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The Effect of K Promoter on Ni-Co (Bimetallic) Catalyst for Dry Methane Reforming

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Abstract

10 wt% (Ni-Co) catalysts with different Ni and Co content : 10%Ni, 9%Ni1%Co, 7%Ni3%Co, 5%Ni5%Co, 3%Ni7%Co, and 10%Co; were prepared using sol-gel method followed by incipient wetness impregnation method. To investigate the catalytic activity including the stability, dry methane reforming were demonstrated over the pelletized catalysts at 620 °C under atmospheric pressure in a CH₄:CO₂:N₂ feedstock for 360 min. The results showed that bimetallic catalysts with the Co content equal to or greater than 3% were more stable than monometallic catalysts (10%Ni and 10%Co). The temperature programmed hydrogenation interpreted that the additional of Co into Ni catalyst improved the carbon resistance from methane cracking. Promoted this type of bimetallic catalyst using 1wt% K (trimetallic catalyst) prevented the carbon formation on the catalyst. The temperature programmed desorption of CO₂ indicated that this trimetallic catalyst has a greater number of strong basic sites. Moreover, the appearance of K lowered the number of weak basic sites and decreased the conversion of methane by 12 %.

Keywords: Dry methane reforming, Bimetallic, Trimetallic, Promoter

1. INTRODUCTION

Dry methane reforming (DMR) is a competitive clean energy generating process because the reaction Eq.(1) converts two greenhouse gases (CH₄ and CO₂) in order to generate H₂ and syngas (mixture of H₂ and CO) on the surface of solid catalyst. Other advantages of DMR are: reactants can be found in natural gas fields at low cost, liquid-

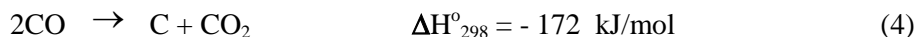
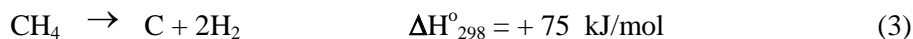
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gas separator is not necessary and reverse-water-gas-shift (RWGS, Eq.(2)) is side reaction increasing H₂ productivity. Considering the high operating temperature, this process has difficulty in commercialization due to catalyst deactivation caused by coke deposition and metal sintering. Carbon deposition is attributed to three reaction including CH₄ fragmentation Eq.(3), Boudouard reaction Eq.(4) and CO hydrogenation Eq.(5). [1]



Although noble metal-based catalysts such as Pt, Ru, Pd, Ir, and Rh provide high activity and selectivity as well as good stability towards coke deposition for DMR, their high cost and low availability are still the drawbacks in comparison with other transition metal based catalyst [2]. Ni-based catalysts are the most appropriate for the process; nonetheless, catalyst deactivated by the carbon formation and loss of active site need to be improved.

This research developed Ni-Co bimetallic catalyst with sol-gel and incipient wetness impregnation. It was found that Ni-Co bimetallic in several metal contents show high selectivity and stability with slightly lower activity compared to Ni monometallic catalyst. In this work, K, an alkali metal promoter, was also applied to evaluate the improvement of carbon tolerance for this bimetallic catalyst. Moreover, our prepared catalysts was analysed to carry out their performance.

2. EXPERIMENTAL

2.1 Catalyst preparations

The catalysts were designed to have a total of 10 wt% of active metal. Firstly, MgO-Al₂O₃ mixed oxide support was prepared by sol-gel method. The support were dried at 45°C overnight, calcined at 800°C for 6 h, then crushed and sieved to particle size 335-710 μm. Secondly, x%Ni_y%Co/MgO-Al₂O₃ (x+y = 10) catalysts were prepared by incipient wetness impregnation using desired amount of aqueous solution of nickel nitrate (Ni(NO₃)₂·6H₂O) and cobalt nitrate (Co(NO₃)₂·6H₂O). After impregnation, the products were dried at 45°C for 24 h, calcined at 650°C for 5 h and then crushed and sieved to 335-710 μm size. Our catalysts include 10%Ni/MgO-Al₂O₃ (10Ni), 9%Ni1%Co/MgO-Al₂O₃ (9Ni1Co), 7%Ni3%Co/MgO-Al₂O₃ (7Ni3Co), 5%Ni5%Co/MgO-Al₂O₃ (5Ni5Co), 3%Ni7%Co/MgO-Al₂O₃ (3Ni7Co), and 10%Co/MgO-Al₂O₃ (10Co).

Promoted 7%Ni3%Co1%K/MgO-Al₂O₃ (7Ni3Co1K) catalyst was prepared by the similar procedure with our catalysts. To do so, 1 wt% K promoter was added into mixed Ni(NO₃)₂·6H₂O and Co(NO₃)₂·6H₂O solution before impregnate this mixture on the surface of the support. The step after impregnation follow the condition of dry, calcination and particle size collection as explain above.

2.2 Catalytic activity test

The catalyst performance on DMR was carried out in a fixed-bed reactor at 620°C for 6 h under atmospheric pressure, using catalyst weight of 200 mg. Activity of catalyst involved reductive treatment with H₂ at 620°C for 12 h under atmospheric pressure. The reactant feed was CH₄:CO₂:N₂ = 3:5:4 in a total flow of 60 ml/min. The composition of outlet gas were determined via an on-line gas chromatograph (Agilent GC7890A) equipped with TCD

2.3 Characterization

Carbon tolerance toward CH₄ decomposition were characterized separately by temperature programmed hydrogenation (TPH) in a plug flow reactor similarly to TPD-CO₂. However, the detector was changed to flame ionization detector (FID) for this experiment. In the experiment, a sample weight of 200 mg were reduced in 30 ml/min of H₂ feed at 620°C for 2 h followed by flushing with 30 ml/min of He for 0.5 h. Isothermal methane cracking was then performed at 620°C over the reduced catalyst surface under CH₄ flow (30 ml/min) for 1 h. After methane cracking, TPH experiment were tested in the range of temperature from 30°C to 900°C at the ramping rate of 10°C/min. During the experiment, carbon produced from methane cracking was subsequently hydrogenated and converted to methane Eq.(6). The TPH profile was recorded as FID signal.



The basic site strength of the catalysts and the support was evaluated by temperature programmed desorption of CO₂ (CO₂-TPD) techniques. A sample weight of 200 mg was packed in a fixed-bed reactor which was coupled to a thermal conductivity detector (TCD). The sample pre-reduced in-situ with H₂ 30 ml/min at 620°C for 1 h before performing CO₂ adsorption at 30°C for 30 min. Subsequently, the sample was flushed by He at a flow rate of 30 ml/min for 0.5 h. Then, CO₂-TPD profile was carried out as TCD signal in the temperature range from 30°C to 900°C using ramping rate of 10°C/min.

3. RESULTS AND DISCUSSION

3.1 Performances and properties of x%Ni/y%Co/MgO-Al₂O₃

Catalytic activity was monitored over 6 h time on steam. CH₄ conversion and product selectivity are shown in Fig. 1 and 2, respectively. According to DMR reaction Eq.(1), The ratio of H₂ selectivity to CO₂ selectivity is unity theoretically. In other word, percentage selectivity of H₂ and CO must be equal to 50%. Although 10Ni catalyst provides highest CH₄ conversion, the conversion drops during the time-on-steam from 78% to 75% and selectivity of CO is 45%. This result indicates that carbon could deposit on 10Ni. The other monometallic catalyst, 10Co, show lowest activity as same as deactivation. The conversion dropped from 48% down to 40% with 42% for the selectivity of CO. Therefore, carbon formation should be considered for 10Co.

In the case of bimetallic catalysts, 7Ni3Co 5Ni5Co and 3Ni7Co can maintain stable CH₄ conversion after the first hour. CH₄ conversion obtained from 7Ni3Co is around 65-70% and that carried out from 5Ni5Co and 3Ni7Co are similar (64%). The sustainable activity of these three catalyst is attributed to the selectivity. Their selectivity almost equal to theoretical value with slightly higher for selectivity of CO. However, 9Ni1Co is not a proper content for our Ni-Co bimetallic catalyst in a comparison to all content. It has a low activity (60%) as well as low selectivity (selectivity of CO = 47%). The carbon resistance results are presents later in the TPH profiles.

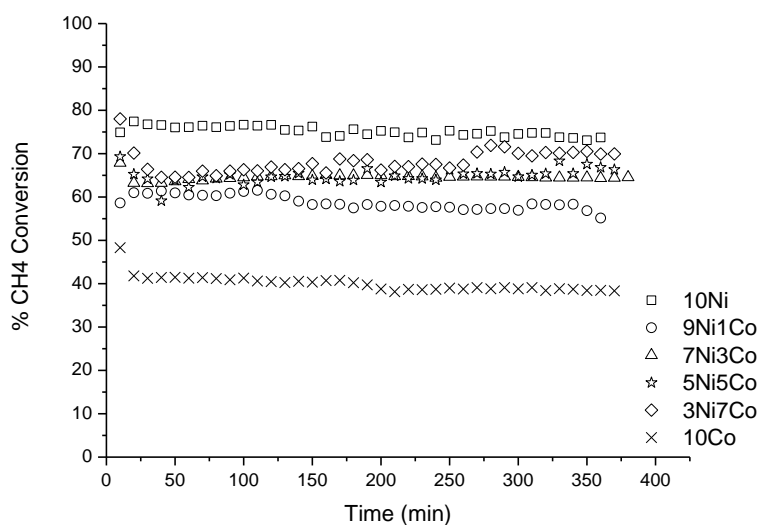


Figure 1. CH₄ conversion versus time on stream for xNi_yCo catalysts under DMR reaction condition (620°C, CH₄:CO₂:N₂ = 3:5:4 with total flow rate of 60 ml/min, 6 h)

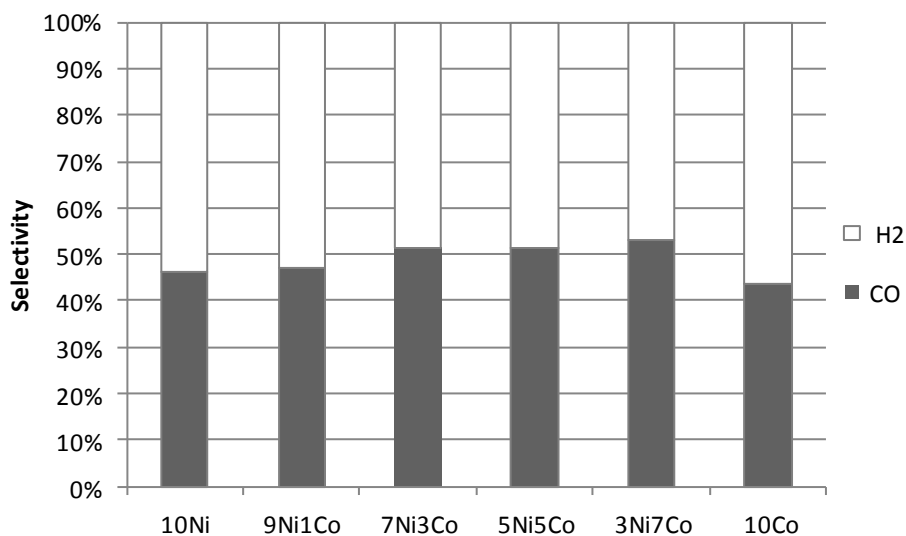


Figure 2. Selectivity of H₂ and CO for xNi_yCo catalysts under DMR reaction condition (620°C, CH₄:CO₂:N₂ = 3:5:4 with total flow rate of 60 ml/min, 6 h)

The carbon generated by CH₄ decomposition over the catalyst surface was revealed via hydrogenation reaction in order to return to CH₄ in TPH technique. The type of carbon species depend on transition metal and reaction condition. CH₄ production peaks in TPH profile (Fig.3) are observed at 570°C and 870°C which correspond to two different carbon surface species. The carbon removed at 570°C could be amorphous/graphitic carbon. The other carbon removed at 850°C and higher could be whisker type carbon [3].

Among all sample, 10Ni is the most appropriate catalyst for whisker carbon. The amount of whisker carbon decreased for 10Co and 9Ni1Co compared to 10Ni. Whisker carbon is stable resulting in most difficult to remove it from the surface of catalysts. Consequently, it can cause catalyst deactivation which

support the results in DMR activity test. Considering carbon surface in Fig.3, it seems that amorphous/graphitic carbon which can be eliminated in the reaction condition are more important for 7Ni3Co, 5Ni5Co, and 3Ni7Co than whisker carbon. Moreover, the amount of amorphous/graphitic carbon forms on 5Ni5Co and 3Ni7Co is almost negligible. Thus, 7Ni3Co, 5Ni5Co, and 3Ni7Co catalysts present sustainable activity.

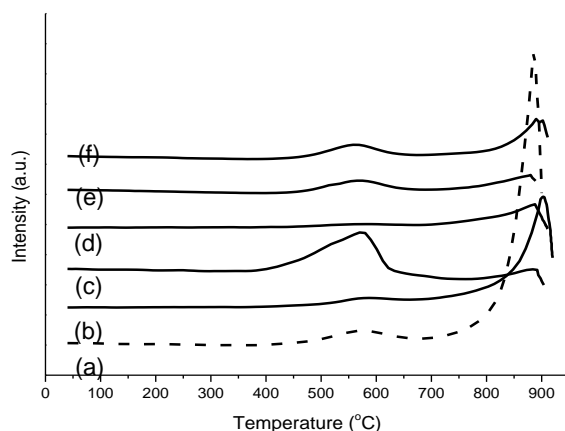


Figure 3. TPH profiles of (a) 10Ni, (b) 9Ni1Co, (c) 7Ni3Co, (d) 5Ni5Co, (e) 3Ni7Co, (f) 10Co catalyst

The CO₂-TPD profiles of the catalysts are shown in Fig.4. Adsorption peaks of CO₂ for all samples show similar patterns. Broad CO₂ desorption peaks are obtained from monometallic catalysts (10Ni and 10Co); whereas, CO₂ desorption peaks appear sharper for bimetallic catalysts (9Ni1Co, 7Ni3Co, 5Ni5Co, and 3Ni7Co). As seen in Fig.4, the main adsorption peak appears at 300°C approximately and the second peak at a high temperature range of 850°C–900°C. Low temperature peaks represent weak adsorption of CO₂ on weak basic sites and high temperature peaks refer to strong adsorption of CO₂ on strong basic sites. CO₂-TPD results indicate that a number of weak basic sites on the surface of bimetallic catalysts is greater than this number on the surface of monometallic catalysts. This result and TPH result indicated that weak basic sites enhance carbon deposition prevention.

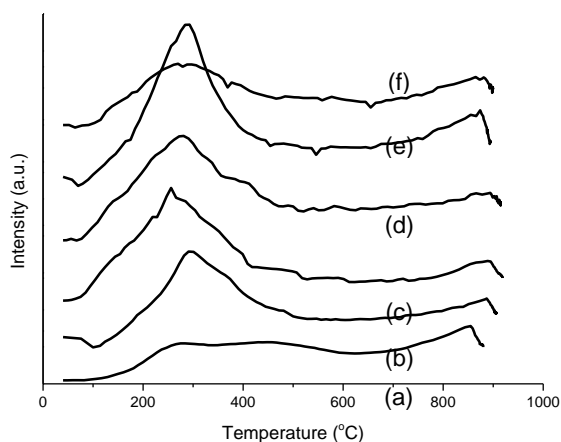


Figure 4. TPD- CO₂ profiles of (a) 10Ni, (b) 9Ni1Co, (c) 7Ni3Co, (d) 5Ni5Co, (e) 3Ni7Co and (f) 10Co

3.2 Performances and properties of 7%Ni3%Co1%K /MgO-Al₂O₃

From the previous results, it can be seen that Ni-Co catalysts show high stability toward whisker carbon surface. Even though 7Ni3Co is considered to be a carbon tolerance catalyst, amorphous/graphitic carbon is still important. During a long period of operating time, amorphous/graphitic carbon could be accumulated and developed into whisker carbon. This part presents the effect of K promoter on performance and property of 7Ni3Co1K.

In Fig.5 and 6, CH₄ conversion of 7Ni3Co sustains at 63%-64%. The additional of 1% K (7Ni3Co1K) lowers the conversion down to (53%) and decreases the selectivity (selectivity of CO₂ =46%)

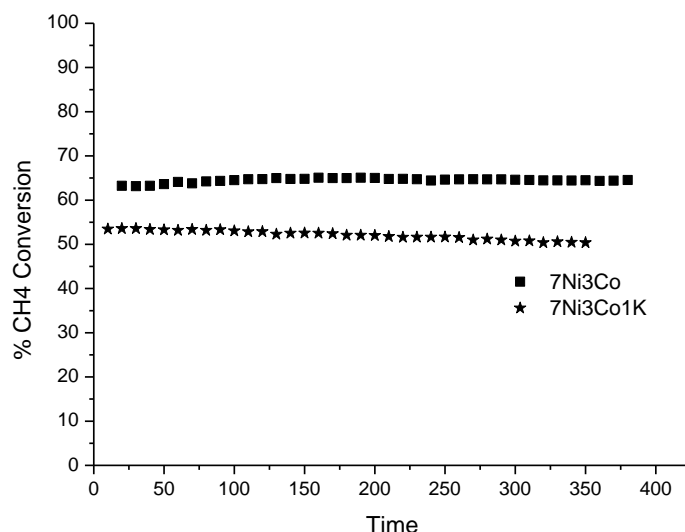


Figure 5. CH₄ conversion versus time on stream over for 7Ni3Co and 7Ni3Co1K catalyst under DMR reaction (620°C, CH₄:CO₂:N₂ = 3:5:4 with total flow rate of 60 ml/min, 6 h)

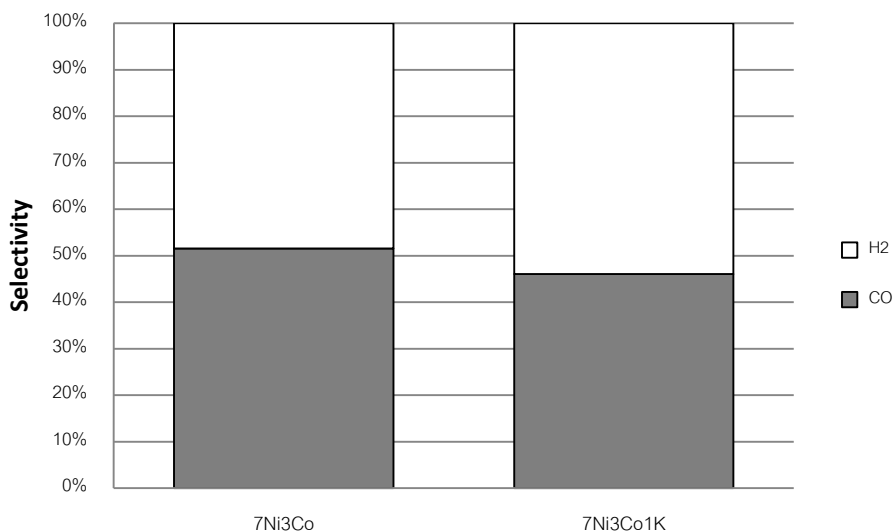


Figure 6. Selectivity of H₂ and CO for 7Ni3Co and 7Ni3Co1K catalysts DMR reaction condition (620°C, CH₄:CO₂:N₂ = 3:5:4 with total flow rate of 60 ml/min, 6 h)

TPH profiles in Fig. 7 reveal that K promoter plays a vital role in carbon resistance property. Adding K on 7Ni3Co surface prevents the formation of carbon not only whisker type but also amorphous/graphitic type. This result may also mention that the additional of K reduces CH_4 adsorption due to the change of surface [4]. Therefore, the CH_4 conversion was decreased during DMR.

The CO_2 -TPD profiles of 7Ni3Co and 7Ni3Co1K are compared Fig. 8. When 1% K is added, the CO_2 desorption peak at low temperature becomes lower and that at high temperature peak becomes higher. It indicated that the number of strong basic sites slightly increase but the number of weak basic site decrease. As a result, strong basic sites because of K promoter prevent carbon deposition over the surface. Because bonding between CO_2 and surface is stronger, it will promote different side reaction causing lower selectivity in catalytic test on DMR.

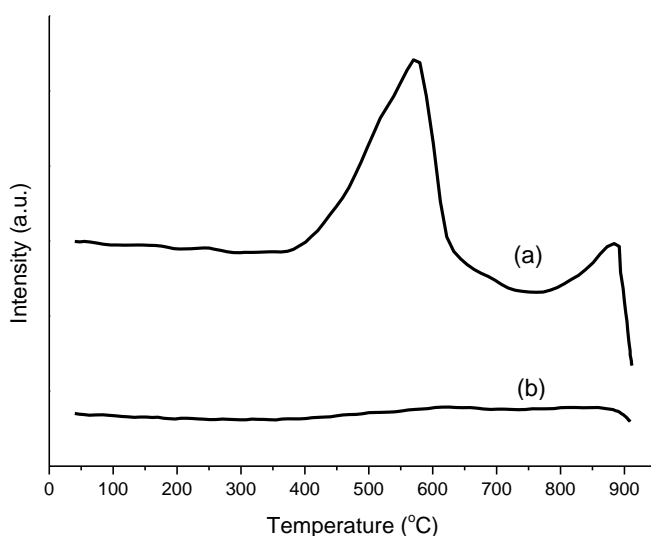


Figure 7. TPH of CH_4 on (a) 7Ni3Co and (b) 7Ni3Co1K catalysts

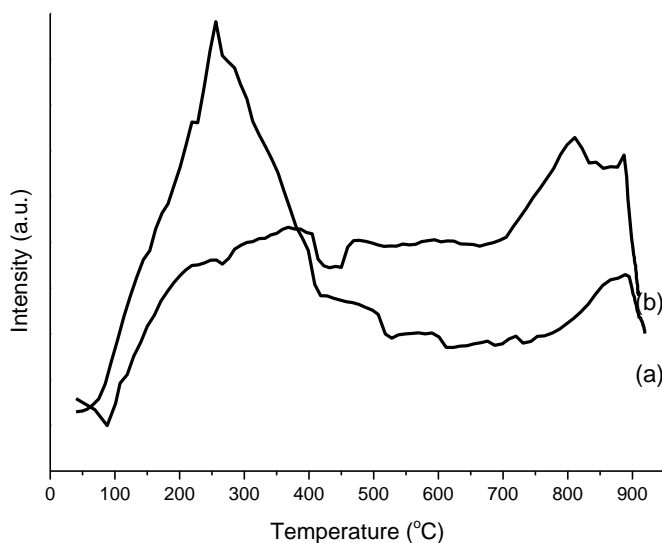


Figure 8. CO_2 -TPD profiles of (a) 7Ni3Co and (b) 7Ni3Co1K

4. CONCLUSION

The Ni-Co bimetallic catalyst show the improvement on stability and selectivity with sufficient activity in several metal fraction using sol-gel and impregnation method. 7Ni3Co 5Ni5Co and 3Ni7Co eliminates whisker carbon effectively due to the increasing of weak basic site compared to 10Ni.

The overall carbon deposition can be prevented by K promoter because of strong basic sites which affect reactant adsorption over the catalyst. Our future work is to investigate the catalyst morphology as well as other chemical properties.

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