Effect of Promoters on Performance of Ni/γ-Al₂O₃ Catalyst in Dry Reforming of Methane

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Abstract
The effect of various promoters (Ca, Ce, Mg, Zr) on the performance of 3%Ni/γ-Al₂O₃ catalysts in dry reforming of methane was investigated in a quartz tubular reactor under the following conditions: 1:1 CO₂/CH₄ ratio, flow rate CO₂/CH₄/Ar = 15/15/3 ml/min, temperature 700°C and at atmospheric pressure. The support, γ-Al₂O₃ was prepared by hydrothermal crystallization of boehmite. Various formulations of the promoted Ni/γ-Al₂O₃ catalysts were synthesized by wet impregnation method followed by drying and calcination at 750°C. The fresh and spent catalysts were characterized by various techniques. The compositions of the reactor inlet and outlet gases were analysed by online gas chromatography. The carbon deposition on the spent catalysts was determined by CHNS analyser. It was observed that the doubly promoted catalyst with Ca-Ce gave the best performance with the least coke deposition. The highest CH₄ and CO₂ conversion were found to be 72% and 79% with 2.247% carbon deposition for 10 hours of stream on run with this catalyst. Triply promoted (Zr-Ca-Ce) catalyst gave better result than doubly promoted Ca-Ce catalyst in activity but not in stability as well as carbon deposition resistance. Rh addition in doubly promoted Ca-Ce catalyst was also investigated that increased the activity (CH₄ conversion 82% and CO₂ conversion 96%) and decreased the carbon deposition (1.93%). This is a new formulation of catalyst which has performed very well in DRM process.

Keywords: dry reforming of methane, Ni/γ-Al₂O₃, promoted catalysts, hydrothermal crystallization, coke deposition

1. Introduction
Catalytic reforming of methane(CH₄) with carbon dioxide (CO₂) known as dry reforming of methane (DRM, Eq. 1) has gained much attention as a means to reduce global warming by utilizing these greenhouse gases (GHG) and to provide a useful feedstock of syngas (H₂/CO mixture).

Thus, DRM process not only reduces the GHG emissions into atmosphere but also converts them to a valuable product syngas. Syngas is a building block for production of chemicals; it can be used itself as a fuel or utilized in the manufacture of useful value-added products of more interest such as: hydrogen (H₂), methanol (CH₃OH), liquid synthetic motor fuels (gasoline (C₅-C₁₂), naphtha (C₆-C₁₂), kerosene (C₁₁-C₁₃) and diesel (C₁₂-C₂₂)), etc. Although, DRM has many environmental and economic incentives, unfortunately, there are no commercial processes for dry reforming of methane [1]. The major issue associated with this process is carbonaceous deactivation of catalysts due to formation of coke at the catalysts surface leading by the side reactions (i) Methane decomposition (Eq. 2) (ii) Boudouard reaction (Eq. 3).
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CH₄ + CO₂ → 2CO + 2H₂  \( \Delta H^\circ = 247.3 \text{ kJ/mol}, \Delta G^\circ = 61770-67.32T \)  (1)

CH₄ ↔ C + 2H₂  (Methane decomposition) \( \Delta H = 75 \text{ kJ/mol}, \Delta G^\circ = 2190-26.45T \)  (2)

2CO ↔ C + CO₂  (Boudouard reaction) \( \Delta H^\circ = -171 \text{ kJ/mol}, \Delta G^\circ = -39810+40.87T \)  (3)

Therefore, industrial application of DRM process is also limited [2-3]. Indeed, there are two processes of this kind which produce synthesis gas called Calcor [4] and Sparag [5]. An economic process generating CO through CO₂ reforming named as Calcor process. Sparag is a sulphur passivated reforming involves the continuous addition of small amounts of a sulphur compound to the reformer feed gas to provide chemisorbed sulphur on the nickel surface at amounts below the saturation level (around 40-50% saturation). This has the effect of blocking the formation and growth of carbon on the surface of the catalyst.

Various types of catalysts are reported in the literature for DRM process such as noble metals, spinels, perovskites, and supported base metals [1-2]. From industrial point of view, supported nickel is the most appropriate catalyst for DRM process due to its availability and low cost but Ni based catalysts are more susceptible to deactivation for high temperature reactions than noble metal catalysts [3]. Noble metals (Pt, Pd, Ru, Rh, Ir) have been found to exhibit promising catalytic activity and good coke deposition resistant but have limited use due to high cost and less availability. This situation lead to the need of developing Ni based catalysts with improved activity and stability. The performance of a catalyst can be affected by many factors such as supports [6], promoters [7], preparation methods [8-9], operating conditions [10] etc.

Wang et al. [11] investigated Al₂O₃, TiO₂, MgO, CaO, SiO₂ supports for DRM process and reported that Al₂O₃, TiO₂ gave high selectivity and stability. Albarazi et al. [12] studied DRM process on Ni/SBA-15 catalysts which also contributed for enhanced activity of Ni catalysts. CO₂ is considered as an acid gas so for high adsorption of CO₂, catalyst basicity increment (Mg, K promoted catalysts) results high activity for DRM process. Al-Fatesh et al. [13] demonstrated that Ce, Ca, Zr promoted Ni/Al₂O₃ catalysts resulted high conversion and very less carbon deposition. Ceria makes intensive interaction with metal active species and has high oxygen storage capacity. During reduction of catalysts, lattice oxygen in cerium oxide phase is eliminated and produces anionic vacancies which are considered as reactive sites of metal oxides. Albarazi et al. [12] proved that the synthesis route has a marked influence on the physicochemical features of the catalyst by the preparation of Ni/SBA-15 catalysts through impregnation, as well as by co-precipitation. Pore blockage was observed in the catalyst that was prepared by co-precipitation. NiO particles with crystal sizes of 9-11 nm were observed outside the mesoporous structure of the SBA-15 support in the case of the catalysts prepared by impregnation [12]. DRM reaction is favoured at high temperatures (endothermic reaction) and low pressures. Gibbs free energy value for DRM reaction is positive at temperature below 643°C (Eq. 1) thus reaction is not spontaneous at lower temperatures [3].

The objective of this work is to prepare Ni-based catalysts that result high activity, selectivity and stability with least coke formation during DRM process. Effect of different promoters on activity, stability and carbon formation is investigated in the present work. Various characterization techniques were employed to substantiate the findings.

2. EXPERIMENTAL

2.1. Support Preparation

Gamma alumina (γ-Al₂O₃) support was prepared via hydrothermal crystallization of boehmite. First boehmite was prepared by Al(NO₃)₃·9H₂O solution which was mixed with
25% aqueous NH₃ solution at pH 8.52. The precipitates were directly transferred to an autoclave and maintained at 121°C and 15 psig for 6 hours [14]. Then the precipitates (boehmite) were washed 5 times with distilled water and after overnight drying, finally it was thermally decomposed at 600°C for 24 hours to form γ-Al₂O₃[15].

2.2. Catalyst Preparation

Wang et al. observed high activity with less carbon deposition for 3% Ni loading on Al₂O₃ [11]. So, in the present investigation Ni/γ-Al₂O₃ catalysts were prepared having 3%Ni loading using Ni(NO₃)₂·6H₂O salt as precursor by wet impregnation method followed by drying at 110°C for 7 h.

Ce(NO₃)₃ · 6H₂O, Ca(NO₃)₂ · 4H₂O, Zr(NO₃)₄ · 5H₂O, Mg(NO₃)₂ · 6H₂O, RhCl₃ · xH₂O precursors were used for incorporation of Ce, Ca, Zr, Mg, Rh promoters respectively. The catalysts were calcined at 750°C for 2h as the optimum calcination temperature reported by Al Fatesh [13]. Six catalysts were prepared and named as Cat1 (3%Ni/γ-Al₂O₃), Cat2 (0.05%Ca-3%Ni/γ-Al₂O₃), Cat3 (0.05%Ca-0.15%Ce-3%Ni/γ-Al₂O₃), Cat4 (0.05%Mg-0.15%Ce-3%Ni/γ-Al₂O₃), Cat5 (0.05%Ca-0.15%Ce-0.15%Zr-3%Ni/γ-Al₂O₃), and Cat6 (0.15Ce-0.05Ca-0.5Rh-3%Ni/γ-Al₂O₃).

2.3. Dry Reforming of Methane

Reforming reaction was carried out in a quartz tubular reactor with 0.75 gm catalyst, volume feed ratio CH₄:CO₂:Ar = 15:15:3 mL/min, constant temperature of 700°C and at atmospheric pressure. The catalysts were reduced in situ with H₂ (40ml/min) at 650°C for 2h followed by flushing with Ar prior to DRM study. The temperature of the catalyst bed was increased to 700°Cand then reactant feed was started. The temperature of the bed was maintained ±0.5°C with the help of a microprocessor temperature controller. Inlet and outlet of the reactor were analysed by an online GC equipped with porapack q-column, methanizer and FID detector. All the catalysts were investigated at 700°C for reactant conversion. The used catalysts were analysed for carbon deposition by CHNS analyser. The conversion of the reactants was calculated as given by Eq. 4, 5.

\[
\text{CH}_4 \text{ conversion (\%)} = \frac{\text{CH}_4^{\text{in}} - \text{CH}_4^{\text{out}}}{\text{CH}_4^{\text{in}}} \times 100
\]
\[
\text{CO}_2 \text{ conversion (\%)} = \frac{\text{CO}_2^{\text{in}} - \text{CO}_2^{\text{out}}}{\text{CO}_2^{\text{in}}} \times 100
\]

2.4. Characterization of Catalysts

The catalysts were characterized by different techniques such as XRD, FTIR, SEM-EDX, TPR etc., to investigate the relationship between their morphology and activity. The amount of carbon deposited on the catalyst after reaction is determined by CHNS analyser.

X-ray measurement of the catalyst was carried out using Rigaku Ultima IVX-ray diffractometer (Germany) for phase identification. The patterns were run with Cu-Kα radiation at 40 kV and 40 mA. The mean crystallite size (d) of the phase was calculated from the line broadening of the most intense reflection using the Scherrer Eq. (6).

\[
d = \frac{0.89\lambda}{\beta \cos \theta}
\]
Scanning electron micrographs (SEM) and SEM-EDX were recorded on Zeiss EVO 18 scanning electron microscope (SEM) instrument. An accelerating voltage of 15 kV and magnification of 5000X was applied. X-ray photoelectron spectroscopy (XPS) was used to monitor the surface compositions and chemical states of the constituent elements and performed on an Amicus spectrometer equipped with Al Kα X-ray radiation. For typical analysis, the source was operated at a voltage of 15 kV and current of 12 mA. The binding energy scale was calibrated by setting the main C 1s line of adventitious impurities at 284.7 eV, giving an uncertainty in peak positions of 0.2 eV.

The hydrogen temperature programmed reduction (H₂-TPR) was carried out in a quartz micro-reactor, equipped with a flow control system, a temperature controller and a mass spectrometer (GSD301, Omnistar TM). Approximately 150 mg of catalyst (40–60 mesh) was dried at 200°C for 1 h in He (>99.999%, 30 cm³/min). The temperature was then decreased to 50°C, and 5% H₂/Ar (30 cm³/min) was flowed through the sample for 30 min. Then the sample was heated at a rate of 10°C/min to 1000°C. The signals for H₂ and H₂O were recorded continuously. CHNS elemental analyzer was used to measure carbon deposited at catalyst surface in dry reforming reaction.

3. Results and Discussion

3.1. X-Ray-Diffraction

Figure 1 Shows XRD pattern of γ-Al₂O₃ prepared by hydrothermal crystallization of boehmite. The structure of γ-Al₂O₃ is traditionally considered as a cubic defect spinel type in which the oxygen atoms are arranged in a cubic close packing and Al atoms occupy the octahedral and tetrahedral sites. Gamma alumina phase was confirmed by matching XRD pattern peaks (figure 1) in JCPDS-ICDD 2003. The intensive and sharp diffraction peaks at 37.538 (3 1 1), 45.667 (4 0 0), 60.545 (5 1 1) and 66.600 (4 4 0) could be primarily attributed to a cubic γ-Al₂O₃ structure (PDF-50-0741 JCPDS file).

Figure 2 represents XRD patterns of all the six catalysts. NiO and NiAl₂O₄ are analysed to be present in the catalyst as it can be seen a very small peak at 2θ = 43.2 corresponding to NiO.
(2,0,0) and the broad peaks at \(2\theta = 31.2-31.5^\circ\), 37-37.4\(^\circ\), 45-45.4\(^\circ\), 59-60\(^\circ\) and 65-66\(^\circ\) suggesting the presence of \(\text{NiAl}_2\text{O}_4\) as reported by Becerra et al. [16] and Xu et al. [17]. Chen and Ren [18] reported that \(\text{NiAl}_2\text{O}_4\) spinel presence in catalysts results high coke deposition resistance but slight fall of activity. Crystallite size of catalysts was calculated by Eq. 6: cat1- 4.9878nm, cat2-4.979nm, cat3-4.5732nm, cat4-4.9844nm and cat5-4.6218nm. All catalysts crystallite sizes (Table 1) are comparable (~5 nm) and the intensity of catalyst peaks are less than support peaks because of Ni impregnation on the support surface [19]. Shalini and Prasad concluded in a recent review that small Ni crystallite size in catalysts (≈5nm) and optimum metal loading (3-12\%) result high activity for DRM process [2].

Catalysts XRD peaks shifted to lower angles as compared to support because of NiO diffusion in to the support structure to form \(\text{NiAl}_2\text{O}_4\).

From XRD pattern it is difficult to discriminate between \(\text{NiAl}_2\text{O}_4\) and \(\gamma\)-\(\text{Al}_2\text{O}_3\) because the reflections of these phases overlap. But the blue colour of calcined catalyst sample (Figure 3) and broad peak at high temperature reduction feature of the TPR pattern (Figure 8), support to this finding that \(\text{NiAl}_2\text{O}_4\) is present in the sample [17-18].
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Figure 4: SEM of a) γ-Al2O3 support, b) Cat1, c) Cat2, d) Cat3, e) Cat4, f) Cat5, g) Cat6
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3.2. Scanning Electron Microscopy (SEM)

Figure 4 shows SEM images of the support and all the catalysts at 5000 magnification. SEM micrographs of all catalyst samples are different in morphology and microstructure. Figure 4 a) shows alumina support particles in which a rough sheet like solid surface was observed. The particles become smaller and segregated by Ni impregnation and doping of promoters (Ca, Ce, Mg, Zr, Rh) (figure 4 b-g). Figure 5 shows SEM images of used Cat3, Cat5 and Cat6 (after 10h time on stream). Carbon deposition in the form of small patches on catalyst surface can be observed and it is clearly noticed that Cat5 seemed to be more affected as compared to Cat3. Rh doped catalyst was named as Cat8 which shows negligible deposition of carbon. Thus, Rh doped noble metal catalyst is highly coke resistant.

Table 1: Crystallite size for all six catalysts

<table>
<thead>
<tr>
<th>S.R</th>
<th>Catalysts</th>
<th>Crystallite size (nm)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Cat1</td>
<td>4.9878</td>
</tr>
<tr>
<td>2</td>
<td>Cat2</td>
<td>4.9790</td>
</tr>
<tr>
<td>3</td>
<td>Cat3</td>
<td>4.5732</td>
</tr>
<tr>
<td>4</td>
<td>Cat4</td>
<td>4.9844</td>
</tr>
<tr>
<td>5</td>
<td>Cat5</td>
<td>4.6218</td>
</tr>
<tr>
<td>6</td>
<td>Cat6</td>
<td>4.3567</td>
</tr>
</tbody>
</table>

Figure 5: Used catalyst SEM images a) Cat3 b) Cat5 c) Cat6

Figure 6: SEM-EDX pattern of Cat5 in two different spectra
EDX result of cat5 at two different locations is shown in figure 5. It was evident from the results of energy dispersive X-ray (EDX) analysis that catalyst sample were pure due to presence of Al, Ca, Ce, Zr, Ni and O peaks there is no other element present in the spectra as shown in figure. It also confirmed the presence of pure oxides phase in the sample which is in good harmony with the XRD and FTIR experiment results. Same thing is noticed for other catalysts.

3.3. Fourier Transform Infra-Red Spectroscopy (FTIR)

Figure 7 (a, b, c) shows broad band around 3500 cm\(^{-1}\) and 1650 cm\(^{-1}\), which are assigned to stretching and bending modes of adsorbed water. The peak at 1400 cm\(^{-1}\) corresponds to NO\(_3^+\)ion which is not present in support as it was not having NiNO\(_3\). The peak corresponding to 900 cm\(^{-1}\) is assigned to Al–O–Al symmetric bending stretching vibrations and around 1160 cm\(^{-1}\) is due to asymmetric bending modes. The bands at 435 and 620 cm\(^{-1}\) are attributable to bending and stretching modes of AlO\(_6\). Peak at 750 cm\(^{-1}\) may be due to Al–O stretching vibrations [20].
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![Graph of FTIR results of catalysts and support](image)

**Figure 7**: FTIR results of catalysts and support

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Transmittance %</th>
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<tbody>
<tr>
<td>425</td>
<td>620</td>
</tr>
<tr>
<td>1075</td>
<td>1650</td>
</tr>
<tr>
<td>3500</td>
<td>425</td>
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<tr>
<td>1650</td>
<td>3500</td>
</tr>
<tr>
<td>620</td>
<td>425</td>
</tr>
<tr>
<td>1650</td>
<td>3500</td>
</tr>
</tbody>
</table>

**b) Cat 4**

**c) Cat 6**

**Cat 5**

**Cat 6**
3.4. Temperature Programmed Reduction (TPR)

To study the NiO reducibility, metal support interaction and to find correct reduction conditions, TPR experiments were performed. Gamma Alumina support was also checked for comparison purpose. Small NiO particles and strongly bonded to the support is normally reduced at higher temperatures than large particles with poor metal–support interaction [19]. In the same way, high Ni loading catalysts also have less reduction temperature due to lack of metal-support interaction. As present study using 3%Ni loading with small NiO particles so TPR peaks are at high temperature values.

Two possibilities are there: NiO bonded to Al$_2$O$_3$ (reduction temperature 400–600°C); and NiO incorporated into Al$_2$O$_3$, i.e., formation of NiAl$_2$O$_4$ (reduction temperature >700°C, with the maximum reduction temperature in the range of 780–835°C) [21]. TPR pattern (figure 8) recorded for cat1 shows two peaks, first broad peak corresponding to NiO and second for NiAl$_2$O$_4$ phase. Thus TPR result and the blue colour of catalyst after calcination (figure 3) favours the statement of presence NiAl$_2$O$_4$ species and it is well known that NiAl$_2$O$_4$ provide more resistance to sintering compared to free NiO species [22-23]. In present work, catalyst was reduced at 650°C means NiO is reduced to metallic Ni (400–600°C) and NiAl$_2$O$_4$ was remained intact in the reduced sample and provide high resistance to sintering as well carbon accumulation (table 2).

![Figure 8: H$_2$ consumption data with temperature](image)

3.5. Catalyst Activity

The activity of all the prepared catalysts in DRM process at 700°C is shown in Figure 9-10. Un-promoted 3%Ni/γ-Al$_2$O$_3$ (cat1) has given maximum 40% CO$_2$ and 35% CH$_4$ conversion and 5.96% carbon deposition for 10h reaction. It is clear from the figure that catalysts containing different promoters (Ca, Mg, Ce, Zr) resulted higher activity than un-promoted catalyst (cat1) due to their oxygen storage capacity which result a significant increase in oxygen deficiency or reaction sites means high CO$_2$ adsorption and high activity. This statement supports the conversion enhancement in cat2 containing 0.05% calcium. With cat2 conversion reached up to 60% CO$_2$ and 47% CH$_4$ but increasing content...
of Ca from 0.15 to 0.30% did not contribute any significant change in conversion. Further, improvement in formulation of CAT2 (0.05%Ca-3%Ni/γ-Al2O3) was made by doping with 0.15%Ce (0.15%Ce-0.05%Ca-3%Ni/γ-Al2O3, Cat3). Cat3 showed higher activity and significant drop in carbon deposition at the same temperature. It increased the conversions up to 78% for CO2 and 72% for CH4 with 2.247% carbon deposition for 10 h reaction. During reduction of catalysts, lattice oxygen in cerium oxide phase is eliminated and produces anionic vacancies which are considered as reactive sites of metal oxides. So, ceria promoted catalysts was considered for further investigation.
Table 2: Carbon deposition and images of the catalysts before & after 10h reaction on stream

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Carbon deposited</th>
<th>CO₂ %</th>
<th>CH₄ %</th>
<th>Figure before Reaction</th>
<th>Figure after Reaction (10h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat1</td>
<td>5.96%</td>
<td>43%</td>
<td>34%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cat2</td>
<td>2.936%</td>
<td>41%</td>
<td>57%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cat3</td>
<td>2.247%</td>
<td>79%</td>
<td>72%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cat4</td>
<td>1.336%</td>
<td>81%</td>
<td>15%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cat5</td>
<td>4.138%</td>
<td>94%</td>
<td>81%</td>
<td></td>
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</tr>
</tbody>
</table>
Cat4 in which Ca was replaced by Mg observed somewhat different in activity as well as in carbon deposition. CHNS analyser results (Table 2) showed catalyst picture before and after the reaction with carbon % deposited on catalyst surface. Cat4 colour is almost same before and after the reaction while all other catalysts became black after the reaction. This was observed may be due to less or no carbon accumulation on this catalyst because cat4 had given high difference between CO₂ (85%) and CH₄ (18%) conversion. This finding is also supported by Al-Fatesh et al. [7]. Due to this much high difference in CH₄ and CO₂ and almost no carbon accumulation, we can say that CH₄ is not reacting with CO₂ but some other side reaction is occurring in this case. So this catalyst was not considered for further study.

Mg replacement results were not good enough so again cat3 is modified with 0.15%Zr (Cat5 0.05%Ca - 0.15%Ce - 0.15%Zr - 3%Ni / γ-Al₂O₃) which analysed under DRM in same process conditions and compared with other catalysts. As shown in figure cat5 gave highest activity 95% CO₂ and 81% CH₄ conversion as compared other catalysts except cat6 but it has not performed well in carbon deposition (Table 2). All these findings are in agreement with results obtained by Al-Fatesh et al. [13].

Then Cat3 was doped with 0.5%Rh which resulted high CH₄ conversion 82% and CO₂ conversion 96% with 1.93% carbon deposition after 10h reaction. Cat6 is better than Cat3 according to the catalytic activity and carbon deposition results.

As mentioned in literature, Noble metals result high activity [24] and less carbon deposition, 0.5 % Rh/γ-Al₂O₃ [25] has been studied as a highly active catalyst for DRM process. But this new formulation Cat6 showing better performance than 0.5 % Rh/γ-Al₂O₃ catalyst for DRM reaction based on activity, SEM, XRD and CHNS results.

### 3.6. Carbon Deposition Analysis (CHNS Analyser)

Table 2 shows CHNS results for all the catalysts and pictorial representation of colour changes before and after the reaction. It was observed that Cat5 which was performed well in activity tests of promoted catalysts resulted 4.138% carbon deposition but only 2.247% carbon was deposited on Cat3, approximately half. It means that Cat3 should be preferred due to high activity with less carbon formation. Cat4 gave less carbon deposition as expected from its colour but it cannot be further used because of less CH₄ conversion. Cat 6 (Rh doped) catalyst resulted very less carbon (1.938%) as clear from CHNS and SEM results. So Cat3 and Cat6 were our best screened catalysts those should be preferred for DRM process.

### 4. Conclusion

The DRM process has gained much attention these days because of reducing GHG (CO₂ and CH₄) from the atmosphere. The main issue associated with this process is its carbonaceous deactivation of catalysts due to carbon formation as by-product. So, to make this process commercialized, an economic and best...
performance (high activity and least carbon deposition) catalyst is required.

Ni based catalyst supported on $\gamma$-Al$_2$O$_3$ with different promoters (Ca, Ce, Mg, Zr, Rh) are prepared and studied for DRM process. Ca and Ce promoted catalyst (Cat3) performs well (CH$_4$ conversion 79% and CO$_2$ conversion 72% with 2.247% carbon deposition for 10 h on stream) because of its high oxygen storage capacity and increment property of active sites. Zr addition with Ca, Ce catalyst (Cat5) is more active than the catalyst without Zr but it results higher carbon accumulation. More selective catalyst even with less activity is often chosen than one which is less selective with high initial activity. Thus, comparative order of catalyst choice is Cat3>Cat4. Mg is also investigated as a promoter (Cat4) in place of Ca in Cat3, but not performed well in the activity test. While Rh addition in Cat3 has given outstanding results of catalytic activity (CH$_4$ conversion 82% and CO$_2$ conversion 96%) as well as least carbon deposition (1.938%). Thus, it has been concluded that Cat6 containing Rh is the best screened catalyst for DRM process. This new formulation of catalyst will be very advantageous and turn this process towards industrial applications.

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