DRY REFORMING OF METHANE OVER SUPPORTED NICKEL CATALYSTS PROMOTED BY ZERCONIA, CERIA AND MAGNESIA

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ABSTRACT

Dry reforming of methane (DRM) is an environmental friendly process to produce synthesis gas (H₂+CO). The catalysts used are often composed of transition metals like nickel, supported on metallic and non-metallic oxides such as alumina along with promoters or without promoters. The deactivation of catalysts is a major problem due to carbon deposition. In the present paper alumina supported nickel catalysts promoted by zirconia, ceria and magnesia are reported for the methane dry reforming in order to improve the activity and stability of the catalysts. Effect of promoters on activity and stability were studied in the detail. The study results indicate the effect of the ZrO₂, CeO₂, and MgO on the activity and stability of catalyst are varying with highest conversion was observed with 10%Ni/5%ZrO₂-Al₂O₃ and stability with 10%Ni/5%CeO₂-Al₂O₃. Characterization of promoted and unprompted catalyst studied was done through XRD, BET, FTIR analysis. Basically pore structure of the support and metal support interaction can affect the catalytic activity and coking resistance.

Key words: CO₂ Reforming of Methane; Carbon Deposition, Promoted and Unprompted Catalyst.


http://www.iaeme.com/IJARET/issues.asp?JType=IJARET&VType=6&IType=10
1. INTRODUCTION

In 2011 report of IEA’s gives the information on world energy; it is prediction that from different source of energy fossil fuels remains on top of the front for our energy requirement [1]. Based on increasing trend of energy requirement of world, CO₂ emission will reach 43 Gt per year under existing or proposed polices by 2035 [1]. CO₂ emission leads to unsustainability of society, that’s why control of CO₂ emission is required.

In existing scenario, carbon capture and storage (CCS) gives approach for CO₂ reduction. CCS is only available technology for CO₂ reduction in upcoming near future. CO₂ reduction by chemical CO₂ utilization is one of interesting area for many sector like industrial and academic. Also there has been a remarkable worldwide interest in developing process to transform natural gas in to products with graded added value in order to obtain economic benefits. In recent years, DRM process is considering as useful route to produce synthesis gas.

\[
\begin{align*}
CH_4 + CO_2 & \leftrightarrow 2CO + 2H_2 \quad (1) \quad (\Delta H = 247 \frac{kJ}{mol}) \\
H_2 + CO & \leftrightarrow CO + H_2O \quad (2) \quad (\Delta H = -39.5 \frac{kJ}{mol}) \\
CO_2 + 4H_2 & \leftrightarrow CH_4 + 2H_2O \quad (3) \quad (\Delta H = -64.9 \frac{kJ}{mol}) \\
2CO & \leftrightarrow C + CO_2 \quad (4) \quad (\Delta H = -171 \frac{kJ}{mol}) \\
CH_4 & \leftrightarrow C + 2H_2 \quad (5) \quad (\Delta H = 75 \frac{kJ}{mol}) \\
CO + H_2 & \leftrightarrow C + H_2O \quad (6) \quad (\Delta H = -131.1 \frac{kJ}{mol})
\end{align*}
\]

These reactions are important as H₂/CO ratio of produced synthesis gas is low which are useful for the production of liquid hydrocarbons in the fischer tropsch reactions [2-4]. In DRM reaction catalyst the deactivation is major roadblock and challenge to develop commercial scale up process. The sintering of catalysts due to high temperature and coke deposition are main cause of the deactivation. DRM reaction network includes reactions 1-6 that methane decomposition (reaction 5), the boudouard reaction (reaction 4) and reverse coke gasification (reaction 6) are main reaction in producing coke [5].

The dry reforming of methane consumes two of the most potent green house gases as reactants [3].

The dry reforming of methane requires the use of catalyst, such as the noble metals rhodium and platinum, supported on metal and non-metal oxide support materials, such as Al₂O₃, MgO, TiO₂, ZrO₂ and CeO₂ [5,6]. Although these noble metals are yield a higher activity and selectivity at same time, they are relatively expensive [7].

As such, transition metals are instead used which include nickel, cobalt, and copper. Nickel is the most suitable catalyst for the reaction due to its availability and low cost, only disadvantage with nickel is its deactivation due to deposition of carbon on active canters [8]. To diminish the carbon formation due to enhancement of the metal/support the active phase incorporation in to support of high oxygen mobility is
proposed. It is required to develop Ni catalyst with superior action in terms of activity and selectivity, in which carbon generation stop or minimize carbon formation, need research in to the below area like (1) the nature of the support, (2) the support and catalyst preparation method and (3) the addition of promoters.

In this paper, the application of the support and catalyst preparation method was examined for DRM. The effect of Ni loading and catalyst preparation method was evaluated.

2. EXPERIMENTAL

2.1 Catalyst Preparation

A series of Ni/Al₂O₃ catalysts were prepared by the wetness impregnated method [9]. The selection of specifics metal and their precursors is dependent on proposed catalyst composition. Ziroconia and ceria and magnesia promoted nickel catalyst were prepared by the wet-impregnation method. Support was impregnated with a solution containing the required amount of nickel nitrate salt Ni(NO₃)₂*6H₂O. 5%, 10% Nickel were impregnated on a alumina, using a nickel nitrate (Ni(NO₃)₂* 6H₂O) solution as a precursor. To study the ZrO₂ loading effect, catalyst prepared, in which nickel nitrate and zirconium nitrate were impregnated onto an Al₂O₃. After the addition of the salt precursor on the support solution was kept for the shaking (6 h). The aim of impregnation is to cover the entire surface of the support of high specific surface with homogenous coating of the active phase. After that transfer the solution into beaker and kept this solution on hot plate at 353 K. Stop the heating when slurry formation takes place. The main aim of evaporation operation used to remove excess of water present in the solution. After the evaporation operation the slurry form solution was kept for overnight (12 h) drying in the Hot air oven at 383 K followed by calcination process, in that the dried catalyst was kept in the open air furnace at 873 K for 4 h. And supply the air after the 20-20 min time interval. Oxidation reaction takes place due to the supply of air in the open air furnace.

2.2. Catalyst activity

The CO₂ reforming of methane was carried out at 923-1073 K and atmospheric pressure, using 1 gm catalyst in a stainless steel tubular fixed-bed reactor. Fixed bed reactor having tube of 18.05 mm inner, 19.05 mm outer diameter and tube length 500 mm.

Activation of the Ni-Catalyst involved reductive treatment with hydrogen at 773 K for 2 hours with heating rate of 10 deg per min. The reactant feed gas was passed in composition of CH₄:CO₂:N₂ – 1:1:1 with total flow rate of 500 ml/min having GHSV of 30000 cm³/g *h.

The exit gases were analysed with gas chromatography equipped with thermal conductivity detector with Porapak – Q and a SA molecular sieve column was used [7]. In this work, conversions of methane and carbon dioxide and yields of hydrogen and carbon monoxide were calculated according to the following formulas.

\[ X_{CH_4} = \frac{C_{CH_4_{in}} - C_{CH_4_{out}}}{C_{CH_4_{in}}} * 100 \]

\[ X_{CO_2} = \frac{C_{CO_2_{in}} - C_{CO_2_{out}}}{C_{CO_2_{in}}} * 100 \]

\[ Y_{H_2} = \frac{C_{H_2_{out}}}{2C_{CH_4_{in}}} * 100 \]

\[ Y_{CO} = \frac{C_{CO_{out}}}{C_{CH_4_{in}} + C_{CO_2_{in}}} * 100 \]
Where $Xi$ and $Yi$ are the conversion of reactants and yields of products, respectively $C_{in}$ is the initial molar fraction of component $i$ in the feed, and $C_{out}$ is the final molar fraction of component $i$ in the product stream [10].

2.3. Catalyst Characterization

2.3.1 Physisorption Analysis

For determining the surface area and pore size distribution of solids, measurement of gas adsorption isotherms are widely used. The identification types of isotherm are required for interpretation of physisorption isotherm. This in turn allows for the possibility to choose an appropriate procedure for evaluation of the textural properties.

Non-specific Brunauer-Emmett-Teller (BET) method is the most commonly used standard procedure to measure surface areas, in spite of the over simplification of the model on which the theory is based. The BET equation is applicable at low $p/p_0$ range and it is written in the linear form: [11]

$$\frac{p}{n_a(p_a - p)} = \frac{1}{n_m C} + \left(\frac{n_m}{n_a C}\right) \frac{p}{p_0}$$

Sample pressure is $p$,
Saturation vapour pressure is $p_0$,
The amount of gas adsorbed at the relative pressure $p/p_0$: $n_a$
The monolayer capacity, and $C$ is the so-called BET constant: $n_a^m$

The adsorption-desorption data to be use for to assess the micro-and mesoporosity and to compute pore size distribution, through number of way has been developed. These are number of assumptions, e.g. relating to pore shape and mechanism of pore filling for same.

2.3.2. XRD

To measure the surface area of fresh and used catalyst, Model: X’PERT MPD, Make: Philips, Holland was used.

Information on crystallographic structure, chemical composition and physical properties of materials and then films; x-ray scattering technique is used. XRD is a part of non destructive analytical techniques [12].

These techniques are based on observing the scattered intensity of on x-ray beam hitting a sample as a function of incident and scattered angle, Polarization and wavelength or energy [10].

2.3.3 Fourier Transforms Infrared Spectroscopy (FTIR)

FTIR spectroscopy gives information on interaction of absorbed molecules, yielding information on [4, 5]

1. The site of interaction, i.e the active centers,
2. The restriction of molecular motion in the adsorbed state.
3. The geometry of the sorption complex and
4. The change of internal bonding due to adsorption.

To obtain an infrared spectrum of absorption, emission, photoconductivity orraman scattering of a solid, liquid or gas fourier transform infrared spectroscopy is a technique used. Over a wide spectral range FTIR spectrometer simultaneously
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collects high spectral resolution data. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time [5].

3. RESULTS AND DISCUSSION

3.1 BET Surface Area

The surface area, pore size and pore volume of the catalysts containing 5%, 10% Ni by weight and promoted with ZrO₂ are presented in table 1.

It appears that catalyst surface area decrease with increased nickel loading from 5% to 10%. As more metal is impregnated, more of the pores originally present are being filled up, this effectively reducing surface area.

This is supported by the decreasing trend in pore volume as nickel loading is increased. As more nickel enters the pores of the support material, the pore volume decreases.

In addition to that, the addition of nickel may also have caused smaller pores to be blocked, effectively increasing the average pore diameter [13, 14].

Addition of promoters reduced the surface area due to pore filling of catalyst support. Furthermore, pore volume decreased by addition of promoters and indicated in Table 1 for ZrO₂. Based on results of activity it is found that promoters enhanced the conversion and stability even if catalyst surface area decreased compared to that of alumina support.

Table 01 Surface Area, Pore Size and Pore Diameter of Promoted catalyst

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET Surface Area (m²/g)</th>
<th>Pore Volume (cm³/g)</th>
<th>Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5%Ni/γ-Al₂O₃</td>
<td>165.60</td>
<td>0.27</td>
<td>5.96</td>
</tr>
<tr>
<td>10%Ni/γ-Al₂O₃</td>
<td>138.10</td>
<td>0.22</td>
<td>6.48</td>
</tr>
<tr>
<td>10%Ni/5%ZrO₂-γ-Al₂O₃</td>
<td>105.25</td>
<td>0.21</td>
<td>7.65</td>
</tr>
</tbody>
</table>

3.2. X-Ray Diffraction of 5% Ni/γ-Al₂O₃ and 10% Ni/γ-Al₂O₃

The XRD patterns for γ-Al₂O₃ supported, wet impregnated catalyst, 5%Ni, 10Ni% and with different promoters (CeO₂, ZrO₂, and MgO) are shown in Fig. 1 to 5. The catalyst containing 5-10%Ni, shows the spectra corresponding to NiO and Al₂O₃.

According to the JCPDS files, the Al₂O₃, Ni, NiO, CeO₂, ZrO₂, MgO, NiAl₂O₄ and MgAl₂O₄ phases can be detected in the XRD patterns [15]. NiAl₂O₄ has spinel structure with a lattice parameter very close to Al₂O₃ that appears at 2θ’s lower than the 2θ of γ-Al₂O₃.

NiO diffraction peaks observed at 2θ = 37.3, 43.4, 44.5, 62.9, 63.0, 75.6 and 79.6. Characteristic diffraction peaks of phases at 2θ of 19.2, 31.6, 45.3, 56.4, 60.0, 66.2 and 2θ of 19.1, 31.4, 37, 45, 59.7, and 65.5 are assigning to MgAl₂O₄ and NiAl₂O₄ respectively.

In Fig. 1, the XRD patterns of 5%Ni/γ-Al₂O₃ shows intense diffraction lines of NiO (2θ = 44.5°) and γ-Al₂O₃ (2θ = 37.4°, 67.3°). In this catalyst two phases of gamma alumina and one crystalline phase of nickel were detected. The smaller amount of Ni interact with alumina and form nickel aluminate (NiAl₂O₄) composite
layer, which is an amorphous phase or a crystalline phase with crystallite sizes smaller than the detection limit of XRD.

Figure 01 X-Ray diffraction patterns of the 5%Ni/Al2O3

In Fig. 2, the XRD patterns of 10%Ni/Al2O3 shows intense diffraction lines of NiO (2θ = 37.2°) and γ-Al2O3 (2θ =45.7°, 66.8°). In this catalyst also two phases of gamma alumina and one crystalline phase of nickel were detected. In this catalyst the dispersion of Ni should be more as compare to 5%Ni/Al2O3, means the active site is more. The smaller amount of Ni interacts with alumina and form nickel aluminate (NiAl2O4) composite layer. Basically a crystallite size of NiAl2O4 is smaller than the recognition limit of XRD.

Figure 02 X-Ray diffraction pattern of the catalyst 10%Ni/Al2O3

XRD spectra shown in Fig. 3 shows intense diffraction lines of NiO (2θ = 37.2°, 43.4°), γ-Al2O3 (2θ = 37.6°, 66.8°) and CeO2 (2θ = 29°). In this catalyst two major phases of gamma alumina, two crystalline phase of nickel and one phase of CeO2 were detected. The amount of CeO2 addition influenced the intensities of Nickel peaks. The weaker and broader the Ni Peak due to the more CeO2 loading on catalyst. It indicates that addition of CeO2 effects the nickel dispersion on catalyst.
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Figure 03 X-Ray diffraction pattern of the catalyst 10%Ni/5%CeO₂-γ-Al₂O₃

The overlap of gamma alumina and nickel oxide form composite layer of NiO-γ-Al₂O₃ which is an amorphous phase. The smaller amount of Ni particle interacts with alumina and form nickel aluminate (NiAl₂O₄). It is clear that strong interaction of nickel metal and alumina lattice to make spinel type solid solution of NiAl₂O₄. There is NiAl₂O₄; the strong interaction is due to the calcination. The presence of Ni in the form of NiO can be observed in XRD patterns as well. The NiO crystallites are small and well dispersed in catalysts samples as the related peak are quite broad. It should be mentioned that NiO crystals are slightly bigger in the presence of CeO₂ and in contrary, alumina peaks lost their intensity after introduction of CeO₂. According to XRD patterns, big crystal of CeO₂ was observed.

In Fig 4, the XRD patterns of 10%Ni/5%ZrO₂-γ-Al₂O₃ shows intense diffraction lines of NiO (2θ = 43.4°, 63°, 75.6°), γ-Al₂O₃ (2θ = 37.6°, 67.3°) and ZrO₂ (2θ = 31°, 51°). In this catalyst two major phases of gamma alumina, three crystalline phase of nickel and two of ZrO₂ were detected. The overlap of gamma alumina and nickel oxide form composite layer of NiO-γ-Al₂O₃ which is an amorphous phase.

Figure 04 X-Ray diffraction pattern of the catalyst 10%Ni/5%ZrO₂-γ-Al₂O₃
In Fig. 05, the XRD patterns of 10%Ni/5%MgO-\(\gamma\)-Al\(_2\)O\(_3\) shows intense diffraction lines of NiO (2\(\theta\) = 37.2\(^\circ\), 62.7\(^\circ\)), \(\gamma\)-Al\(_2\)O\(_3\) (2\(\theta\) = 37.6\(^\circ\), 45.7\(^\circ\), 66.8\(^\circ\)) and MgO (2\(\theta\) = 62.4\(^\circ\), 74.8\(^\circ\)). As Ni\(^{2+}\), Mg\(^{2+}\), Al\(^{3+}\), fall in to the same lattice, the formation of solid solution of spinel type of MgAl\(_2\)O\(_4\) and NiAl\(_2\)O\(_4\) is favored under high temperature calcination.

Characteristic diffraction peaks of spinel phases at 2\(\theta\) of 19.2 and at 2\(\theta\) of 65.5 assigning to MgAl\(_2\)O\(_4\) and NiAl\(_2\)O\(_4\) respectively [15].

![Figure 05 X-Ray diffraction pattern of the catalyst 10%Ni/5%MgO-\(\gamma\)-Al\(_2\)O\(_3\)](image)

### 3.3 FTIR Analysis

FTIR analysis is shown in Fig. 6 (a-c). For a more precise IR characterization, spectra were reported in a wide range of frequency 400-4000 cm\(^{-1}\).

The IR spectra in all cases, exhibit metal-oxygen stretching frequencies in the range 470-900 cm\(^{-1}\) associated with the vibration of M-O, Al-O and M-O-Al bonds (M=Ni, CeO\(_2\), MgO and ZrO\(_2\)). Peaks of stretching vibration of structured O-H at 3450 cm\(^{-1}\), and stretching vibration at 1640 cm\(^{-1}\) is due to the physically adsorbed water and clear form the spectrum of the catalysts.

![Figure 6(a): FTIR Spectrum of 10%Ni/5%CeO\(_2\)-\(\gamma\)-Al\(_2\)O\(_3\)](image)
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Figure 6(b) FTIR Spectrum of 10%Ni/5%ZrO2 - γ-Al2O3

Figure 6(c): FTIR Spectrum of 10%Ni/5%MgO - γ-Al2O3

The residual nitrate compounds present in the catalyst after heat treatment and especially nitrogen used for the reaction is responsible for the appearance of N-O and N-C peaks at 1525 cm⁻¹.

The peaks at 415 cm⁻¹ corresponds to the metal-oxygen – metal band. This band can also be related to the stretching vibration absorption spectrum of Ni. Absorption peaks of metal oxides (NiO, ZrO2, CeO2 and MgO) arising from inter atomic vibrations are below 1000 cm⁻¹. An absorption peaks at 1400, 1649 and 3450 cm⁻¹ are related to adsorbed water for all materials [4, 5, 25].

Effect of Ni loadings with different promoters at different temperatures
Activity of Ni/Al2O3 catalyst was presented in connection to reactant conversion and synthesis gas yield given in Figs 07 & 08 and 09.

At amount of 10% Ni loading conversion of both CH₄ and CO₂ were substantially increased. At less Ni-loading low conversion of CH₄ and CO₂ are observed. It is due to that less active metal and the formation of NiAl₂O₄ nevertheless their surface area
is comparatively high. From XRD it is clear that at 10% Ni loading higher conversion of CH\textsubscript{4} and CO\textsubscript{2} observed, and it is because of number of active Ni content high.

**Figure 7** CH\textsubscript{4} conversion (%) over different temperature (K) in Dry Reforming of methane.

**Figure 8** CO\textsubscript{2} conversion (%) over different temperature (K) in Dry Reforming of methane.

**Figure 9** H\textsubscript{2}/CO Ratio over different temperature (K) in Dry Reforming of methane.
When Zirconia added, both CH$_4$ and CO$_2$ conversions were strongly increased. Due to effect of ZrO$_2$, the formations of NiAl$_2$O$_4$ reduced and/or reach to negligible. Seo et al. [16] has found similar results, that ZrO$_2$ inhibits the integration of nickel species into the lattice of Al$_2$O$_3$, and avoid the formation of metallic nickel particles in between the reaction step.

Basically presence of ZrO$_2$, inhibits the coke formation on 10Ni%/γ-Al$_2$O$_3$. Pompeo et al. explained the coke reduction capability of ZrO$_2$ [17]. However, due to presence of ZrO$_2$ the Al$_2$O$_3$ surface is modified. Ni is deposited near to ZrO$_2$; it is not directly onto the Al$_2$O$_3$ and because of this CO$_2$ dissociation improves. This causes gasification of the dissociated oxygen and unsaturated intermediates and promotes the formation of carbon deposit precursors, prevents coke formation in the system [7, 18].

It is also clear that CeO$_2$ promoted catalyst has higher CH$_4$ conversion then unsupported at all temperature. High conversion of CH$_4$ because of the surface basicity. Surface basicity of CeO$_2$ is high compare to alumina.

There are a number of carbons like species because of interaction between CeO$_2$ with CO$_2$ [19]. Basically the above phenomenon is due to the nature of different supports and the interaction between metal and support/promoters. CeO$_2$ has oxidative properties and a good capacity for oxygen storage reaction [19]. DRM reaction starts with hydrocarbon species and carbon atom, it is first steps of reaction. CH$_4$ dissociation give carbon and it was deposited on catalyst. Generated carbon react with oxygen from the dissociation of adsorbed CO$_2$, it is due to the effect of CeO$_2$, and finally gives less carbon deposition. With Ni/CeO$_2$-γ-Al$_2$O$_3$ catalyst reaction rate of carbon species formed is high. These systems exhibited higher activity then Ni/γ-Al$_2$O$_3$ catalyst.

It is worth noting that, excellent performance of MgO in raising of basic sites concentrations and consequently, promoting the adsorption rate of acidic CO$_2$ [4]. MgO can improve catalytic activity due to the formation of MgAl$_2$O$_4$ phase and surface rearrangement [20].

### 3.5 Effect of temperature

For all impregnated catalyst the consequence of temperature on the conversion of reactant and product gas (H$_2$ and CO) yields are given in Fig. 07 to 09.

DRM is highly endothermic reaction as temperature increased conversion of CH$_4$ and CO$_2$ is increased and also the yields of H$_2$ and CO [21].

Over all the catalyst and all examined temperatures, the conversions of CO$_2$ were higher than those of CH$_4$ which can be due to the existence of RWGS (reaction 2) reaction. Highest 84.56% and 89.34% conversion of CH$_4$ and CO$_2$ achieved at 1073 K respectively with 10%Ni loading with effect of ZrO$_2$.

The RWGS is also contributed to higher CO$_2$ conversion then CH$_4$ conversion at low temperature, as reported [22]. CH$_4$ dissociation is also increased and greatly enhanced at higher temperatures. It leads to formation of coke, as conversion of methane is increased. In sort at higher temperature the CH$_4$ dissociation is a strongly favoured reaction. Increase in H$_2$/CO ratio was detected when temperature raised, though in all cases ratio was below unity, it indicates that RWGS was always taking place but in lower extent when the temperature increased.
3.6. Effect of GHSV

Fig. 10 & 11 show the effect of space velocity for conversion of the CH$_4$ and CO$_2$, H$_2$/CO ratio on the nickel catalyst with ZrO$_2$, CeO$_2$ and MgO promtes on γ-Al$_2$O$_3$ as support. The space velocity was diverted by altering the total flow rate maintains at molar feed ratio of one and catalyst amount of 1 g.

![Figure 10 CH$_4$ (%) and CO$_2$ (%) Conversion over different GHSV (cm$^3$/g*h)](image)

**Figure 10** CH$_4$ (%) and CO$_2$ (%) Conversion over different GHSV (cm$^3$/g*h)

![Figure 11 H$_2$/CO Ratio over different GHSV cm$^3$/g*h)](image)

**Figure 11** H$_2$/CO Ratio over different GHSV cm$^3$/g*h

Moreover, the CH$_4$ and CO$_2$ reforming reaction were conducted at constant temperature of 1073 K. As the space velocity increase, yields of H$_2$ and CO monotonically decrease. Since contact time becomes shorter, methane reforming with CO$_2$ could not completed under this reaction conditions. For reaction it is required to interaction between reactant and active Ni particles inside the catalyst pores, in case of high GHSV, the residence time is limiting factor for reaction. In such situation number of reactant remain un-reacted. As shown in Fig. 11 the H$_2$ and CO yields decreases as GHSV increases for all impregnated catalyst.

At higher GHSV there is external diffusion resistance that lead reduction in both CH$_4$ and CO$_2$ conversion, similar to observation of Mark and Maier [23]. Decrease in CH$_4$ and CO$_2$ conversions is attributed to reverse reaction such as CO hydrogenation to CH$_4$ at high GHSVs [24].
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3.7 Stability test

High activity alongside excellent stability can be properties of a promising catalyst. Fig. 12 & 13 gives the methane and carbon dioxide conversion at different time on stream over the three promoted catalysts prepared by impregnated method. The stability improvement can be estimated by the ratios between the CH$_4$ and CO$_2$ conversion after 12 hr (720 min) of time on stream (C12/C1) ratios were 0.79, 0.74, 0.77 for 10Ni%/5%CeO$_2$-γ-Al$_2$O$_3$, 10Ni%/5%ZrO$_2$-γ-Al$_2$O$_3$ and 10Ni%/5%MgO-γ-Al$_2$O$_3$ respectively. All of the impregnated catalyst samples illustrated the satisfactory stability and acceptable performance during reaction time. There is deactivation in all three catalysts upto certain extent. The stability was better over the CeO$_2$ promoted catalyst compared to other promoted catalyst. If deposited carbon having filamentous structure then it’s does not deactivate the nickel sites. In reaction performance, reactant accessible to active metals carried on the top, and as a result the activity remains constant.

![Figure 12](http://www.iaeme.com/IJARET/index.asp) Comparison of stability test of different catalyst over time (h) in terms of CH$_4$ conversion (%).

![Figure 13](http://www.iaeme.com/IJARET/index.asp) Comparison of stability test of different catalyst over time (h) in terms of CO$_2$ conversion (%).

In order to authenticate of this witnessing a look over the mechanism of DRM might be useful. It is indicated that the CH$_4$ decomposition occurs on the surface of the active metals while CO$_2$ adsorption take place on the support. Adsorbed CO$_2$ reacts with carbon species derived from dissociative adsorption of CH$_4$. Therefore, CO releases and deposited carbon removes. As a result of smaller particle size and
enhanced dispersion, higher surface area obtained and subsequently the rate of the carbon removal promotes [8, 24].

The rate of the atomic carbon gasification by CO$_2$ is limited than the rate of atomic carbon formation, and carbon will be polymerized, is the major reason for deactivation and it lead to coke formation.

These polymerized carbon atoms can deactivate Ni particle via two ways: a) encapsulating carbon or diffusing through the Ni after dissolving and b) detaching Ni particles from the support.

If bond between metal and support is not strong and structure remains weak, then carbon formation via methane decomposition is more probable. Excellent stability of the catalyst can be ascribed to the uniform particle size distribution and to metal support interaction effect. ZrO$_2$ and MgO promoted catalysts indicate reducing trend in conversion of reactant and product yield. According to literature, it is clear that coke formation is a major significant root cause for catalyst deactivation.

4. CONCLUSION

Attaining the promising catalyst is the most significant obstacle facing DRM commercialization. High specific surface area, uniform particle size distribution, high dispersion of active metal, and metal support interaction effect are some of the favorable properties of the catalyst for DRM which were compared in between promoted and un-promoted catalyst, prepared by wet impregnation.

Dry reforming reaction was favored at 1073 K, over all prepared catalyst and promoted catalyst and over all temperature range of 823-1073 K.

In addition to DRM reactions dissociation of CH$_4$ took place that lead to coke deposition over catalyst. Promoters (CeO$_2$, ZrO$_2$ and MgO) inhibit the deactivation. The different promoters CeO$_2$, ZrO$_2$ and MgO are added to improve activity and stability of the prepared Ni/γ-Al$_2$O$_3$ catalyst and to understand its effect over DRM.

Moreover 10%Ni/5%ZrO$_2$-γ-Al$_2$O$_3$ catalyst has better activity in CH$_4$ and CO$_2$ conversion and also in H$_2$ and CO production.

Catalyst 10%Ni/5%ZrO$_2$-γ-Al$_2$O$_3$ gives H$_2$/CO ratio close to unity and higher than two other promoted catalysts.

The presence of ZrO$_2$ promoter improve dissociation of CO$_2$ forming oxygen intermediates near the contact between ZrO$_2$ and Nickel.

Due to that on surface coke deposition are gasified.

Further, physicochemical characterization of catalyst confirmed the high dispersion of the Ni particles on 10%Ni/5%ZrO$_2$-γ-Al$_2$O$_3$ catalyst.

A higher dispersion, surface area of Ni particles results in high activity of 10%Ni/5%ZrO$_2$-γ-Al$_2$O$_3$ catalyst prepared by impregnation method in the dry reforming of Methane. Introduction of CeO$_2$ enhances the dispersion of nickel particles and reducibility of Ni/γ-Al$_2$O$_3$ also inhibited NiAl$_2$O$_4$ formation, and it is also clear form XRD.

However addition of CeO$_2$ in to 10%Ni/γ-Al$_2$O$_3$ system not also suppressed the carbon deposition, because CeO$_2$ enhanced the Ni dispersion and reactivates of carbon deposition.

Present investigation confirms that at high GHSV the conversion of CH$_4$ and CO$_2$ in declined trend, as reactant does not have sufficient time to react over the surface of Ni.
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