the impregnating products were dried at 45 °C for 24 h, the catalysts were also calcined at 650 °C for 5 h and pelletized in a sequence.

2.2 Catalyst characterization

The reducibility of catalysts was studied using temperature programmed reduction of hydrogen (H_2 -TPR) in a conventional TPR set-up with a stainless steel tubular reactor. The fresh catalysts (200 mg) were cleaned in the flow of argon at 220 °C for 2 h. Then, catalysts were cooled to ambient temperature. The flow of argon was replaced by the flow of reducing gas (5 % H_2/Ar) and the temperature was increased from room temperature to 900 °C at a rate of 10 °C/min. The hydrogen consumption was measured by a gas chromatograph (Agilent Technologies, 6820 GC system) equipped with a thermal conductivity detector (TCD). The active metal dispersion on the catalysts surface was analyzed by temperature programmed desorption of hydrogen (H_2 -TPD) in the same reactor set-up used for TPR analysis. The reactor was charged with 200 mg of samples. After reduction in hydrogen flow at 620 °C for 2 h, the samples were cooled to room temperature in argon flow and isothermal hydrogen adsorption was taken for 0.5 h at room temperature. The surface of samples was purged with the flow of argon for 0.5 h. The catalysts were then heated to 900 °C at the rate of 10 °C/min. The similar procedure was used for temperature programmed desorption of carbon dioxide (CO_2 -TPD) in order to investigate the performance of CO_2 adsorption for all catalysts.

The carbon resistance of catalyst according to CH_4 decomposition (or CO_2 decomposition) was evaluated by temperature programmed hydrogenation (TPH) in the same device as was used for TPR analysis. Prior to the experiment, the as-prepared catalysts were reduced in hydrogen flow at 620 °C for 2 h followed by purging with helium flow for 0.5 h. Isothermal CH_4 decomposition (or CO_2 decomposition) was then conducted at 620 °C for 1 h. The catalysts were cooled in helium flow to room temperature after decomposition reaction. To compare the amount and to analyze the species of carbon deposition, the samples were hydrogenated when they were heated from room temperature to 900 °C at a rate of 10 °C/min in the flow of hydrogen. The signal corresponding to CH_4 formation during the hydrogenation of carbonaceous material on the catalysts was recorded.

2.3 Catalyst testing

The fixed-bed stainless steel reactor was loaded with 200 mg of catalysts. The catalysts were reduced *in situ* with H_2 at 620 °C for 12 h. Then, the DMR tests were carried out under atmospheric pressure at 620 °C for 6 h with a total feed flow rate of 60 mL/min (CH_4 : CO_2 : N_2 = 3:5:4). The composition of outlet gas was analyzed using an on-line gas chromatograph (Agilent GC7890A) equipped with TCD. To investigate the influence of alloy formation on DMR performance, the similar procedure was used with different reduction temperature (620 °C for 8 h followed by 800 °C for 4 h at the heating rate of 10 °C/min).

3. Results and discussion

3.1 Catalyst characterization

The H_2 -TPR profiles are displayed in Figure 1. Three reduction peaks were observed in Ni/MA catalyst. The H_2 -uptake corresponding to the first peak (150 - 350 °C) is attributed to the reduction of NiO located on MA surface and the second peak (370 - 500 °C) can be ascribed to the reduction of NiO having an interaction with MA. The third reduction peak (> 600) is caused by the reduction of Ni^{2+} in spinel phase, the form of strong metal-support interaction (SMSI) (Li et al., 2010). The H_2 -TPR profiles of Co/MA also present three reduction peaks. The first peak (250 - 460 °C) and second peak (450 - 650 °C) can be attributed to the multi step reduction of Co_3O_4 ($\text{Co}_3\text{O}_4 \rightarrow \text{CoO} \rightarrow \text{Co}^0$). The reduction of Co species in spinel structure takes place at

the temperature higher than 650 °C (Hong et al., 2009). For Ni-Co/MA catalyst, the shoulder on its TPR profile at low temperature can be associated with the reduction of Ni or Co from metal oxide. The almost one stage reduction with a broad peak can be associated with the formation of Ni-Co alloy during the reduction (Zhang et al., 2008 and Lin et al., 2011). Compared with monometallic catalysts, bimetallic catalyst presents more hydrogen consumption and greater reduction peak ending at higher temperature. The results indicate that Ni-Co/MA provides a greater metal dispersion due to the formation of alloy and SMSI. The better dispersion of bimetallic catalyst can be confirmed by H₂-TPD results, displayed in Figure 2. A larger amount of hydrogen is desorbed from the surface of bimetallic catalyst compared with those of monometallic catalyst. The CO₂-TPD profiles are presented in Figure 3. Ni/MA catalyst has a small broad desorption peak, which corresponds to a low CO₂ adsorption performance as well as a less number of basic sites. A significant desorption peak (80 - 480 °C) was observed for Co/MA and Ni-Co/MA catalyst. This peak is caused by low-to-medium strength basic sites. As seen in Figure 3, Ni-Co/MA provides higher number of basic sites compared with Co/MA. Accordingly, the basic site strength and CO₂ adsorption performance can be arranged in the following order: Ni-Co/MA > Co/MA > Ni/MA.

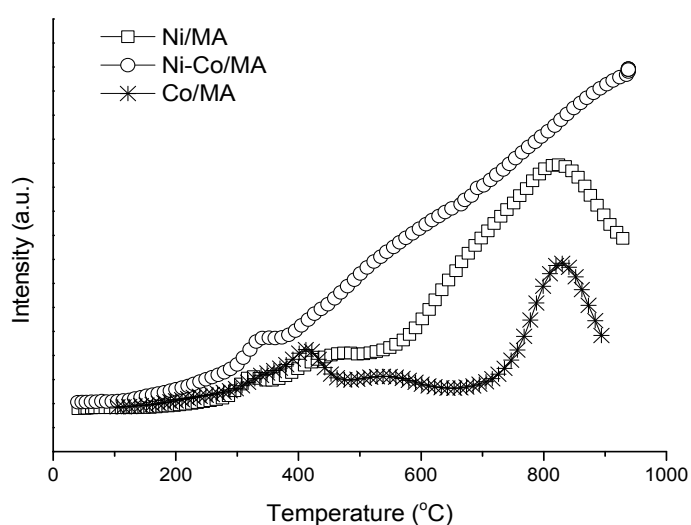


Figure 1: H₂-TPR profiles of Ni/MA, Ni-Co/MA and Co/MA.

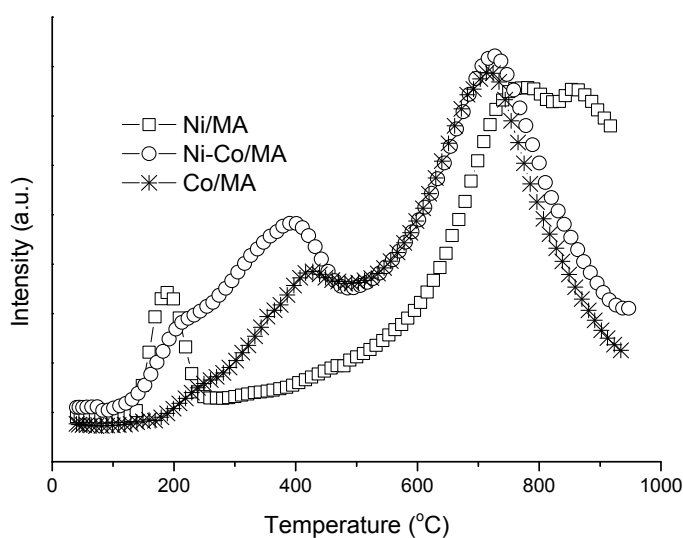


Figure 2: H₂-TPD profiles of Ni/MA, Ni-Co/MA and Co/MA.

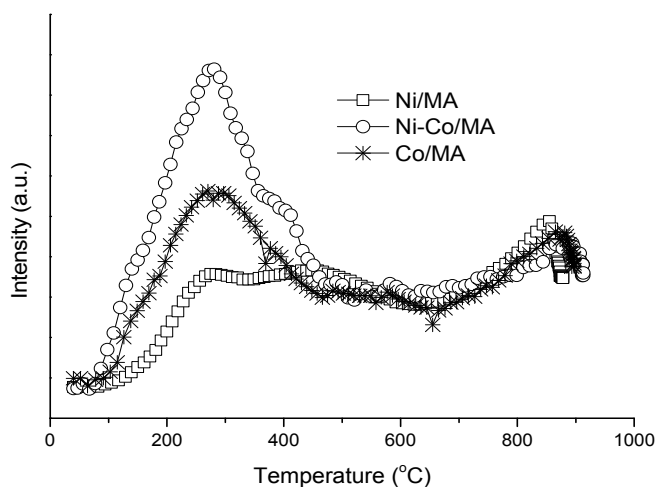


Figure 3: CO_2 -TPD profiles of Ni/MA, Ni-Co/MA and Co/MA.

Because coke can form easily under the decomposition reaction, the carbon resistance of all catalysts according to the decomposition reactions was evaluated in this work. After the decomposition of CH_4 (or CO_2) at 620°C for 1 h, the analysis of carbon deposition was conducted using TPH method. Figure 4 shows TPH profiles after CH_4 decomposition. TPH profile of Ni/MA establishes the large amount of coking with appearance of two peaks. The lower temperature peak (at 570°C) is attributed to amorphous/graphite carbon whereas the higher temperature peak (at 870°C) is assigned to whisker carbon over Ni/MA catalyst (Kambolis et al., 2010). The similar carbonaceous materials were also found for Co/MA but in a small amount of total carbon deposition. It can be seen from Figure 4 that Ni-Co/MA presents an excellent anti-coking performance for CH_4 decomposition. The carbon formation regarding to CO_2 decomposition was investigated using the same analysis (Figure 5). The TPH profile of Co/MA after CO_2 decomposition shows a significant amount of amorphous/graphite carbon due to a good CO_2 adsorption performance. In contrast, coking on the surface of Ni/MA after CO_2 decomposition is negligible. Although Ni-Co/MA also has a great CO_2 adsorption performance, carbon deposition can be prevented from its surface. The carbon resistance of Ni-Co/MA can be related to a good metal dispersion, which correlates to small metal particles (Hao et al., 2009).

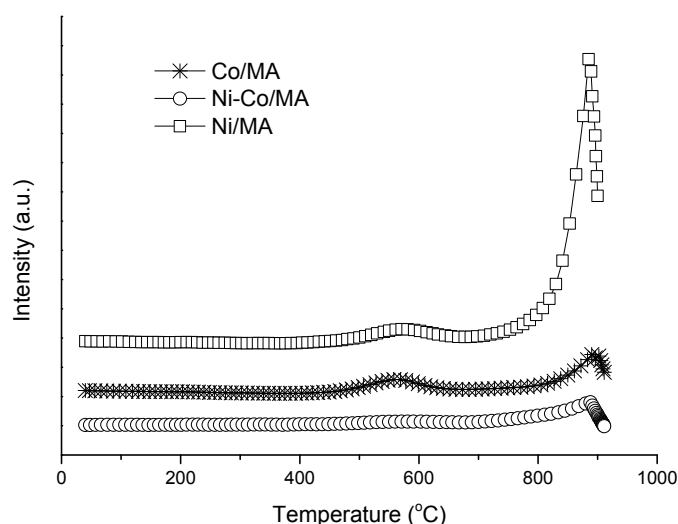


Figure 4: TPH profiles of Ni/MA, Ni-Co/MA and Co/MA after CH_4 -decomposition.

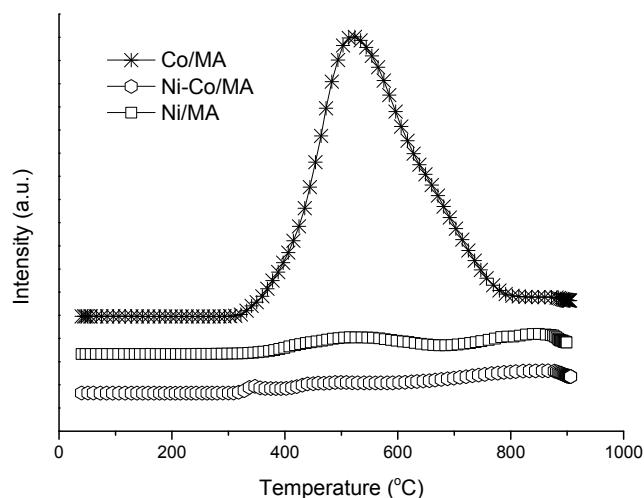


Figure 5: TPH profiles of Ni/MA, Ni-Co/MA and Co/MA after CO₂-decomposition.

3.2 Catalyst testing

The catalytic performance of the catalysts was investigated as methane conversion and H₂/CO ratio. The methane conversions (tested at 620 °C for 6 h) versus the time on stream are depicted in Figure 6 and the average H₂/CO ratios are showed in Table 1. The Ni/MA catalyst shows the highest CH₄ conversion and Co/MA catalyst exhibits the lowest CH₄ conversion. The results reveal that both monometallic catalysts are slowly deactivated as CH₄ conversion decreases from 78 % to 75 % for Ni/MA and from 42 % to 40 % for Co/MA. This deactivation can be caused by carbon deposition because the average H₂/CO ratios of monometallic are higher than unity (Tungkamani et al., 2013), which agrees with the TPH results. A stable CH₄ conversion of 65% and the H₂/CO ratio of 0.94 (almost unity) were observed for Ni-Co/MA catalyst due to a good CO₂ adsorption performance and carbon tolerance.

To monitor the influence of alloy formation on DMR performance of Ni-Co/MA catalyst, the DMR process was demonstrated over Ni-Co/MA after the *in situ* reduction at higher temperature (reduced at 620 °C for 8 h followed by at 800 °C for 4h in a sequence). The Ni-Co alloy formation of Ni-Co/MA that was occurred in the different reduction temperature from 620 °C to 800 °C provides similar CH₄ conversion (Figure 6). It was found that more alloy formation plays an important role in the catalytic selectivity as H₂/CO ratio for Ni-Co/MA reduced at higher temperature is 0.99 which is closer to unity than those of Ni-Co/MA reduced isothermally at 620 °C. In addition, Zhao et al. also reported the H₂/CO ratio of 0.98 for their Ni-Co bimetallic catalyst (Zhao et al., 2013)

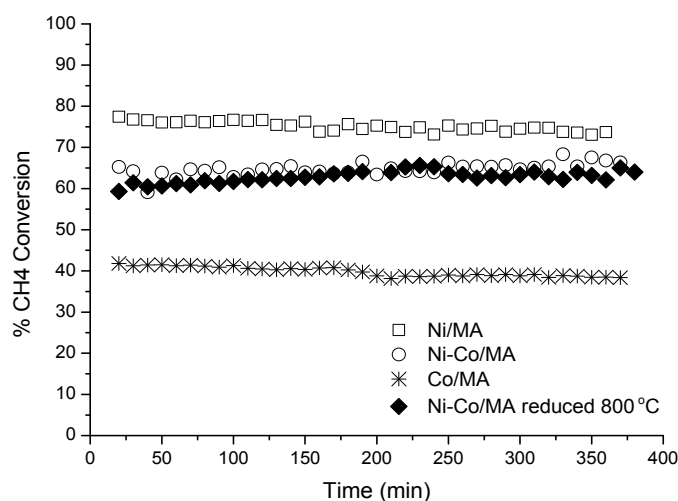


Figure 6: CH₄ conversion with time on stream for DMR of Ni/MA, Ni-Co/MA and Co/MA (reduced at 620 °C for 12 h) and Ni-Co/MA (reduced at 620 °C for 8 h followed by at 800 °C for 4 h)

Table 1: The average H₂/CO ratio for DMR of Ni/MA, Ni-Co/MA and Co/MA (reduced at 620 °C for 12 h) and Ni-Co/MA (reduced at 620 °C for 8 h followed by at 800 °C for 4 h)

| Catalyst | Ni/MA | Co/MA | Ni-Co/MA (reduced at 620 °C) | Ni-Co/MA (reduced at 620 and 800 °C) |
|--------------------------|-------|-------|------------------------------|--------------------------------------|
| H ₂ /CO ratio | 1.17 | 1.29 | 0.94 | 0.99 |

4. Conclusions

In conclusion, Ni-Co/MA catalyst shows high reducibility with practical SMSI and Ni-Co alloy formation. These properties of the bimetallic catalyst result in the great metal dispersion and the excellent carbon resistance of Ni-Co/MA catalyst can be due to small metal particles. A good performance of CO₂ adsorption with an excellent carbon elimination of Ni-Co/MA catalyst causes a high catalytic selectivity on DMR. More alloy formation on the surface of Ni-Co/MA help to reach the remarkable DMR selectivity without the change in the catalytic activity.

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