Preparation and evaluation of mesoporous nickel and manganese bimetallic nanocatalysts in methane dry reforming process for syngas production

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Abstract. In this paper, Ni-Mn catalysts supported on mesoporous nanocrystalline γ -Al₂O₃ were prepared and employed in carbon dioxide reforming of methane for the production of synthesis gas. The physicochemical properties of the catalysts were determined by XRD, BET, TPO and SEM techniques. The obtained results revealed that the Mn-promoted catalysts exhibited higher activity and stability and lower degree of carbon formation compared to unpromoted nickel catalyst. The catalytic results showed that the 10 (wt%) Ni-3 (wt%) Mn/Al₂O₃ catalyst possessed the highest catalytic activity. The XRD results confirmed that the addition of Mn improves the dispersion of the active metal species on the catalyst or incorporates into the support due to a decrease in the crystallite size of Ni and consequently causes an increase in Ni dispersion. The 10 (wt%) Ni-3 (wt%) Mn/Al₂O₃ catalyst was stable during 20 hour on stream without any decrease in methane conversion.

Keywords. Dry reforming; Ni catalyst; syngas; nanocrystal; Mn promoter; mesoporous material.

1. Introduction

The increase in the concentration of CH₄ and CO₂ (greenhouse gases) causes a continuous increase in the surface temperature of the earth (Global warming), which is a serious atmospheric problem all over the world. These two greenhouse gases could be eliminated from the atmosphere by catalytic reactions such as dry reforming of methane.^{1,2}

The other preference for this reaction is producing synthesis gas. Syngas, the abbreviation of synthesis gas, is a fuel gas mixture consisting primarily of hydrogen and carbon monoxide. One of the uses of this syngas is as a fuel to manufacture steam or electricity. But the main usage is in petrochemical and refining processes as a feedstock for the production of methanol, H₂, liquid hydrocarbons, *etc.*³⁻⁵ The gasification process is applied to convert light hydrocarbons to longer hydrocarbon chains.

During the dry reforming of methane process, methane combines with carbon dioxide to generate synthetic natural gas (SNG). Dry reforming of methane is

shown by the reaction below, and it is highly endothermic (above 800 °C) and requires high amount of energy to achieve high conversion of both reactants due to the strong endothermic nature of the reaction.⁶⁻⁸

Until now, the wide range of mono metallic components and alloys have been used for the dry reforming reactions.^{7,9} Availability and low price of the nickel-based catalysts has led to the widespread use of it and also have attracted significant interest for the dry reforming reaction.¹⁰ However, the major objection to the use of Ni-based catalysts is the rapid deactivation of these catalysts in this reaction. For instance, sulfur poisoning and carbon formation due to Boudouard or methane decomposition decrease the catalytic activity and also reverse the water gas shift reaction (RWGS) that consumes the H₂, which causes the decrease in H₂ selectivity.¹⁰⁻¹³ As mentioned, the coke forms mainly from two reactions⁹:

The methane decomposition:

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The Boudouard reaction:

These two carbon formation reactions can destroy the catalyst particles and block the reactor and deactivate the catalysts employed in dry reforming reaction.¹³ In addition, the RWGS reaction is ascribed by the equation below^{14–16}:

The deposited carbon was the main reason for catalyst deactivation as indicated by the analysis in dry reforming of methane. The deposited carbon can accumulate on the catalyst surface and cover the active sites and consequently deactivate the employed catalysts.⁵ To suppress carbon formation over Ni-based catalysts, many attempts have been made.^{17–22}

Using the bimetallic catalysts could be a good option for enhancing activity and stability and also inhibiting coke formation in dry reforming, which could be attributed to the synergic interactions between the metals.^{11,12} Choi and co-workers²³ investigated the promotion effect of second metals such as Mn, Ti, Mo, Co, Zr, Cu, Sr and Ag on Ni/Al₂O₃ catalysts. It was found that the modified Ni-Co/Al₂O₃, Ni-Cu/Al₂O₃ and Ni-Zr/Al₂O₃ catalysts are non-resistant in coke formation but had better performance in activity. Although the Mn-promoted catalyst showed a remarkable reduction in coke deposition but it sacrificed the catalytic activity.^{10,23,24} Seok²⁴ reported that the addition of Mn to Ni/Al₂O₃ catalysts decreased the amount of deposited carbon in dry reforming reaction. The Ni/MnOx/MnAl₂O₄ catalyst prepared by a coprecipitated method exhibited higher resistance against carbon formation and higher catalytic stability than the same catalyst prepared by impregnation method.^{10,24} Borowiecki *et al.*,²⁵ reported that the addition of Mo to Ni/Al₂O₃ catalysts decreased the rate of deactivation in reforming reaction. They also showed that the addition of molybdenum as promoter significantly reduced the carbon formation and improved the activity of catalysts in steam reforming of methane.^{12,25} Quincoces *et al.*,⁵ showed that the addition of molybdenum to nickel catalyst increased the interaction between the catalyst support and nickel, and also inhibited the growth of Ni particles.

Castro Luna and Iriarte⁴ reported the positive effects of different promoters (Mn, K, Ca and Sn) on the catalytic performance of the Ni/Al₂O₃ catalyst. The results showed that the addition of Mn, Sn and Ca caused a significant decrease in catalytic activity and a dramatic increase in carbon formation. Alumina and SiO₂ have

been considered as support for Ni-based catalysts due to high availability and high specific surface.² In particular, mesoporous Al₂O₃ supported Ni catalysts exhibited excellent catalytic performance for the dry reforming reaction.²⁶

In this paper, the effect of Mn promoter on the structural and catalytic properties of nickel catalysts supported on mesoporous nanocrystalline alumina is reported. In addition, the coke formation was studied over the promoted catalysts to investigate the inhibiting effect of Mn promoter on carbon formation.^{10,24,27}

2. Experimental

2.1 Sample preparation

The γ -Al₂O₃ support was prepared by the sol-gel method using the aluminium tri-isopropylate as Al precursor based on the method described in our previous work.⁹ In this sol-gel method, the aluminium precursor was hydrolyzed (at 80–85 °C for 1 h) in distilled water. After this step, the nitric acid (HNO₃ to Al molar ratio = 1:1) was added to the prepared solution to obtain the sol after aging the obtained mixture at 98 °C for 12 h. For gel formation, the prepared sol was maintained at 98 °C for 2 h in the atmosphere. Then the prepared gel was dried at 80 °C and calcined at 600 °C for 4 h. The catalysts with 10 wt% Ni and various Mn contents were prepared by wet impregnation method. For this purpose, the catalyst support (γ -alumina) was impregnated with an aqueous solution of Mn(NO₃)₂ · 4H₂O with appropriate concentration at room temperature to obtain the desired content of Mn. After impregnation, the suspension was dried at 80 °C overnight and calcined at 450 °C in air. After that, the promoted support was impregnated by an aqueous solution of Ni(NO₃)₂ · 6H₂O with the same method described above and calcined at 500 °C for 4 h.

Ni–Mn bimetallic catalyst was also prepared by a coprecipitation method. The metal salt precursors with desired contents (Ni(NO₃)₂ · 6H₂O, Mn(NO₃)₂ · 4H₂O and Al(NO₃)₃ · 9H₂O) were dissolved in deionized water under stirring. Then, an aqueous solution of NaOH was added dropwise to the prepared solution at room temperature and the pH was adjusted to 11. The prepared suspension was filtered, washed and dried at 85 °C overnight and calcined at 500 °C for 4 h.

2.2 Characterization

The BET surface area, pore volume and average pore diameter of the catalysts were determined via N₂ adsorption at boiling temperature of liquid nitrogen at –196 °C using a BELSORP Mini II analyzer. The pore size distribution was calculated from the desorption branch of the isotherm by the Barrett-Joyner-Halenda (BJH) method. The crystal structures of the prepared samples were obtained using an X-Ray diffractometer (PANalytical X'Pert-Pro) by a Ni filter in the range of

Table 1. Textural properties of various samples.

Catalyst	Active metal composition (wt%)		S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Average pore diameter (nm)	Crystal size (nm)
	Ni	Mn				
10Ni 1Mn	10	1	167.1	0.4	10.2	5.8
10Ni 3Mn	10	3	166.3	0.4	10.6	7.8
10Ni 5Mn	10	5	150.1	0.4	10.1	8.7
10Ni	10	0	171.7	0.5	10.6	—
5Mn	0	5	182.9	0.5	10.8	—
γ -Alumina	0	0	185.9	0.5	10.7	—

$2\theta = 10\text{--}80^\circ$ using the Cu-K α monochromatized radiation source. The reduction properties of the calcined catalysts were evaluated by the temperature programmed reduction (TPR) analysis with a Micromeritics chemisorb 2750 instrument. In this analysis, a specific amount of catalyst (100 mg pretreated under an inert atmosphere (Ar) at 200°C for 1 h) was subjected to a heat treatment ($10^\circ\text{C}/\text{min}$), while a reducing gas flow ($30\text{ mL}/\text{min}$) containing a mixture of H_2 : Ar (10:90) was passed over the catalyst surface. A thermal conductivity detector (TCD) measured the H_2 consumption during the reduction process. Temperature-programmed oxidation (TPO) analysis of the spent catalysts was performed with a similar instrument as described for TPR analysis. In this analysis, a gas flow ($30\text{ mL}/\text{min}$) of O_2 :He (5:95) mixture was passed over 25 mg of the spent catalyst and the temperature increased at a heating rate of $10^\circ\text{C min}^{-1}$ up to 800°C . A VEGA TESCAN microscope operated at 30 kV was used for studying the morphology the prepared samples.

2.3 Catalytic evaluation

A quartz tubular fixed-bed reactor was used for determining the catalytic performance of the prepared catalysts under atmospheric pressure. The calcined catalyst powders were pressed, crushed and sieved to obtain catalyst particles with specified sizes. The quartz reactor was loaded with 200 mg of the catalyst particles (35–60 mesh) and the catalysts were reduced *in situ* at 600°C for 4 h in an H_2 stream ($25\text{ mL}/\text{min}$). Later, the reactant gas mixture containing methane and carbon dioxide with the desired ratio was introduced into the reactor, and the activity tests were carried out at various reaction temperatures in the range of $550\text{--}700^\circ\text{C}$. The mole percent of different components in reactants and products was determined using a gas chromatograph equipped with a TCD and a Carboxen 1000 column. The conversion of methane and carbon dioxide and the yields of hydrogen and carbon monoxide were obtained from the following equations^{14,28}:

Methane conversion:

$$X_{\text{CH}_4} = \frac{\text{CH}_{4(\text{in})} - \text{CH}_{4(\text{out})}}{\text{CH}_{4(\text{in})}} \times 100\% \quad (5)$$

Carbon dioxide conversion:

$$X_{\text{CO}_2} = \frac{\text{CO}_{2(\text{in})} - \text{CO}_{2(\text{out})}}{\text{CO}_{2(\text{in})}} \times 100\% \quad (6)$$

$$\text{Hydrogen yield: } \frac{\text{H}_{2(\text{out})}}{2\text{CH}_{4(\text{in})}} \times 100\% \quad (7)$$

3. Results and Discussion

3.1 Physicochemical properties

The results of BET analysis are summarized in Table 1. It is seen that the catalyst support exhibited high specific surface area and pore volume with a small average pore size around 10 nm. The addition of nickel to catalyst support decreased the BET area and pore volume due to partial blockage of the pores of the alumina with NiO particles.^{4,15,29} Furthermore, the addition of Mn promoter, increasing in its content caused decrease in BET area and pore volume. However, the addition of nickel and Mn does not have a significant effect on the average pore size. The lowest BET area was observed for the 10Ni-5Mn/ Al_2O_3 catalyst, due to the highest amount of nickel and Mn promoter. The Mn/ Al_2O_3 catalyst also exhibited high specific surface area and pore volume with small pore size, which are close to those observed for Al_2O_3 .

The N_2 adsorption/desorption isotherms and pore size distributions are shown in Figure 1a and b, respectively. According to the IUPAC classification, the isotherms of all catalysts can be categorized as type IV with H_2 hysteresis loops, which is related to mesoporous materials with cylindrical shaped pores.^{16,29}

As the size of pores increased, the hysteresis loop shifted to the right in the diagram. At high relative pressures, nitrogen adsorption occurs in larger mesopores. It is seen that the type of the isotherm of the alumina support was not affected by the addition of Ni and Mn.

Pore size distributions of all catalysts are presented in Figure 1b. All catalysts show a narrow single modal

Figure 1. (a) N₂ adsorption/desorption isotherms and (b) pore size distributions of the prepared samples.

pore size distribution with a maximum centered around 4 nm (pore radius). The observed pore radius of all catalysts was located between 2–6 nm. Such mesoporous structures played a significant role for a metallic catalyst to prevent the agglomeration of active phase through the confined effect, which restricts the growth of Ni crystallites during high temperature reaction.²⁹

X-ray diffraction analysis was used for identification of bulk phase features of the Ni-Mn bimetallic supported catalysts. The XRD patterns of the calcined Ni-Mn/Al₂O₃ catalysts with different contents of Mn are shown in Figure 2.

The characteristic diffractions at 37°, 45° and 67° are corresponding to the spinel-like structure NiAl₂O₄ (JCPDS Card No = 077-1877) phase that has a coincidence with γ-Al₂O₃ (JCPDS Card No = 010-0425) phase. The peaks at 37°, 43° and 63° are related to the NiO (JCPDS Card No = 073-1519) phase. The low intensity of these peaks can be related to the low percentage of this phase and it may overlap with other peaks due to the same particle size.^{2,14,17,28}

There are two new diffraction peaks observed in the XRD pattern of 10Ni5Mn/γ-Al₂O₃ and 5Mn/Al₂O₃ catalysts. The first peak at 28.7° and the second one at 56.9° are attributed to the formation of MnO₂ solid phases. It displays the MnO₂ species afforded through the catalyst construction. According to the JCPDS Code No (004-0779), the MnO₂ phase is a tetragonal crystalline phase.^{2,9,30} The intensity of MnO₂ diffraction patterns differs and increases with the increase in Mn content. Also at the high amount of Mn promoter, the intensity of NiO and NiAl₂O₄ phases decreased, indicating that Mn improves the dispersion of the active metal species on the catalyst or incorporates into the support due to a decrease in Ni crystallite size and consequently causes an increase in Ni dispersion.³¹ The other reason can be the competition formation of crystalline phases like NiMn₂O₄ or even amorphous phase of Mn-Ni. The crystalline NiMn₂O₄ phase was observed at 2θ = 35°, 43°, 57° and 62° (Reference code No = 001-1110) and overlaid with the MnO₂ phase of Mn.

Some other phases like MnAl₂O₄ are not recognized because these species need a high temperature to form while the calcination temperature of these samples was 600 °C.^{2,9,17} The active metal crystallite size was determined using the Scherrer equation and the results are reported in Table 1.

$$D = \frac{R \times \lambda}{\beta \times \cos \theta} \quad (8)$$

In this equation, D is the active metal particle size, R is the Scherrer constant (0.89), λ is the wavelength of X-ray (1.5408 Å), θ is the diffraction angle, and β is the line broadening at half the maximum intensity (radian). The results showed that increase in Mn content increased the NiO crystallite size.¹⁶

Hydrogen temperature-programmed reduction (H₂-TPR) experiments were applied to investigate the reducibility of the catalysts. TPR analysis is a technique for the characterization of solid components and is used to find the most efficient reduction conditions. In this experiment, an oxidized catalyst precursor is submitted to a programmed temperature rise while a reducing gas mixture flows over it.

The TPR profiles of the calcined catalysts are shown in Figure 3. The peak temperature of the TPR profile usually indicates the combined status of the active metals and the support.

The TPR analysis showed the presence of several reduction peaks at various temperatures. For the Ni/Al₂O₃ catalyst, the first small reduction peak at around 480 °C is related to the reduction of nickel oxide with weak interaction with catalyst support. The

Figure 2. XRD patterns of Ni-Mn/Al₂O₃ catalysts with different loadings.

main reduction peak observed at 650 °C is related to nickel oxide with strong interaction with Al₂O₃ and the shoulder peak at 800 °C is assigned to the reduction of nickel aluminate. It seems that the addition of Mn promoter shifted the $T_{\max}$ of the first and second reduction peaks to lower temperatures. For the 10Ni-1Mn/Al₂O₃ catalyst, no peaks were observed for reduction of manganese oxide, due to the low content of that. However, for the catalysts with Mn content higher than 1 wt%, two reduction peaks appeared at 350 °C–450 °C were related to the reduction of different species of manganese oxide. In 10Ni-3Mn/Al₂O₃ catalyst the first reduction peak at 300 °C is associated with the reduction of MnO₂ to Mn₂O₃ and the second reduction peak at a higher temperature (350 °C) is related to the reduction of Mn₂O₃ to MnO. For better understanding, the TPR profile of the 5Mn/Al₂O₃ catalyst is also shown in Figure 3. As can be seen, two reduction peaks were observed at 300 °C and 400 °C, which are related to the reduction of MnO₂ to Mn₂O₃ and Mn₂O₃ to MnO, respectively. Increase in Mn content intensified the peaks related to the reduction of manganese oxide species.^{3,14,16,27,28,32,33}

3.2 Catalyst performance

As indicated in Figure 4a and b with an increase in the reaction temperature, the conversion of CH₄ and CO₂ increased, because of the endothermic nature of methane reforming with carbon dioxide.

Figure 3. TPR profiles of Ni-Mn/Al₂O₃ catalysts.

It is also obvious that the conversion of CO₂ is higher than that of CH₄ on the unpromoted and promoted catalysts due to the reverse water-gas shift reaction.

To investigate the catalytic performance of the bimetallic catalysts, the catalytic results of single-metal catalysts are also shown in Figure 4a and b. It is seen that the addition of Mn as second metal influences the reactants conversion, specifically the methane conversion. This could be due to the revenue of the catalyst in the reaction. The procedure of the main reaction demonstrates that the methane molecules decomposed on the

Figure 4. (a) CH₄ conversion; (b) CO₂ conversion; and (c) H₂/CO ratio. Reaction conditions: CH₄/CO₂ = 1/1, GHSV = 12,000 (mL/h · g_{cat}).

surface of nickel and carbon dioxide molecules on the support. Mn addition causes the significant structural influences on the catalyst which enhanced the NiO dispersion and the formation of NiMn₂O₄ resulting in the

Figure 5. Short time stability of 10Ni3Mn/Al₂O₃ catalysts with various Mn loadings. (a) Methane conversion, (b) carbon dioxide conversion. Reaction conditions: CH₄:CO₂ = 1:1, T = 700 °C and GHSV = 12000 mL/(g_{cat} · h).

Figure 6. Long-term stability of the optimal 10Ni3Mn/Al₂O₃ catalyst, CH₄:CO₂ = 1:1, T = 700 °C and GHSV = 12000 mL/(g_{cat} · h).

Figure 7. (a) Effect of GHSV, (b) effect of feed ratio on the catalytic activity, and (c) effect of feed ratio on the catalytic performance of 10Ni-3Mn/Al₂O₃. Reaction condition: T = 700 °C.

stronger interaction of NiO with the support. So by increasing the dispersion of nickel and due to reaction mechanism, obviously the conversion of methane in the

Figure 8. TPO profiles of Ni-Mn/Al₂O₃ catalysts with different loadings; (1) 10Ni, (2) 10Ni2.5Mn, (3) 10Ni8Mn, (4) 10Ni1Mn, (5) 10Ni3Mn and (6) 10Ni5Mn.

case of the bimetallic catalyst is higher than the single mode.¹⁰

Since the manganese applies only structural changes in the catalyst and is not an active metal so the 5Mn catalyst did not show a high catalytic activity. In addition, the catalytic activity of the promoted catalysts with different Mn contents is very close together.

The catalysts were exposed to the reaction atmosphere for 300 min at 700 °C to study the catalytic stability of the prepared catalysts. The results showed that all the catalysts had a very high stability without decreasing in CH₄ conversion over the test period of 300 min, Figure 5a. Long-term stability the optimal 10Ni3Mn/Al₂O₃ catalyst was performed (Figure 5b).

The results representing the high stability of this catalyst during 20 h time on-stream under the reaction conditions (Figure 6).

GHSV is one the most important process parameters that affect the catalyst performance. With the increase in GHSV, the residence time of reactants on the catalyst decreases and causes a decrease in conversion of reactants (Figure 7a).

The effect of feed ratio on the catalytic performance of 10Ni3Mn/Al₂O₃ catalyst at 700 °C is plotted in Figure 7b. The acquired results show that with the increase in the CO₂/CH₄ ratio, the CH₄ conversion increased, whereas the CO₂ conversion decreased, due to the presence of excess CO₂ in the main reaction (1). As previously mentioned, the excess CO₂ in this reaction increased the rate of RWGS reaction, which led to a decrease in H₂/CO ratio, Figure 7c.³⁴

Figure 9. SEM images of (a) 10Ni/Al₂O₃, and (b) 10Ni₃Mn/Al₂O₃. Reaction conditions: CH₄/CO₂ = 1, GHSV = 12000 mL/(g_{cat} · h), time on the stream = 300 min.

The substantial purpose of working on an extra metal besides the nickel is to suspend the coke formation. Therefore, to evaluate the impressment of the manganese as a second metal, the TPO analysis was done.³⁵ Temperature-programmed oxidation patterns of the spent catalysts are represented in Figure 8. All the samples have one oxidation peak which indicates the

type of formed carbon in the process of dry reforming of methane. The peak at approximately 700 °C can be related to the filamentous form of carbon. Other species such as activated carbon and amorphous carbon are formed at lower temperatures and have not been observed in the TPO profiles of these catalysts.^{7,9}

Figure 9a and b shows the SEM images of the spent 10Ni/Al₂O₃ and 10Ni₃Mn/Al₂O₃, respectively. In both the samples, the whisker-type carbon was observed. However, the SEM analysis showed that the promoted catalyst with 3 wt% Mn exhibited a lower degree of carbon formation compared to the unpromoted catalyst, which is in agreement with TPO analysis.^{7,9,18,28}

4. Conclusions

The Ni-Mn/Al₂O₃ bimetallic catalysts with different loadings of Mn were prepared and employed in the dry reforming reaction. The results showed that the bimetallic catalysts exhibited higher activity and stability with no severe coke deposition compared with the monometallic sample.

The results indicate that the 10Ni₃Mn/Al₂O₃ catalyst was the optimal catalyst among the prepared catalysts. According to the XRD patterns, the addition of Mn promoter caused a decrease in the intensity of NiO and NiAl₂O₄ diffraction patterns, indicating that Mn improves the dispersion of the active metal species in the catalyst or incorporates into the support due to a decrease in the crystallite size of Ni and consequently causes an increase in Ni dispersion.

With the increase in GHSV, the residence time of reactants on the catalyst decreases and causes a decrease in conversion of reactants. The acquired results show that with the increase in the CO₂/CH₄ ratio, the CH₄ conversion increased, whereas the CO₂ conversion decreased, due to the presence of excess CO₂ in the main reaction. The SEM analysis showed that the promoted catalyst with 3 wt% Mn exhibited a lower degree of carbon formation compared to unpromoted catalyst.

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