Performance of Ni/Al$_2$O$_3$-MgO catalyst for Dry Reforming of Methane: Effect of preparation routes

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Abstract. Nickel based nano-catalysts, supported on bimetallic oxide support (i.e. Ni/Al$_2$O$_3$-MgO) were prepared by the co-precipitation (one step, Catalyst-A) and co-precipitation followed by impregnation (two steps, Catalyst-B) techniques separately. The catalysts were then tested for the dry reforming of methane (DRM) reaction. The effect of catalyst synthesis technique on their performance has been analysed. The Ni/Al$_2$O$_3$-MgO nano-catalyst prepared by co-precipitation followed by impregnation method (two steps) technique was found to be superior to the one synthesized by co-precipitation (one step) method. The elevated CO$_2$ and CH$_4$ conversions and stable H$_2$/CO ratio have been observed throughout the DRM reaction at atmospheric pressure (i.e., 1atm), 800°C for Catalyst-B. Catalyst-B was better in terms of activity, conversion to syngas, stability, and reduced coke formation comparatively.

Keywords — DRM. Co-precipitation. Impregnation. Bimetallic oxide. Syngas.

1. Introduction
The rising population is posing numerous challenges that is being faced by the whole world. An increasing trend in the worlds energy consumption (i.e. nearly 100 % increase over the past decades) has been observed as per BP statistical review of world energy 2014. One of these challenges is the accumulation of greenhouse gases (GHGs) causing a global climate change which leads to disturbing climatic patterns across the landscapes. These type of alterations caused by human interference in nature causes the ecosystems to diminish and finally collapse, leading to a loss of biodiversity. The fossil fuels are mainly responsible for the increased concentration of world GHGs (carbon dioxide and methane) concentration in the atmosphere as per the reports of climate council. Around140 billion cubic meters (BCM) of CO$_2$ is emitted into the atmosphere as a result of flaring large volume of natural gas (NG), globally [1][2].
The Paris Agreement was also signed by 195 nations so as to control the adverse effects of climate change and global warming on the planet [3]. To control the rising global temperature (i.e., beneath 2°C) as per past industrial balance and to restrict its rise by next century. Radical measures need to be taken to curb the global temperatures and GHG’s emissions regarding the energy sector. This global treaty for controlling greenhouse gas (GHG) emissions demands some drastic amendments in energy sector. This bold objective can be achieved by sustainable, efficient, green, and assimilated approaches, that are emerging and are on the verge of transformation in as the energy sector. These objectives and goals can be envisioned by practicing the sustainable approach for energy resources, while keeping a check on CO₂ emission by its storage (CCS) and utilization (CCU) [4].

Carbon dioxide (CO₂) is a major GHG ambushing the infrared rays, which is emitted by various human activities such as deforestation and burning fossil fuels. It also gets released by natural phenomenon like respiration of animals and volcanic eruptions. The global CO₂ concentration is rising at an alarming scale and it reached all-time high as per the recordings from last five decades till date. As per the latest data released, the global CO₂ concentration reached 415.39 ppm which is highest recorded CO₂ concentration level in last two centuries. Similarly, the CH₄ concentration is also rising by human interference in exploiting the natural resources, such as natural gas processing, coal seam gas and leakage of more methane hydrates from ocean beds due to rise in ocean temperatures [5–7].

Global CO₂ emissions hit all time high level in 2018, emitting 33.1bn tons CO₂ in atmosphere [8], hence a need to fix the CO₂ emissions to put a check on Global warming. Variety of conventional technologies has been suggested for the separation of CO₂ from multicomponent gaseous stream such as chemical absorption (amine), adsorption, membrane separation and cryogenic fractionation. Malaysia is among the top 20 NG producers in the world with estimated natural gas reserves of 107.0 trillion square cubic feet (tscf) and some of these reservoirs contain very high CO₂ level (i.e. around 87 %) [9]. This high amount of CO₂ needs to be separated and stored or processed so as to avoid its emission in the atmosphere. CO₂, when present in natural gas, reduces the energy content of natural gas and due to its acidic property, cause corrosion in pipeline when water is also present. The CO₂ concentration of NG differs depending upon the geographical location in the prevailing gas reserves. Therefore, CO₂ reforming of methane is a promising area of research [10–12].

CO₂ is one of the major contributors to GHGs which is causing the greenhouse effect, nonetheless it may also be considered as natural source of carbon. This allows us to investigate various methods to produce green fuels and beneficial chemicals with simultaneously cutting the carbon emissions. With the recent discovery of huge shale gas reserves, and easily available exploitable techniques of fracking, CH₄ has become one of the chosen source of energy [13, 14]. The foul gasses emitted by anaerobic bacteria by decomposition of waste from landfills along with biogas are the considerable sources of GHGs other that shale gas reserves [15]. Apart from utilization of major GHGs and reducing their concentration, the dry reforming of methane (DRM) also produces a value-added product (i.e. synthesis gas of syngas). Syngas is an industrially important feedstock for manufacture of a wide range of value-added products [9]. CO₂ and Methane are to two major GHG’s which pose a grave environmental threat worldwide [16]. Although methane concentration is very in environment (i.e. in parts per billion), but its presence may cause great enhancement in global temperatures, since it is 28 times more captivating for infrared heat radiations then CO₂ [17].

In the process of CO₂ reforming of methane, the noble metals are suitable as they are both catalytically active and coke resistant; however noble metals are highly pricey; hence it is not economic to commercialize them. Successively, researchers spotlight the d-block metals, specially Ni and Co because of the fact that they are economic and has high activity and selectivity [18]. The major hurdles in the way of DRM commercialization are carbon formation causing catalyst deactivation and sintering at high reaction temperatures [10]. The role of the catalyst support is basically to provide high surface area to the active metals and enhanced dispersion with elevated metal support interactions [19]. The scheme of the reaction is shown below.

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298K} = +247 \text{ kJ/mol} \quad (1)
\]
One of the eye-catching features of DRM is its low H₂/CO ratios for syngas, which is highly pertinent for hydrocarbons synthesis via Fischer-Tropsch process. On the other hand, the syngas with high hydrogen content (as obtained from steam reforming of methane) is inferior to DRM process. Stoichiometric DRM H₂/CO ratio is unity but, reverse-gas shift reaction often slightly lower the ratio [20].

$$\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298K} = +41.2 \text{ kJ/mol} \quad (2)$$

Alumina is the most apt support for many catalytic materials but, it has limitations due to high coke formation. Nickel over magnesia have good coke resistance due to formation of Ni–Mg–O solid solution, but the activity of Nickel over magnesia was low compared with Nickel over alumina under the same reaction conditions. Nonetheless the high thermal stability and basicity of Mg make it suitable for use into the highly endothermic reaction of DRM [21]. A mixed oxide support (Al₂O₃ and MgO) is a promising approach. [22], studied the effect of Mg:Al ratio in catalyst support for Ni based catalyst and concluded that Mg:Al ratio of unity gives the best activity and stability for the DRM reaction.

In present work, we investigate the influence of method of catalyst synthesis on textural properties of catalyst, coke formed characterized by XRD and CO₂ and CH₄ conversions for Al₂O₃-MgO supported Ni catalyst. The catalysts are synthesized by co-precipitation method (one step, viz. Catalyst A) and co-precipitation followed by impregnation method (two steps, viz. Catalyst B) and have been for tested for DRM.

2. Methodology

2.1. Materials Required

Ni(NO₃)₂.6H₂O was used as Ni precursor whereas Al(NO₃)₃.9H₂O and Mg(NO₃)₂.6H₂O were used as catalyst support precursors. Ammonia solution with 28 wt.% in water was used as a precipitating agent and to maintain the value of pH at about 9.5, with constant stirring for ageing time of 10 hours. The temperature of the reaction mixture is maintained at 80°C for 10 hours. The reaction mixture is aged for 10 hours with constant stirring at 80°C. The reaction mixture is aged for 10 hours with constant stirring at 80°C. The reaction mixture is aged for 10 hours with constant stirring at 80°C. The reaction mixture is aged for 10 hours with constant stirring at 80°C. The reaction mixture is aged for 10 hours with constant stirring at 80°C.

| Chemical Name           | Linear Formula | Supplier    | Mass Fraction Purity |
|-------------------------|----------------|-------------|----------------------|
| Nickel Nitrate Hexahydrate | Ni(NO₃)₂.6H₂O  | Sigma Aldrich | >99.9%               |
| Magnesium Nitrate Hexahydrate | Mg(NO₃)₂.6H₂O | Sigma Aldrich | >99%                |
| Aluminium Nitrate Hexahydrate | Al(NO₃)₃.9H₂O | Sigma Aldrich | >99%                |
| Ammonia solution        | NH₄OH          | Sigma Aldrich | 28%                 |

2.2. Preparation of catalyst

2.2.1. Co-precipitation method (One step technique): Stoichiometric quantity of precursor chemicals i.e., Mg (NO₃)₂.6H₂O, Al (NO₃)₃.9H₂O and Ni (NO₃)₂.6H₂O were gradually dissolved in distilled water all together and ammonia solution (28 wt.% aqueous solution) is added drop wise to the mixture as a precipitating agent and to maintain the value of pH at about 9.5, with constant stirring for ageing time of 10 hours. The temperature of the reaction mixture is maintained at 80°C (figure 1). Thereafter, the precipitate was filtered and washed thoroughly with deionized water. The resulting slurry was dried at 110°C for 12 hours in the oven, and then calcined at 850°C for 5h in muffle furnace (ramping rate of 5°C/min) [23]. The calcined catalyst is then crushed by agate and mortar into fine powdered form.

2.2.2. Co-precipitation followed by impregnation (two steps technique): Aluminium and Magnesium oxide support is prepared by co-precipitation method. Stoichiometric quantity of precursor chemicals i.e. Al(NO₃)₃.9H₂O and Mg(NO₃)₂.6H₂O were dissolved in distilled water and ammonia solution (28 wt.% in water) is added drop wise to the mixture as a precipitating agent with constant stirring to maintain the value of pH at about 9.5. The reaction mixture is aged for 10 hours with constant stirring at 80°C. After that the precipitate was filtered and washed with deionized water; the resulting slurry was...
dried at 110°C for 12 hours and then calcined at 850°C for 3h in oven (ramping rate of 5°C/min) for Al₂O₃-MgO support material [24][20].

The supported metal (Ni) catalyst is prepared by impregnation of the previously prepared Al₂O₃-MgO support with Nickel Nitrate hexahydrate precursor salt solution to give nearly 10 wt.% Ni in the final catalyst. The required volume of the metal solution measured by adding water to the known amount of support. The procedure is the addition of water on the support until the first drop of water appeared on the surface of the support which indicated that the catalyst support is saturated and is not able to absorb water anymore. The mixture is aged for 6 hours under constant stirring at 80°C. Then the excess water is
evaporated and dried at 110°C for 12 hours and then calcined at 850°C for 3 hours. The process flow diagram is shown in figure 2.

2.3. Catalyst Performance Evaluation and Testing for DRM
The catalysts are evaluated in a tubular furnace reactor as shown in the figure 4 below. To evaluate the activity and the stability of the catalysts, 100 mg of each catalyst is loaded in the middle of the reactor. Before the real reaction, the catalysts are reduced in the presence of H₂ and N₂ at 800°C for 2h. It is then cooled to 600°C in a flow of nitrogen. After that, a mixture of CH₄ and CO₂ are introduced, and the activity test is performed at 800°C. The loss in catalyst activity at 800°C was monitored up to 6h on stream. The product stream has been analysed using a gas chromatography unit equipped with thermal conductivity detector (GC-TCD). The following schematic diagram shows the reactor system.

![Figure 3. Schematic diagram of the DRM reactor](image)

3. Results and discussions

3.1. GC-TCD analysis
The gas chromatography results confirm the occurrence of the DRM reaction over the prepared catalysts. The characteristic TCD peaks for different gases i.e., H₂, N₂, CO₂, CH₄ and CO₂ has been detected for both the catalysts as depicted in figure 4. It is evident from the figure 5 that the exit gas stream from the reactor composed of different gases. The peaks between 1.5-2.0 mins and 5.0-5.5 mins confirms the existence of hydrogen and carbon mono oxide.

![Figure 4. The GC-TCD results for catalyst B.](image)

Finally, methane and carbon monoxide conversions with the syngas ratio were calculated using the following expressions:

\[
X_{CH_4}(\%) = \left( \frac{F_{CH_4_{in}} - F_{CH_4_{out}}}{F_{CH_4_{in}}} \right) \times 100
\]  
(1)

\[
X_{CO_2}(\%) = \left( \frac{F_{CO_2_{in}} - F_{CO_2_{out}}}{F_{CO_2_{in}}} \right) \times 100
\]  
(2)
\[ \frac{H_2}{CO} = \frac{F_{H_2\text{out}}}{F_{CO\text{out}}} \]  

(3)

3.2. Coke formation

The catalysts prepared by two different routes were tested for DRM reaction in the reactor and the spent catalysts are weighed. It has been observed that for 100mg of catalyst used the coke formation for the catalyst A (i.e., prepared by single step co-precipitation method) was 75mg whereas for the catalyst B (i.e., prepared by two step co-precipitation followed by impregnation method) was only 5mg.

Table 2. Coke formation after 6 hours of DRM reaction for Ni/Al₂O₃-MgO catalysts prepared by different routes

| Catalyst                        | Catalyst amount used (mg) | Final Wt. of catalyst (mg) | Coke formation (mg) |
|---------------------------------|---------------------------|---------------------------|---------------------|
| Ni/Al₂O₃-MgO (catalyst A)       | 100                       | 175                       | 75                  |
| Ni/Al₂O₃-MgO (catalyst B)       | 100                       | 110                       | 10                  |

3.3. Textural properties of the synthesized catalyst

Table 3. Textural properties of the synthesized catalyst

| Catalyst                        | BET surface area \(^a\) (m²/g) | BJH average pore size (nm) | Pore volume \(\text{cm}^3/g\) | Average Crystal Size \(^b\) (nm) |
|---------------------------------|-------------------------------|----------------------------|-----------------------------|-------------------------------|
| Catalyst A                      | 25.1                          | 30                         | 29                          | 55.7                          |
| Catalyst B                      | 39.6                          | 21.4                       | 0.15                        | 40.6                          |
| Al₂O₃-MgO (support, Mg:Al=1)    | 96.1                          | 12.5                       | 0.26                        | -                             |

\(^a\) surface area computed by BET method.  
\(^b\) Debye–Scherrer equation used for XRD peaks of MgO for crystal size evaluation

The surface area and porosity analysis of catalyst A, catalyst B and the catalyst support has been done as shown in table 3. It can be seen clearly that for two step synthesis technique the initial surface area of catalyst support is high i.e. 96.1 \(m^2/g\). However, on adding the Ni on catalyst support the surface area reduced to 39.6 \(m^2/g\). The opposite pattern is observed for the average pore size and pore volume results obtained. On the other hand, the catalyst prepared by single step co-precipitation technique has very low surface area and big pore size and pore volume. This big pore size leads to the high coke formation [25], and is found consistent with the coke formed in the previous weight analysis. Further, the crystal size has been calculated employing the Debye-Scherrer equation along the plane of MgO. It has been found that Catalyst B has bigger particle size when compared to Catalyst A.

3.4. X-Ray diffraction pattern of the spent catalysts

The XRD pattern of the spent Catalyst A and Catalyst B has been recorded to determine the characteristic crystals phase present in the spent catalyst from 2θ range of 10-80º (figure 6). The sharp peaks corresponding to 2θ values has been obtained for catalyst A as compared to catalyst B. The 2θ peaks at 26º, 44 º, 52 º corresponding to NiAl₂O₄ phase [ICDD 01-077-3527] whereas the peaks at 37º and 67º is corresponding to MgO phase [ICDD 03-065-0476], which can be seen in both the catalysts and confirms the presence of alumina and magnesia. The NiAl₂O₄ phase is more prominent in catalyst A, since complex oxide of Ni is formed with alumina, because of one step synthesis technique. The NiO is also covered under the MgO peaks (due to similar MgO and NiO peak patterns) and characteristic peak for Ni alone is not visible, which is found consistent with the literature [26]. A peak at 2θ value of 45º corresponding to complex Al₂O₃-MgO (i.e., Al₂MgO₄) phase can be seen in Catalyst A. Another peak at 2θ value of 27º corresponds to graphitic carbon formed [ICDD 03-065-6212] in spent Catalyst A, which may have blocked the active sites of the catalyst, this is also found consistent with literature [27]. The graphitic carbon peak is however not significant in case of Catalyst B. It can hence be concluded from XRD results of spent Catalyst A and Catalyst B that, the for one step synthesis technique, the association of Ni metal was more with the support metals (i.e., Al and Mg). This was the reason of existence of complex Ni metal oxide crystals with alumina and magnesia. Hence, the
availability of active metal sites is low in single step synthesis technique when compared to 2-step synthesis technique.

Figure 5. XRD pattern of spent catalysts A and B

3.5. Performance evaluation of prepared catalysts

Figure 6. Performance curve of Catalyst A and B in terms of (a) CH₄% conversion (b) CO₂% conversion and (c) H₂:CO ratio

It has been observed that catalyst B proved out to be better than catalyst A in terms of CH₄ and CO₂ conversions and H₂/CO ratio. The mean CH₄ and CO₂ conversions for catalyst B was 64.7 % and
62.28% respectively and H₂/CO ratio varying between 1.1 to 0.9; whereas for catalyst A, CH₄ and CO₂ conversions were 45.8% and 56.8% respectively with H₂/CO ratio dropping from 0.8 to 0.6 for 6 hours of reaction (figure 6 (a-c)).

4. Conclusion
The synthesis and performance evaluation testing of 10 wt.% Ni supported on Al₂O₃-MgO (with Al:Mg = 1) catalyst prepared by one step synthesis (i.e., co-precipitation) and two step synthesis (co-precipitation+ impregnation) techniques are investigated. It has been found that the catalyst synthesized by two step method i.e., co-precipitation followed by impregnation showed superior results for DRM in terms of activity, coke formation, stability, surface area and conversion of CH₄ and CO₂. This is because in one step synthesis most of the active metal (Ni) gets encapsulated in alumina-magnesia lattice structure and some amount of Ni combines with Mg to form MgNiO₃, which is very stable and does not get reduced even at 800°C during activation step. Hence the two-step synthesis methodology is found to be better compared to one step synthesis technique.

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