Reforming of Methane by CO$_2$ over Bimetallic Ni-Mn/$\gamma$-Al$_2$O$_3$ Catalyst

Anis Hamza Fakeeha, Muhammad Awais Naeem, Wasim Ullah Khan, Ahmed Elhag Abasaedd, Ahmed Sadeq Al-Fatesh*

Chemical Engineering Department, College of Engineering, King Saud University, P.O. Box 800, Riyadh 11421, Kingdom of Saudi Arabia

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$\gamma$-Al$_2$O$_3$ supported Ni-Mn bimetallic catalysts for CO$_2$ reforming of methane were prepared by impregnation method. The reforming reactions were conducted at 500–700 °C and atmospheric pressure using CO$_2$/CH$_4$/N$_2$ with feed ratio of 17/17/2, at total flow rate of 36 mL/min. The catalytic performance was assessed through CH$_4$ and CO$_2$ conversions, synthesis gas ratio (H$_2$/CO) and long term stability. Catalytic activity and stability tests revealed that addition of Mn improved catalytic performance and led to higher stability of bimetallic catalysts which presented better coke suppression than monometallic catalyst. In this work, the optimum loading of Mn which exhibited the most stable performance and least coke deposition was 0.5wt%. The fresh and spent catalysts were characterized by various techniques such as Brunauer-Emmett-Teller, the temperature programmed desorption CO$_2$-TPD, thermogravimetric analysis, X-ray diffraction, scanning electron microscope, EDX, and infrared spectroscopy.

Key words: CH$_4$, CO$_2$, Bimetallic, Dry reforming, Ni/$\gamma$-Al$_2$O$_3$, Mn and H$_2$/CO

I. INTRODUCTION

Steam reforming, carbon dioxide reforming and partial oxidation of methane are the dominant routes to convert methane into syngas (mixture of H$_2$ and CO). Methane is one of the major greenhouse gases that contribute to global warming (4%–9% of green-house gases). The other green-house gases include carbon dioxide (9%–26%) and water-vapor (36%–70%) [1]. Production of syngas by catalytic CO$_2$ reforming of methane, also called dry reforming, has attracted a great attention from last decade due to simultaneous utilization and/or reduction of two greenhouse gases i.e., CH$_4$ and CO$_2$. The other advantage of dry reforming is the production of low H$_2$/CO ratio, close to unity that favors the synthesis of methanol and other valuable liquid hydrocarbons (Fischer Tropsch synthesis) [2, 3]. Mostly group VIII metals (Ru, Ir, Pd, Pt) and Ni-based catalysts in combination with various supports and promoters have been studied for CO$_2$ reforming of methane [4]. It was found that the Boudouard reaction and/or methane decomposition hinder the successful industrial application of the process. In fact these side reactions deactivate the catalyst due to coke formation over its surface. In order to overcome this obstacle, it is necessary to develop a coke resistant catalyst. The noble metal based catalysts are found to be more active and higher coke resistant than nickel based catalysts but the main limitation of noble metals is their high cost and scarcity. Therefore, it is beneficial to develop improved Ni-based catalysts which are coke resistant, highly active and exhibit stable operations for long periods [4, 5]. Alumina supported nickel which is the usual component of commercial steam reforming catalyst, has been tested for CO$_2$ reforming of methane; it showed high initial activity but encountered severe carbon deposition [6–8]. Different modifiers like Co, Cu, Zr, Mn, Ti, and Ag were added to Ni/Al$_2$O$_3$ catalyst to reduce the carbon deposition and increase activity. Mn has already attracted considerable interest because of its unique properties in different areas of catalysis. During the reaction, Mn undergoes oxidation reduction cycles due to its ability of altering oxidation states. This distinctive property of Mn is catalytically very advantageous [9–12].

Park et al. studied steam reforming of liquid petroleum gas over Mn promoted Ni/$\gamma$-Al$_2$O$_3$ catalysts [13]. They reported that the catalytic activity and stability was strongly influenced by addition of Mn and its impregnation sequence in Ni/$\gamma$-Al$_2$O$_3$ catalyst. Wang et al. found that the catalytic activity and stability of the nanocrystalline Co-Co-Zr-O$_2$ catalyst increased with Mn addition [14]. They revealed that improved activity and stability is credited to the presence of surface oxygen species and their mobility. Luna and Iriarte studied the effect of adding 0.5wt% of metals including K, Ca, Sn, and Mn to Ni-Al$_2$O$_3$ catalyst and concluded that K-modified Ni-Al$_2$O$_3$ catalyst exhibited excellent stability with slight decrease in activity for 30 h re-

*Author to whom correspondence should be addressed. E-mail: aailfatesh@ksu.edu.sa, Tel.: +9661-4676859, FAX: +9661-4678770

action [15]. Choi et al. inferred that modification of Ni/Al$_2$O$_3$ catalyst using Mn led to excellent coke suppression. Moreover they concluded that Mn promoted catalyst exhibited very stable performance with only slight decrease in activity during dry reforming reaction for 100 h time on stream (TOS) [16].

Moreover, in addition to dry reforming, role of Mn as coke suppressing promoter for various catalytic reactions such as steam reforming of naphthalene and dehydrogenation of ethane has also been studied and showed very promising results. In the former reaction, Mn doping to ceria-zirconia supported Ni catalyst enhanced oxygen storage capacity which resulted in coke gasification while in dehydrogenation of ethane addition of Mn increased CO$_2$ activation and thus enhanced catalyst resistance to coke deposition [17, 18].

In the present work, a set of γ-Al$_2$O$_3$ supported Ni-Mn bimetallic catalysts with different Ni/Mn molar ratios were developed and tested in carbon dioxide reforming of methane, in order to suppress carbon formation by coke suppressing promoter for various catalytic reactions such as dry reforming of naphthalene and dehydrogenation of ethane [17].

II. EXPERIMENTS

A. Catalyst preparation

The 5wt% nickel/support catalysts were prepared by wet impregnation method using nickel nitrate salts as Ni precursor and γ-Al$_2$O$_3$ ($S_{BET}$=196 m$^2$/g) as a support. Solutions containing known amount of nitrate salts were prepared in distilled water, then γ-Al$_2$O$_3$ was impregnated with the previously prepared solution of active metal. The Ni-Mn bimetallic catalysts with different loadings of Mn (0, 0.5wt%, 1wt%, 2wt%, 4wt%, 5wt%) were prepared by co-impregnation of nitrate salts of the Ni and Mn with γ-Al$_2$O$_3$ support using the same procedure mentioned above. After impregnation the prepared catalysts were dried at 120 °C for 16 h and subsequently calcined at 700 °C for 3 h. For simplicity, Ni-Mn-Al bimetallic catalyst was denoted as Ni-xMn-Al (where $x$ denotes the percent of Mn in the catalyst; the reference catalyst, i.e., with 0%Mn will be as Ni-Al).

B. Catalyst characterization

The catalysts (before and after reaction) were characterized by various experimental techniques. The specific surface area of catalysts was determined by nitrogen (N$_2$) adsorption at −196 °C by using standard Brunauer-Emmett-Teller (BET) method in an automated gas adsorption instrument (Micromeritics Tristar II 3020). The structure of the synthesized catalysts was examined by X-ray diffraction (XRD), Rigaku (Miniflex), using Cu Kα radiation. Diffraction peaks recorded in a 2θ range of 10°−80° were used to identify the structure of the samples. Carbon formation on the surface of used catalysts was quantified by thermogravimetric analysis (TGA) in air atmosphere using EXSTAR SII TG/DTA 7300 analyzer. The used catalyst sample 10−20 mg in quantity was heated from room temperature to 800 °C at a heating rate 20 °C/min. The morphology of the catalysts was analyzed by scanning electron microscope (SEM), JEOL JSM-6360A. For estimation of basicity the temperature programmed desorption (CO$_2$-TPD) measurements were carried out on Micromeritics Auto Chem II 2920 apparatus. Fourier transform infrared spectroscopy (FTIR) experiments of samples were analyzed with a Bruker Vertex 70 spectrometer in the range of 4000−400 cm$^{-1}$.

C. Catalytic reaction

The CO$_2$-CH$_4$ reforming reaction was carried out at atmospheric pressure in a 9.4 mm i.d. and 48 cm long stainless steel fixed-bed tubular microreactor (2000 AMI Zeton altimira) using 0.3 g of the catalyst. The reaction temperature was measured by a thermocouple placed in the center of the catalyst bed. The volume ratio of the feed gases (CH$_4$:CO$_2$:N$_2$) was 17:17:2. The total flow rate and space velocity were 36 mL/min and 120 mL/min·g$_{cat}$, respectively. Prior to the reaction the catalyst was activated by passing H$_2$ at 650 °C for 2 h (30 mL/min). The reforming activity was studied at temperature range from 500 °C to 700 °C. The effluents were analyzed using an online gas chromatograph (3400 cx,Varian Star) equipped with a thermal conductivity detector. Details of experimental setup and procedure can refer to Ref.[19].

III. RESULTS AND DISCUSSION

A. Specific surface area and X-ray diffraction

The results of specific surface areas ($S_{BET}$) of both fresh and spent catalysts are shown in Table I. The surface areas for all mono- and bimetallic fresh catalysts are very close (181.3−190.9 m$^2$/g) except Ni-5Mn-Al catalyst, which showed the smallest surface area (159.7 m$^2$/g) that contributed to lower activity. Moreover 10%−20% decrease in surface area occurred after 7 h of operation at 700 °C. The decrease in area might be originated from two sources; thermal sintering of active metal and carbon deposition [20].

The XRD patterns of fresh catalysts are shown in Fig.1. From the given diffractograms, it is difficult to distinguish between γ-Al$_2$O$_3$ and NiAl$_2$O$_4$ due to peak broadening and overlying of alumina and metal-aluminate phases. The diffraction peaks detected at 2θ=45.6° and 2θ=66.7° are ascribed to γ-Al$_2$O$_3$
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FIG. 1 XRD patterns of $\gamma$-Al$_2$O$_3$ supported on mono- and bi-metallic fresh catalysts.

TABLE I Catalytic performance of xwt%Mn+5wt%Ni/$\gamma$-Al$_2$O$_3$ catalysts.

<table>
<thead>
<tr>
<th>Mn</th>
<th>$S_{BET}$/$\text{m}^2/\text{g}$</th>
<th>Coke$/%$</th>
<th>$S_{BET}$/$\text{m}^2/\text{g}$</th>
<th>DF$/%$</th>
</tr>
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<tr>
<td>0.0</td>
<td>181.3</td>
<td>9.73</td>
<td>161.9</td>
<td>2.89</td>
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<td>0.5</td>
<td>188.2</td>
<td>4.86</td>
<td>157.5</td>
<td>1.12</td>
</tr>
<tr>
<td>1.0</td>
<td>190.9</td>
<td>7.89</td>
<td>170.3</td>
<td>1.75</td>
</tr>
<tr>
<td>2.0</td>
<td>186.6</td>
<td>8.96</td>
<td>159.2</td>
<td>2.20</td>
</tr>
<tr>
<td>4.0</td>
<td>189.9</td>
<td>9.23</td>
<td>156.1</td>
<td>2.37</td>
</tr>
<tr>
<td>5.0</td>
<td>159.7</td>
<td>9.66</td>
<td>150.3</td>
<td>2.64</td>
</tr>
</tbody>
</table>

a Fresh catalyst.  
b Determined by TGA after 7 h of reaction at 700 °C.  
c Spent catalyst.  
d Deactivation factor = [(initial CH$_4$ conversion-final conversion CH$_4$)/initial conversion of CH$_4$]×100%.

(JCPDS: 00-029-0063) and/or NiAl$_2$O$_4$ spinel phase (JCPDS: 00-010-0339), whereas the diffraction peak observed at $2\theta$=37.2° corresponds to NiO (JCPDS: 01-073-1519). It is worthwhile to note that in all these catalysts, no MnO diffraction peak was detected, which may be due to its homogeneous dispersion throughout the catalyst and/or its small concentration of Mn, which is beyond the detection limits of XRD.

B. Temperature programmed reduction

To understand the effect of Mn loading on the reducibility of bimetallic catalysts, temperature-programmed reduction (TPR) experiments are used to investigate the degree of interaction between active metal and support. The TPR profiles of the fresh mono and bimetallic catalysts are shown in Fig.2. In comparison, for Ni-Al and Ni-0.5Mn-Al catalyst only one dominant peak is observed at 810 and 825 °C respectively, which can be associated to Ni species having strong interaction with support. However, at higher Mn loadings two main reduction peaks are observed; one broad peak at lower temperature <400 °C, while the other at higher temperature >800 °C. These higher temperature reduction peaks can be assigned to reduction of NiO species having strong interaction with support, while lower temperature reduction peaks could be related to reduction of MnO$_x$ species and/or reduction of NiO species which weakly interact with support respectively. Moreover, the lower temperature reduction peak in Ni-4Mn-Al catalyst is much bigger than Ni-Al and Ni-2Mn-Al catalysts, which suggested that more reduction of MnO$_x$ species took place at higher Mn loading. The reduction of MnO$_x$ species at current observed temperature is in agreement with the data reported in Ref.[21]. Generally, the reduction peaks at higher temperature (>800 °C) correspond to reduction of NiAl$_2$O$_4$ spinel species as reported in Ref.[22]. These spinel species are formed during calcination as a result of strong metal-support interaction. In case of Ni/Al$_2$O$_3$ impregnated catalysts, Richardson and Twigg revealed that impregnation of Al$_2$O$_3$ support with Ni(NO$_3$)$_2$ solution progresses gradually so that NiO crystals deposited during drying and decomposed in the early phase of calcination to produce a very acidic environment that dissolved Al$^{3+}$ ions from the Al$_2$O$_3$ surface [23]. These ions then attach the NiO, either by incorporation into the crystallite or by accumulation in the adjacent vicinity, and are responsible for lower reducibility. The increase in Mn loading decreases the reducibility of Ni-Al catalysts up to 1wt%Mn while at higher loadings, such as 4wt%Mn, reducibility increases, which may be ascribed to the slightly weak interaction between metal and support due to presence of Mn.

C. CO$_2$-TPD and FTIR

The basicity of mono- and bi-metallic fresh catalysts was estimated by CO$_2$-TPD (Fig.3). It is obvious from figure that Ni-Al showed the least capacity of CO$_2$ adsorption with two desorption peaks centered at 100 and 295 °C corresponding to weaker and medium strength basic sites respectively. In comparison with Ni-Al, all
Mn doped bimetallic catalysts showed two similar peaks at the same temperatures, but for the peaks at higher temperature, they show stronger intensities. Additionally, it is apparent that as Mn content increases, the TPD peak intensity becomes higher which indicates the increase in CO\textsubscript{2} adsorption capacity. The higher adsorption of CO\textsubscript{2} (acidic gas) over Mn added bimetallic catalysts confirms that these catalysts are more basic. It is well known that the basic catalyst could improve the adsorption of CO\textsubscript{2} that supplied the surface oxygen for gasification of coke, during dry reforming reaction, hence improved coke resistance. However, catalytic activity and coke resistance cannot be evaluated only on the basis of basic strength because catalytic performance also depends on several other key factors including active metal particle size, metal support interaction, dispersion and reduction degree [24].

The surface properties of fresh and spent catalysts are determined by FTIR spectra and results are shown in Fig.4. For both the fresh and spent catalysts, the broad band at 3400–3600 cm\textsuperscript{-1} and bands in the range of 1200–1700 cm\textsuperscript{-1} may be assigned to bending, combination, and symmetric/asymmetric stretching modes of O–H, while the strong absorption in the region from 500 cm\textsuperscript{-1} to 1000 cm\textsuperscript{-1} is owing to the vibration modes of oxides of Al(Al–O), Ni(Ni–O), and Mn(Mn–O). The FTIR spectrum of the spent samples also showed well-resolved bands of O–H stretching and bending indicating occurrence of water gas shift reaction. For example, appearance of O–H band peak, in addition to peaks presented in fresh catalyst, in case of Ni-Al spent catalyst at 2300–2400 cm\textsuperscript{-1} confirmed the existence of reverse water gas shift (RWGS) reaction during dry reforming reaction which further leads to H\textsubscript{2}/CO ratio less than unity (Fig.4(c)). It was reported that surface adsorbed water as a result of RWGS reaction also favors the gasification of coke deposited over catalyst surface [25, 26]. Moreover, the presence of O–H peak, at 2300–2400 cm\textsuperscript{-1}, in Ni-Al spent catalyst indicated that surface water did not contribute in coke gasification as well as it did in Mn doped catalysts, since Ni-Al showed the highest amount of coke deposition. On the other hand, the absence of O–H peak, at 2300–2400 cm\textsuperscript{-1}, in spent Ni-0.5Mn-Al catalyst suggests that water formed in RWGS reaction has been consumed in coke gasification, since this catalyst showed minimum carbon deposition (Table I). These findings are in agreement with TGA results in which it can be seen that more carbon deposited over Ni-Al than Ni-0.5Mn-Al (Table I).

D. Activity and stability

The effect of Mn promoter on a 5wt% Ni/\gamma-Al\textsubscript{2}O\textsubscript{3} supported catalyst, in terms of activity and stability are presented in Figs. 5 and 6. From the Fig.5 (a) and (b), it is apparent that the conversions of both CH\textsubscript{4} and CO\textsubscript{2} increase as the reaction temperature increases. For instance, at 500 °C, Ni-0.5Mn-Al catalyst showed 6.8% CH\textsubscript{4} conversion, while at 600 and 700 °C the same catalyst showed 35.1% and 80.6% CH\textsubscript{4} conversion, respectively. This increase in activity with temperature is in agreement with thermodynamicity of the process. At all reaction temperatures, CO\textsubscript{2} conversions are higher than the corresponding CH\textsubscript{4} conversions which indicates the occurrence of reverse water gas shift (RWGS) reaction (CO\textsubscript{2}+H\textsubscript{2}=CO+H\textsubscript{2}O). This aspect could increase surface coverage with hydroxyls which are beneficial to the decrease of carbon formation by gasifying it.

The long run stability in terms of CH\textsubscript{4} and CO\textsubscript{2} conversions, for Mn added mono- and bi-metallic catalysts, was evaluated at 700°C for 7 h TOS and their results are presented in Fig.6. From Fig.6(a) it is observable that monometallic Ni-Al catalyst showed the highest drop in methane conversion TOS while all other Mn added bimetallic catalysts showed relatively stable behavior with small decline in conversion. The decrease in activity for mono-metallic and bimetallic catalysts is due to effect of coking over catalyst surface which is confirmed later on by TGA results (Table I). It is worthy to note the increase in catalytic activity at low Mn loadings (Ni-0.5Mn-Al and Ni-
The negative effect of Mn addition, at higher loadings, on the catalytic activity may be attributed to reduction in specific surface area (Table I) and to the partial coverage of Ni particles (active component) with Mn which is relatively less active. Similar coverage or blockage of active metal component with several promoters which caused a slight decrease in activity was also reported by other researchers [27]. The results of CO$_2$ activation versus TOS (Fig.6(b)) reveal that addition of Mn in catalyst has a significant effect on CO$_2$ conversion. These enhancements in CO$_2$ activation are attributed to the improved basicity of the bimetallic catalysts. Moreover, the higher CO$_2$ conversion is also responsible for H$_2$/CO ratio lower than unity (Fig.5(c)), since it increases the yield of CO in system which causes reduction in H$_2$/CO ratio [28, 29]. The initial and final conversions of methane and carbon dioxide, at 700 °C, for the Ni-Al catalyst changed from 79.4% to 77.1% and 82.7% to 79.4%, respectively; whereas, for Ni-0.5Mn-Al, the initial and final conversions of methane and carbon dioxide changed from 80.6% to 79.7% and 85.6% to 84.2%, respectively. The higher and stable conversions of both methane and carbon dioxide assured the better performance of Ni-0.5Mn-Al bimetallic catalyst than monometallic Ni-Al. The deactivation factors (DF) of CH$_4$ conversion, estimated after 7 h of reaction at 700 °C, for mono and bimetallic catalysts are summarized in Table I.

Since DF can be taken as a function of stability which further depends upon deactivation. In this work deactivation mainly resulted from carbon deposition. Thus DF is a measure of how stable (or resistant to carbon deposition) a catalyst remains during the course of reaction. It is obvious that DFs for Ni-Mn-Al bimetallic catalysts are smaller than the DF for monometallic Ni-Al catalyst which leads to the fact that Mn addition improved coke resistance and thus more stable performance of bimetallic catalysts as compared to monometallic catalyst. Similar results have also been reported. Yao et al. revealed that the addition of Mn to Ni/SiO$_2$ catalyst improved metal support interaction and active metal dispersion and led to smaller NiO size which consequently reduced carbon deposition over Mn modified catalyst for a temperature range of 600–800 °C [30]. In addition to dry reforming reaction, modification of Ni/Al$_2$O$_3$ catalyst with Mn also presented excellent coke resistance in steam reforming of tar from biomass to produce syngas [31]. Additionally when Ni-Al catalyst was doped with Mn, the DF initially decreased as the amount of Mn is increased from 0 to 0.5%. However, further increase of Mn (>0.5wt%) caused the DF to increase but still this increase in DF.
is less than that of monometallic catalyst. Therefore the optimum loading of Mn in this work was 0.5wt%. Therefore, the presence of a small amount of Mn in the Ni/γ-Al₂O₃ catalyst system improves its activity and stability.

The CH₄ and CO₂ conversions for Ni-Al and Ni-0.5Mn-Al were very close to each other. So, to investigate the real time catalytic activity difference between them, both of these catalysts were tested under different conditions of gas space velocities (GSV). The study of GSV was carried out, at 700 °C and at 1 atm pressure, by using fixed total gas flow rate (36 mL/min) and different weights of catalyst samples were used. The results are shown in Fig.7. It can be seen from the figure that the increase in GSV causes a decrease in catalytic activity due to shorter contact time and endothermicity of the reaction. To retain the conversion of reactants and yield of products constant, extra thermal energy is required at higher GSV values [32]. All the catalytic activity tests were repeated three times to assess the percentage error of <1.2% in the calculations. Based on these results, it can be inferred that Ni-0.5Mn-Al bimetallic catalyst is better than Ni-Al monometallic catalyst in both activity and stability under similar reaction conditions.

E. Thermogravimetric analysis

Carbon deposition is the crucial problem for the reforming reaction, which could lead to catalyst deactivation by blocking the pores of the catalyst support and/or covering the active metal component. The quantitative measurement of carbon deposition over spent catalysts was performed by employing TGA and their results are summarized in Table I. The highest (9.73wt%) amount of carbon deposited after 7 h of reaction at 700 °C was observed on Ni-Al catalyst, whereas Ni-0.5Mn-Al bimetallic catalyst showed the least (4.86wt%). From the TGA results it inferred that carbon deposition decreases up to 0.5wt% Mn loading, however further increase in Mn loading increases the amount of carbon deposition.

F. SEM and EDS

The SEM micrographs and energy dissipative spectroscopy (EDS) results of fresh and spent catalysts with and without addition of Mn in Ni-Al catalyst are shown in Fig.8 and Table II. From the SEM micrographs, it is apparent that the used Ni-Al catalyst (Fig.8(a)) showed significant amount of carbon deposition with filamentous structure. On the other hand, Ni-0.5Mn-Al spent catalyst (Fig.8(b)) showed insignificant signs of carbon deposition. The EDS results for the fresh and spent catalysts are listed in Table II. The EDS results for the fresh catalysts confirmed the amount of Ni and Mn present in the catalyst. Moreover, the EDS results of the Ni-Al and Ni-0.5Mn-Al fresh catalysts, as shown in Table II, clearly proved the absence of carbon deposition. On the other hand, from the EDS results for Ni-Al and Ni-0.5Mn-Al spent catalysts tested at 700 °C for 7 h, the occurrence of the carbon deposition is evident. In comparison with Ni-Al catalyst the carbon deposition over Ni-0.5Mn-Al catalyst is less, which is conforming that Ni-0.5Mn-Al is a better catalyst than Ni-Al.

IV. CONCLUSION

5wt%Ni/γ-Al₂O₃ catalysts modified with Mn were prepared by impregnation method and were used for
TABLE II Elemental analysis of catalyst by EDS.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Element</th>
<th>Energy/keV</th>
<th>Mass/%</th>
<th>Error/%</th>
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<tbody>
<tr>
<td>Ni-Al(^a)</td>
<td>O</td>
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</tr>
<tr>
<td></td>
<td>Al</td>
<td>1.486</td>
<td>55.89</td>
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<td>Ni</td>
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<td>Al</td>
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<tr>
<td></td>
<td>Mn</td>
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<td>Ni-Al(^b)</td>
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<td>Ni</td>
<td>7.471</td>
<td>4.65</td>
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\(^a\) Fresh catalyst.
\(^b\) Spent catalyst.

methane reforming with CO\(_2\). The activity, stability and amounts of carbon deposited on the catalysts were estimated based on the Mn/Ni ratio. Among all the tested catalysts, Ni-0.5Mn-Al bimetallic catalyst i.e., with the lowest Mn/Ni ratio has exhibited excellent catalytic performance with least carbon deposition, dictating higher stability for dry reforming reaction. On the contrary, the catalysts with higher Mn loadings showed decrease in catalytic activity; however somehow these catalysts contributed better in terms of carbon suppression than that of monometallic catalyst. Higher basicity, in case of Mn doped catalyst, is the key factor which favors the gasification of coke deposition from catalyst surface during reaction.

V. ACKNOWLEDGMENTS

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