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Research Article

Effect of Strong Metal Support Interactions of Supported Ni and Ni-Co Catalyst on Metal Dispersion and Catalytic Activity toward Dry Methane Reforming Reaction

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Abstract

This work studied the effect of interaction between active metal species (Ni and Ni-Co species) and different support (Al_2O_3-MgO and SiO_2) on the catalyst properties and catalytic performance in dry methane reforming reaction. Supports were synthesized by sol-gel method, then the catalyst samples were prepared by incipient wetness impregnation with a salt solution of active metal(s). The fresh catalysts were characterized via Scanning Electron Microscopy (SEM), Temperature Programmed Reduction (TPR) and Temperature Programmed Desorption (TPD) techniques. Dry Methane Reforming (DMR) activities were tested in a conventional fixed-bed reactor at 620°C. The SEM images and H_2-TPR results reveal that the Strong Metal Support Interaction (SMSI) takes place in the catalysts based on Al_2O_3-MgO support. The metal dispersion and average metal particle size were evaluated using TPD results. It was found that a Ni-Co bimetallic catalyst provides higher metal dispersion and smaller average metal particle size than Ni monometallic catalysts due to the effect of metal-metal interaction. The bimetallic catalyst with weaker metal-support interaction improve the metal-metal interaction resulting in increasing higher metal dispersion. DMR test presented that sites of strong metal-support interaction enhanced CH_4 activity. The stronger metal-metal interaction in Ni-Co bimetallic catalyst with SiO_2 support promoted CO_2 activity.

Keywords: Dry methane reforming, Metal dispersion, Metal-support interaction, Metal-metal interaction

1 Introduction

Dry Methane Reforming (DMR) is a relative low cost hydrogen/syngas production as compared to other thermochemical processes. DMR is an environmental friendly process. It converts two greenhouse gases into an alternative fuel gas (H_2) and the industrial feedstock (synthesis gas, H_2 and CO) as written in equation (1). This process is suitable for the natural gas discovered in Thailand because this natural gas contains a significant amount of carbon dioxide (>10%) [1].

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \quad \Delta H^\circ_{298} = 246.2 \text{ kJ/mol} \quad (1)$$

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DMR normally take place upon heterogeneous catalyst. The heterogeneous catalysts which have been widely used for DMR are supported nickel catalysts due to a compromise between cost and activity. In order to develop the DMR performance of these catalysts, the influence of the interactions in the catalysts on their properties and activity is necessary to be understood. For example, it has been pointed out that metal-support interaction of catalysts plays a vital role on DMR activity and coking resistance. The Ni/Al_2O_3-MgO catalyst has a stable spinel-like structure which inhibits carbon formation. In this structure, nickel has a strong interaction with support. Ni-Co/Al_2O_3-MgO catalysts provide relative high metal dispersion and small metal particle [2]. Cobalt in Ni-Co bimetallic catalyst promotes CO_2-adsorption [3]. Ni/SiO_2 establishes a good activity and stability for DMR [4]. However, the activation of DMR over Ru/SiO_2 occurs only on metal surface and this catalyst deactivates rapidly [5].

The aim of this work is to study the effect of strong metal support interactions of supported Ni and Ni-Co catalyst on metal dispersion and catalytic activity toward dry methane reforming reaction.

2 Experimental

2.1 *Preparation of supports and catalysts*

The Al_2O_3-MgO and SiO_2 supports, were synthesized by a sol-gel method. The gel products were dried at 45°C for 24 h, and then calcined in air at 800°C for 6 h. The catalyst samples were prepared by impregnating supports with desired amount of an aqueous solution of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$, UniLab) or a mixed aqueous solution of nickel nitrate and cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, QRëC). After drying at 60°C for 48 h, the samples were calcined in air at 650°C for 5 h and pelletized. The list of prepared catalysts with their chemical composition are summarized in Table 1.

Table 1: Chemical composition of the catalysts

Sample ID	Composition (wt.%)[a]			
	Ni	Co	SiO_2	Al_2O_3-MgO
10NS	10.0	0.0	90.0	0.0
10NAM	10.0	0.0	0.0	90.0
5N5CS	5.0	5.0	90.0	0.0
5N5CAM	5.0	5.0	0.0	90.0

[a] as expected after reduction

2.2 *Catalyst characterization*

Temperature programmed reduction of hydrogen (H_2-TPR) is applied to investigate the metal-support interaction which corresponds to the reducibility of catalyst samples. The measurement was performed in a stainless steel tube reactor. The sample was first pretreated in Ar flow at 200°C for 1 h, followed by cooling in Ar to room temperature. The hydrogen assumptions for the reduction of the catalyst were measured in a reduced gas (5%H_2/Ar) at a heating rate of 10°C/min from room temperature to 900°C using a thermal conductivity detector (TCD, Agilent GC6820).

The metal dispersion and metal particle size of fresh catalysts were characterized using temperature programmed desorption of hydrogen (H_2-TPD) on a chemisorption apparatus (BELCAT-Basic system). The sample was pre-reduced in a H_2 flow at 600°C for 2 h before it was cooled at the rate of 10°C/min to 100°C in Ar flow. At this temperature, chemisorption of hydrogen was performed until saturation was reached. Then, the H_2-TPD was carried out in the range of 40°C to 900°C at a ramping rate of 10°C/min in Ar flow.

Scanning Electron Microscope (SEM) images of catalyst surface were taken by mean of JSM-6610LV (JEOL) operated at 200 kV to investigate the surface morphology of catalyst.

2.3 *Catalytic tests*

The activity of catalyst samples for DMR were tested in a fixed-bed stainless steel reactor. Prior to the reaction test, the catalyst was reduced in-situ in H_2 flow at 620°C for 2 h. The total feed flow rate of CH_4-CO_2-N_2 mixture (CH_4:CO_2:N_2 molar ratio of 3:5:4) was 60 ml/min which was introduced into the reactor at 620°C under atmospheric pressure. The composition of the product stream was analysed by an on line gas chromatograph (Agilent GC7890A) equipped with TCD detector. The conversion of CH_4 and CO_2 were described using equations (2)–(3):

$$x(CH_4)\% = \frac{\dot{n}_{CH_4 in} - \dot{n}_{CH_4 out}}{\dot{n}_{CH_4 in}} \times 100\% \qquad (2)$$

$$x(CO_2)\% = \frac{\dot{n}_{CO_2 in} - \dot{n}_{CO_2 out}}{\dot{n}_{CO_2 in}} \times 100\% \qquad (3)$$

where x (i) and $\dot{n}_i$ are the conversion and the molar flow rate of the molecule i, respectively.

3 Results and Discussion

3.1 *Physicochemical properties of the catalysts*

H_2-TPR profiles of catalyst samples are shown in Figure 1. The reducibility of nickel in 10NAM exhibits three different phases. The lowest temperature peak (370°C) corresponds to the reduction of free NiO [3]. The peak at higher temperature (470°C) is attributed to the reduction of NiO that is interacting with Al_2O_3-MgO support. The reduction beginning at the temperature higher than 600°C can be ascribed to the reduction of nickel in spinel phase, which suggests the Strong Metal-Support Interaction (SMSI) effect between Ni and support [3], [6]. The H_2-TPR profile of 10NS also showed two H_2 consumption peaks according to the reduction of free NiO and NiO-support interaction. Nonetheless, the metal-support interaction in 10NS is not as strong as SMSI in 10NAM. In the case of Ni-Co bimetallic catalyst (5N5CAM and 5N5CS), the first peak starts at the temperature lower than Ni monometallic catalysts (10NAM and 10NS). For 5N5CS, the lowest temperature peak at 270°C was found separately from other peaks. This peak referred to the reduction of free Co_3O_4 to CoO without the evidence of SMSI species. The reduction of free Co_3O_4 phase was not observed in 5N5CAM. The higher temperature board peak in H_2 consumption curves for 5N5CS and 5N5CAM can be associated with multiple reductions (reduction of Co Ni and Ni-Co species). However, two overlap peaks at 660°C and 850°C in H_2-TPR profile for 5N5CAM attempts to SMSI of the Ni-Co complex [7], [8].

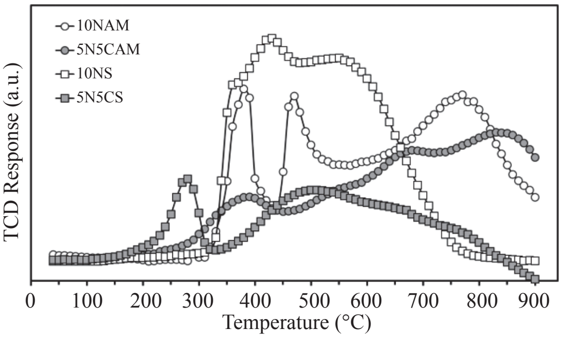

Figure 1: H_2-TPR profile of 10NAM, 5N5CAM 10NS and 5N5CS catalysts.

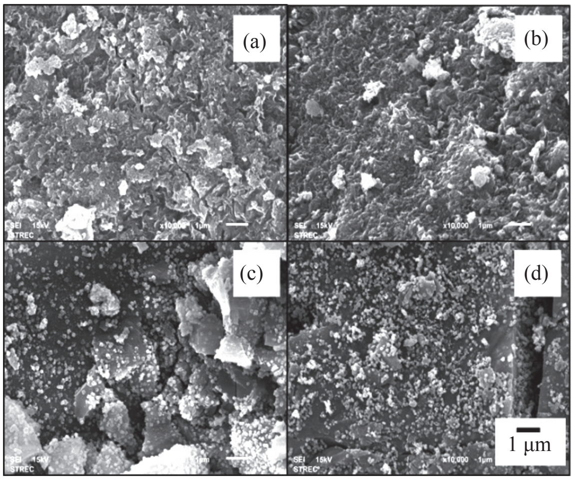

Figure 2: SEM images of (a) 10NAM (b) 5N5CAM (c) 10NS and (d) 5N5CS catalysts.

Figure 2 shows the SEM images of calcined catalysts. The effect of SMSI in 10NAM [Figure 2 (a)] and 5N5CAM [Figure 2 (b)] allows metal oxide particle of active metal (Ni, Co) to combine with Al_2O_3-MgO support. As a result, the active metal(s) in oxide form can hardly be identified from Al_2O_3-MgO support in SEM image for 5N5CAM. The surface morphology of catalysts based on SiO_2 support is different from the surface of catalysts based on Al_2O_3-MgO support. In 10NS [Figure 2 (c)], a number of nickel oxide particles are dispersed and separated from the SiO_2 support because of weak metal-support interaction. Metal oxide particle size of active metals decreases, which illustrates a greater dispersion for 5N5CS [Figure 2 (d)] as compared to 10NS. It means that metal-metal interaction for Ni-Co bimetallic catalyst assists catalysts in the dispersion of active metal species. The metal dispersion and average metal particle size for reduced catalysts were conducted from the H_2-TPD measurement (Table 2). Monometallic catalysts, 10NAM and 10NS, exhibits almost similar metal dispersion. Thus, this catalyst presents the same average size of metal particle. The appearance of second metal (Co) in bimetallic (Ni-Co) catalysts promotes the metal dispersion. The TPD results and SEM results show similar trend. Therefore, the higher metal dispersion of Ni-Co catalyst can be attributed to interaction between metal and metal [7], [9].

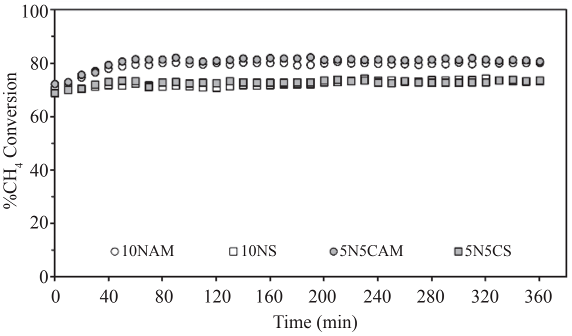

Figure 3: DMR performance of CH_4 conversion of 10NAM, 10NS, 5N5CAM and 5N5CS catalysts.

The weaker metal-support interaction improves the metal-metal interaction as it was observed that 5N5CS has higher metal dispersion and smaller average metal particle size than those of 5N5CAM catalysts.

Table 2: Metal dispersion and average metal particle size of all catalysts

Sample	Metal dispersion (%)	Average metal particle size (nm)
10NAM	19.58	3.23
10NS	18.66	3.39
5N5CAM	21.49	2.94
5N5CS	25.71	2.46

3.2 *Catalytic activities*

DMR were carried out over catalyst samples at 620°C for 6 h. The activities in terms of CH_4 and CO_2 conversions are presented in Figure 3 and 4, respectively. As seen in to Figure 3, the catalyst based on Al_2O_3-MgO support (10NAM and 5N5CAM) achieves CH_4 conversion as high as 80%. The catalysts with weaker metal support interaction (10NS and 5N5CS) provide lower CH_4 conversion of about 72%. It can be indicated that CH_4 conversion is more active over the sites of strong metal-support interaction. 10NAM and 5N5CAM show similar activity for CO_2 conversion. Unlikely, 5N5CS presents higher CO_2 conversion than 10NS. The ratio of CO_2 consumption to CH_4 consumption (Figure 5) discloses that Ni-Co interaction plays an important role on CO_2 conversion for a case of weak metal-support interaction catalyst due to the improvement of metal-metal interaction. These results are in good agreement with the discussion in H_2-TPD results. Consequently, the ability of cobalt to adsorb CO_2 [3] appears more effective in 5N5CS.

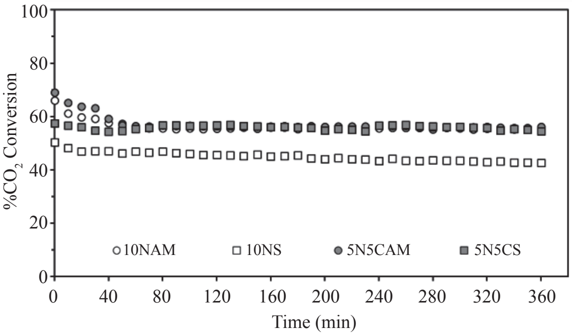

Figure 4: DMR performance of CO_2 conversion of 10NAM, 10NS, 5N5CAM and 5N5CS catalysts.

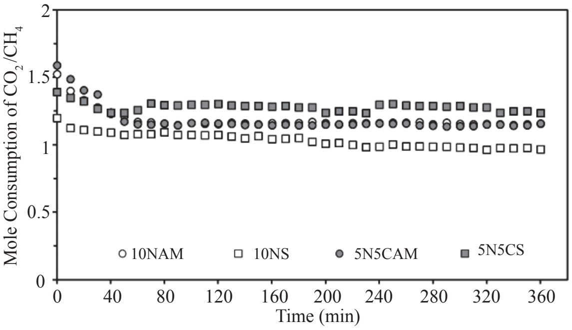

Figure 5: DMR performance of mole consumption of CO_2/CH_4 of 10NAM, 10NS, 5N5CAM and 5N5CS catalysts.

4 Conclusions

The Ni and Ni-Co catalysts based on different supports causes unequal metal-support interactions which lead to the opposite metal-metal interaction effect for bimetallic catalysts. Strong metal-support interaction occurred between nickel (nickel-cobalt) and Al_2O_3-MgO support (10NAM and 5N5CAM catalysts). The catalysts based on SiO_2, 10NS and 5N5CS, show weaker metal-support interaction without SMSI. Weak interaction between active metal species and support results in increasing the effect of Ni-Co interaction in the bimetallic catalyst. Consequently, higher metal dispersion was observed in 5N5CS as compared to 5N5CAM. For DMR activity, strong metal-support interaction enhance CH_4 conversion. The improvement of Ni-Co interaction was found to enhance CO_2 conversion.

Acknowledgments

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