



## Effect of the FSP-inserted Co in the Ni-based catalyst on the dry reforming of methane

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### Abstract

The carbon dioxide reforming of methane (DRM) over silica-supported Ni catalyst was studied at 750 °C and 1 atm. The cobalt was added in the silica support during preparation by flame spray pyrolysis (FSP). The Co loading was varied as 5, 10 and 20 wt % while the impregnated Ni loading was fixed as 5 wt %. The XRD peaks of NiO disappeared when the cobalt was introduced in the catalyst. It was implied to a good dispersion of Ni particles on the catalyst surface. The FSP-inserted Co decreased significantly the BET surface area but the pattern of adsorption-desorption isotherms indicating the slit-shaped pores was rather similar. The TPR results showed the reduction peaks at high temperature relating to strong interaction of the cobalt and the silica. This affected loss of ability to chemisorb hydrogen for the 5 wt% Co insertion. This catalyst promoted the DRM activity and maintained the product ratio of hydrogen and CO. The excess of cobalt showed high metal active sites consisting of both Ni and Co sites. However, the 10 and 20 wt% Co loadings retarded the catalytic activity and the hydrogen yield. They promoted the reverse water gas shift reaction as well.

**Keywords:** Dry reforming of methane, Silica supported nickel catalyst, FSP-inserted cobalt

### Introduction

In the present, petroleum fuels are main resource of energy and the requirement of fuels has continuously increased. To reduce the reliance on petroleum fuels, new alternative energies are searched and studied. One of them is biogas consisting of methane (CH<sub>4</sub>) and carbon dioxide (CO<sub>2</sub>). It damages the environment so that several researches interest in apply it. High efficiency technology is dry reforming of methane (DRM). The use of CH<sub>4</sub> and CO<sub>2</sub> are reactant to produce the syngas, hydrogen (H<sub>2</sub>) and carbon monoxide (CO), with a relatively low H<sub>2</sub>/CO ratio (1:1). The greatest challenge against the industrial application of CO<sub>2</sub> reforming of methane is coke via methane decomposition and CO disproportionation, which causes deactivation of the catalyst and plugging of the reactor.

The common catalyst in the dry reforming of methane is transition metal, especially Ni and Co [1]. The nickel based catalyst is the most effective metal due to its high DRM activity. Many factors such as nickel dispersion, support property and metal-support interaction affect the catalytic activity and stability of the catalyst [2]. The silica is a common support that shows high specific surface area. When a surface area of silica increases, the nickel dispersion is increased, which can improve the catalytic performance [3]. However, the interaction of nickel and silica is rather weak leading to aggregation of nickel particles. In this work, the cobalt was added into the silica during the preparation by flame spray pyrolysis (FSP) to increase active sites and enhance the strong metal-support interaction.

## Materials and methods

### Catalyst preparation

Nickel nitrate, tetraethyl orthosilicate, and cobalt (II) nitrate hexahydrate were used as the catalyst precursors. The Co-SiO<sub>2</sub> support was prepared by flame spray pyrolysis in a single step. The Co and Si precursors were diluted by ethanol solvent with a fixed concentration at 0.5 M. This mixture was injected through the flame by syringe pump with a flow rate of 5 ml/min. The catalyst powder was collected on a glass microfiber filter with the aid of vacuum pump. The cobalt loading was adjusted as 5, 10 and 20 wt %. The 5 wt % nickel was loaded on the FSP-made Co-SiO<sub>2</sub> support by incipient wetness impregnation (IWI). The catalyst was dried at 120 °C overnight and calcined in air at 500 °C for 4 h.

### Catalyst characterization

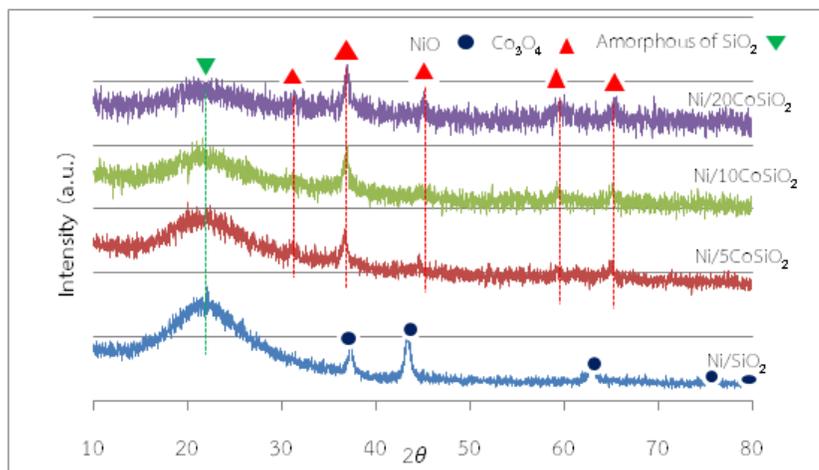
XRD measurement was performed in the range 2θ from 10° to 80° using a Bruker AXS Model D8 Discover instrument equipped with Cu Kα. The N<sub>2</sub> physisorption was conducted by Micromeritics ASAP 2010. Before analysis, the catalyst was pretreated in helium with 50 ml/min at 180 °C for 3 h. H<sub>2</sub>-chemisorption and H<sub>2</sub>-TPR were performed using a Micromeritics AutoChem 2910 instrument. For H<sub>2</sub>-chemisorption, a 0.1 g of catalyst was packed in a quartz U-tube. The catalyst was reduced in H<sub>2</sub> with 30 ml/min at 500 °C for 2 h. After reduction, the catalyst was pretreated at 750 °C for 20 min. The metal active sites were measured at 100 °C in N<sub>2</sub> flow with injected-pulses of H<sub>2</sub> until the sample was saturated. For H<sub>2</sub>-TPR, a 0.1 g of catalyst was packed in a quartz U-tube. The catalyst was pretreated in N<sub>2</sub> with 30 ml/min at 750 °C for 1 h. The reduction profiles were recorded from 100 to 800 °C with a heating rate of 10 °C/min under a flow of 10% H<sub>2</sub> in N<sub>2</sub>.

### Catalyst evaluation

The catalytic properties were performed by the DRM test at 750 °C and 1 atm. The catalyst was packed in a fixed-bed quartz reactor. Prior to reaction test, the catalyst was reduced by H<sub>2</sub> at 500 °C for 2 h. The feed stream was the mixture of CH<sub>4</sub> and CO<sub>2</sub> with the molar ratio as 1. The gas hourly space velocity (GHSV) was fixed as 12000 h<sup>-1</sup>. The reaction was held for 10 h. The effluent products were analyzed by GC-TCD equipped with Porapak Q packed-column.

## Results and discussion

The XRD pattern of the Ni/SiO<sub>2</sub> and Ni/CoSiO<sub>2</sub> is shown in Figure 1. The Ni/SiO<sub>2</sub> catalyst showed the peaks of NiO [4] and amorphous SiO<sub>2</sub> [5]. When the cobalt was added in the SiO<sub>2</sub> support, the peaks of NiO disappeared. Only the XRD peaks of Co<sub>3</sub>O<sub>4</sub> [6] and amorphous SiO<sub>2</sub> were found. It was implied that in this case the NiO particles were well dispersed on the catalyst surface. When increasing Co loading, phase appeared and the crystalline size of Co<sub>3</sub>O<sub>4</sub> was constant about 22 nm as shown in table 1.



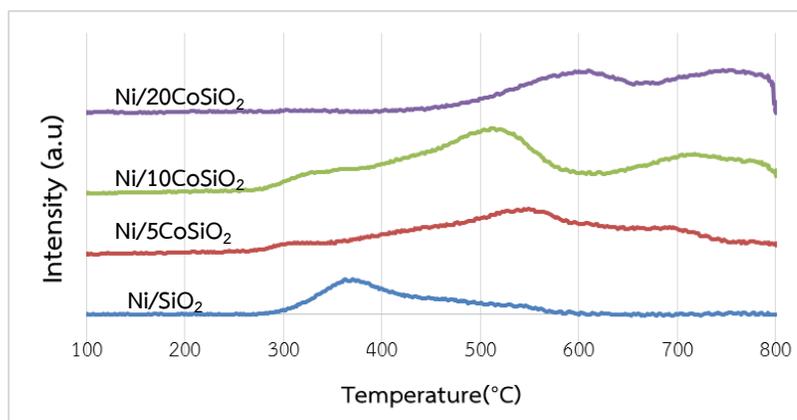
**Figure 1** The XRD pattern of the Ni/CoSiO<sub>2</sub> catalyst with various Co loadings

**Table 1** The crystalline size from the XRD data and BET surface area of the Ni/CoSiO<sub>2</sub> catalyst with various Co loadings

Catalyst	Crystalline size (nm)		BET surface area (m <sup>2</sup> /g)
	NiO	Co <sub>3</sub> O <sub>4</sub>	
Ni/SiO <sub>2</sub>	16.2	n.d.	218
Ni/5CoSiO <sub>2</sub>	n.d.	22.5	195
Ni/10CoSiO <sub>2</sub>	n.d.	22.6	162
Ni/20CoSiO <sub>2</sub>	n.d.	22.5	193

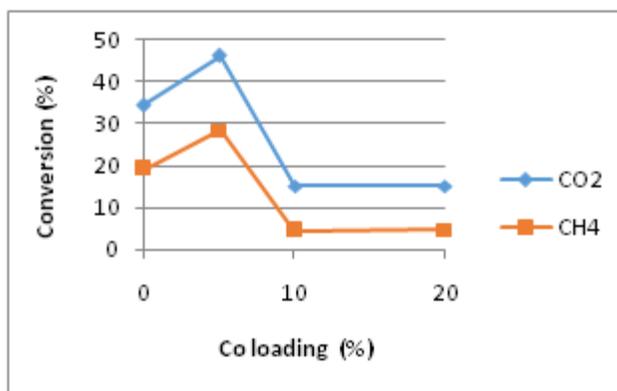
The BET surface area was determined by N<sub>2</sub> physisorption as shown in table 1. The surface area of Ni/SiO<sub>2</sub> was higher than that of all Ni/CoSiO<sub>2</sub> catalysts. The adsorption-desorption isotherms of all catalysts was also measured but not shown here. For all catalysts, the isotherms showed hysteresis loop with H4-type that was typical of aggregated plate-like particles giving rise to slit-shaped pores.

Figure 2 shows TPR profiles for the Ni/SiO<sub>2</sub> and Ni/CoSiO<sub>2</sub> catalysts. The Ni/SiO<sub>2</sub> showed a broad peak with a shoulder around 300 to 580 °C with a maximum at 375 °C. It was corresponding to the reduction of NiO to Ni [7]. When the cobalt was added, the reduction began at 280 °C and finished at more than 800 °C. Three reduction regions were observed. A small peak at low temperature (< 400 °C) and a broad peak at moderate temperature (400-650 °C) was assigned to the overlap reduction of NiO to Ni and Co<sub>3</sub>O<sub>4</sub> to Co. Another broad peak at high temperature (> 650 °C) was addressed as the reduction of cobalt oxides strongly interacted with the SiO<sub>2</sub>. It was indicated that the FSP-inserted Co enhanced a strong interaction of nickel and support, especially the 20 wt % Co loading. An increase of the reduction temperature in Ni-Co alloy compared with Ni alone was attributed to the very strong interaction between Ni-Co and silica [8]. The reducibility calculated from the TPR data and the metal active sites measured by H<sub>2</sub>-chemisorption are summarized in Table 2. Loss of reducibility in the Ni/CoSiO<sub>2</sub> catalyst was because some of cobalt was embedded in the SiO<sub>2</sub> or the non-reducible cobalt silicate was possibly formed during the FSP preparation. When the 5 wt % Co was loaded, a strong metal-support interaction inhibited the chemisorption ability of hydrogen on the catalyst surface. However, the metal active sites were increased with increasing cobalt loading.

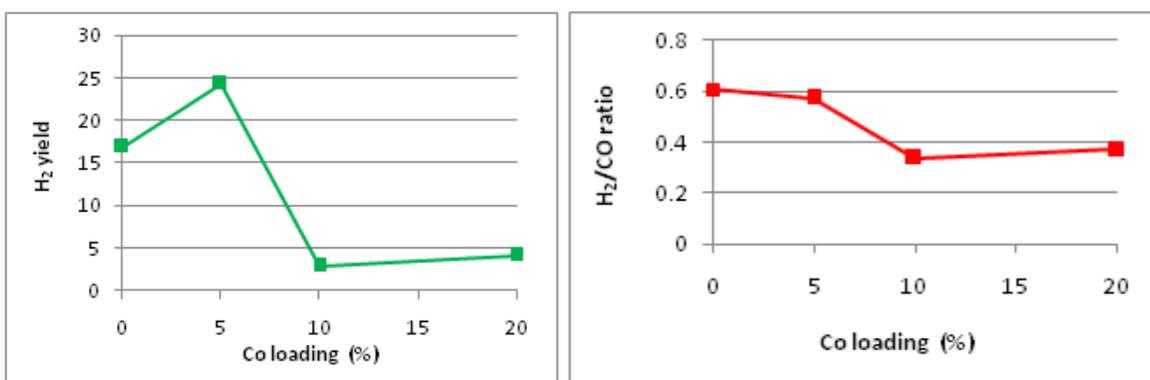
**Figure 2** TPR profiles of the Ni/CoSiO<sub>2</sub> catalyst with various Co loadings**Table 2** The reducibility and the metal active sites of the Ni/CoSiO<sub>2</sub> catalyst with various Co loadings

Catalyst	Reducibility (%)	Metal active sites × 10 <sup>-19</sup> (atom/g cat)
Ni/SiO <sub>2</sub>	100.0	1.2
Ni/5CoSiO <sub>2</sub>	67.1	0.7
Ni/10CoSiO <sub>2</sub>	18.7	1.4
Ni/20CoSiO <sub>2</sub>	39.4	2.6

Figures 3 and 4 show the results from the DRM testing for 10 h. CO<sub>2</sub> conversion was higher than CH<sub>4</sub> conversion because the reverse water gas-shift reaction was also occurred. The addition of only 5 wt % cobalt enhanced both conversion and H<sub>2</sub> yield. Also, the H<sub>2</sub>/CO ratio was still maintained for this catalyst. It was speculated that the promotional effect was a strong interaction of nickel and support. The aggregation of nickel particles was retarded and therefore the well-dispersed nickel metals can promote the DRM activity. On the other hand, high cobalt loading (10 and 20 wt %) showed the negative effect for the DRM. The dispersed cobalt metals were possible to accelerate the coke formation due to effect of the ensemble sites on the catalyst surface. The cobalt species can also promote the reverse water gas-shift reaction.



**Figure 3** CH<sub>4</sub> and CO<sub>2</sub> conversions for the DRM on the Ni/CoSiO<sub>2</sub> catalyst with various Co loadings



**Figure 4** H<sub>2</sub> yield and H<sub>2</sub>/CO ratio in the product for the DRM on the Ni/CoSiO<sub>2</sub> catalyst with various Co loadings

## Conclusion

The dry reforming of methane on the SiO<sub>2</sub>-supported nickel catalyst was investigated. The cobalt was loaded in the SiO<sub>2</sub> support during the preparation by flame spray pyrolysis. The FSP-inserted cobalt affected a well dispersed NiO and a strong interaction of nickel and support. The introduction of only 5 wt % Co was suitable to promote the DRM reaction. The excess of FSP-inserted cobalt showed more cobalt active sites. They inhibited the DRM activity but promoted the reverse water gas-shift reaction.

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