1. Introduction

In the present environment, high thermal energy required for the reaction of abundant and thermodynamically stable methane and carbon dioxide molecules which are main constituents of greenhouse gases. These greenhouse gases are produced from combustion of bio-fuel and petroleum products. In order to maintain the CH$_4$ and CO$_2$ concentration within the threshold value limit in the atmosphere, there is a need to reduce emission of CH$_4$ and CO$_2$. However, required and obtained energy from fossil fuel for daily and long run purposes could not be met from other sources in the present scenario. Therefore, consumption of coal, bio-fuel and petroleum are inevitable. Dry reforming of CO$_2$ with CH$_4$ is the promising reaction and also important reaction in view point of reuse of carbon and hydrogen. As results, catalytic conversion of CO$_2$ and CH$_4$ into value added molecules is an alternative way to reduce...
their emission.

In the literature, the conversion of CO$_2$ by H$_2$ over γ-Al$_2$O$_3$-supported Rh; SiO$_2$-supported Ni, Ru, Co and Fe; nickel oxide doped platinum; and copper-zinc-chromium catalysts were investigated. Thermodynamically reductive conversion of CO$_2$ by using an excess H$_2$, CH$_4$ and H$_2$O were also investigated [1-14]. In addition, a partial oxidation of methane by nitrous oxide in presence of water was reported over silica supported molybdenum oxide catalyst [15-17]. However, dry reforming of carbon dioxide by methane gave C$_2$ hydrocarbons and syngas (CO and H$_2$). Dimerization of methane was observed during the carbon dioxide activation over Li/MgO catalyst. Dry reforming of CO$_2$ by CH$_4$ simultaneously gave ethylene and syngas. Moreover, catalytic reaction was reported of carbon oxides to hydrocarbon at atmospheric pressure over a ceria promoted copper containing cobalt catalysts [18-20]. However, the detail studies of de-oxygenation of CO$_2$ by using H$_2$, carbon and CH$_4$ are lacking.

Therefore, in this paper, de-oxygenation of CO$_2$ by either individual or/and combination of hydrogen, carbon and methane over reduced alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalysts were reported.

2. Materials and Method

2.1. Chemicals and apparatus

In the experiments, alumina-supported ruthenium, rhodium, platinum, molybdenum, vanadium, and magnesium catalysts were prepared by using the chemicals ruthenium chloride (ruthenium content 45-55%), rhodium chloride (98%), platinum chloride (99.99%), ammonium molybdate (99%), vanadate and magnesium nitrate (99%) (Aldrich Chemicals, CO.,) over alumina. In addition, the alumina support was prepared by the calcination of (Böhmite) aluminium oxide hydroxide (γ-AlO(OH)) at 500 °C for 1.5 h. Moreover, the high purity hydrogen, carbon dioxide, helium gases (Deluxe India Ltd.) and methane (Alphagaz) were used to explore the activation of carbon dioxide over alumina supported catalysts. The supported catalysts were calcined at 700 °C for 4 h in a furnace (Thermax Co. Ltd.). The reduction of alumina-supported ruthenium, rhodium, platinum, molybdenum, vanadium, and magnesium catalysts were carried out in hydrogen atmosphere. The de-oxygenation of CO$_2$ was carried out in a split furnace (Carbolite USA). Carbon dioxide, hydrogen, carbon monoxide, and methane were analyzed by using Porapak-Q as column, TCD and FID as detectors equipped with GC (Nucon India Ltd). The reactants and products of the de-oxygenation reactions of CO$_2$ were presented in terms of % conversion and % selectivity, respectively.

2.2. Characterization of catalysts

The alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalysts were characterized by X-Ray diffraction (Philips Power XRD) for XRD patterns. Particle sizes of catalysts were examined by SEM (QUANTA 200 3D).

2.3. Set up and procedure for the de-oxygenation of CO$_2$

The de-oxygenation of CO$_2$ was carried out over the reduced supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalysts in a split furnace as illustrated in Figure 1. A variable ratio was used of a mixture of carbon dioxide, H$_2$ or/and CH$_4$ in helium gas. A quartz fixed bed reactor was used with dimension 6 mm OD. The quartz reactor was modified at the center with dimension 10 mm OD and 10 cm length. In order to make complete set up, 4 mm OD stainless steel tubes, four three ways valves, a gas sampling valve, a carbolite split furnace with temperature
controller, a Nucon GC and flow control valves were used. With four three way valves, flow of hydrogen, helium and carbon dioxide gases were controlled (Figure 1). For flushing a catalyst bed, helium gas was used. For reduction of alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalyst a gas mixture of hydrogen and helium in 1:1 mol ratio was used at 500 °C for 1 h. De-oxygenation of carbon dioxide was carried out by using H$_2$, carbon, or/and CH$_4$ over reduced alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalysts at a temperature by keeping a molar ratio of CO$_2$ and helium 1:1. The analysis of carbon dioxide, hydrogen, methane and carbon monoxide was carried out by pulse technique by using Porapak-Q column with a Nucon GC equipped with TCD and FID (methane) detectors.

The alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalysts 0.1 to 0.5 gm with particle size -22 to -30 mesh was placed in the quartz reactor at centre with support of quartz wool. A certain temperature of catalyst bed was fixed with a temperature controller. Catalyst bed was flushed with helium gas in order to remove the stresses of other gases. After that, catalyst bed was reduced by using a mixture of hydrogen and helium gases in mol ratio 1:1 at 500 °C for 1 h. Then, catalyst bed was cooled down. The reactions of carbon dioxide were carried out by using hydrogen or/and CH$_4$ at certain temperature by passing a mixture of carbon dioxide and hydrogen or/and CH$_4$ in presence of helium. Further, the product was analyzed by online GC using a Porapak-Q column and also a thermal conductivity and flame ionization detector (methane). However, the results were confirmed by means of three runs. Furthermore, the results of the de-oxygenation reaction of CO$_2$ were presented as % conversion for reactants and % selectivity for products.

3. Results and discussion

The results of de-oxygenation reaction of carbon dioxide by using hydrogen or/and methane over alumina-supported ruthenium or rhodium or platinum or molybdenum or vanadium or magnesium catalysts are described in the following sections.

3.1 Characterization of catalysts

The catalyst particle size and the crystalline phases are important for the de-oxygenation of CO$_2$ over supported catalyst. Therefore, the alumina supported ruthenium, rhodium, platinum, molybdenum and vanadium catalysts were characterized by SEM images and XRD patterns. Characterized the 1 wt% Ru/Al$_2$O$_3$, 5 wt% Ru/Al$_2$O$_3$, 1 wt% Rh/Al$_2$O$_3$, 4 wt% Rh/Al$_2$O$_3$, 2 wt% Pt/Al$_2$O$_3$, 4 wt% Pt/Al$_2$O$_3$, 4 wt% Mo/Al$_2$O$_3$, 4 wt% V/Al$_2$O$_3$ and 7.5 wt% Mg/Al$_2$O$_3$ catalysts by SEM for particle size (Figure 2(a-i)). The SEM images clearly show the particle sizes of alumina supported noble metals catalysts. The particle size of catalyst is an important factor the de-oxygenation reaction of CO$_2$ because the reaction of CO$_2$ with hydrogen, methane, carbon and combining the mixture of hydrogen, methane and carbon could occur on the supported catalysts. Therefore, the large number of fine particles in the same amount of catalyst with their uniformity and uniform distribution enhances the de-oxygenation reaction of CO$_2$ with reactants hydrogen, methane and carbon. Here, the alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalysts were observed with fine and uniform particles as shown in the Figure 2(a-i). The observed de-oxygenation reactions of CO$_2$ with reactants hydrogen and methane are efficient (activities of catalysts are good) over alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalysts in the studied temperature range 500 to 650 °C.

The status of supported catalyst is observed by the XRD pattern of metal catalyst component over the alumina support. In order to identify the crystalline phases of catalysts, the XRD patterns for alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium were recorded for different loadings of these metals over alumina (Figures 3-5). In the Figure 3, the XRD patterns for the alumina supported molybdenum, vanadium and magnesium catalysts were recorded. However, the results show that as the loading of ruthenium increases over alumina from the 0.5 to 5 wt.%, the intensities of 2θ values of ruthenium were increased. The XRD patterns of 4 wt.% Pt/Al$_2$O$_3$ and 2 wt.% Rh/Al$_2$O$_3$ were shown in the Figure 4. In the Figures 3-5, it was observed that as the loading of metal catalyst component ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium over the alumina support increases, the crystalline phases of these metal catalyst component increases indicating that the de-oxygenation reaction of CO$_2$ with hydrogen and methane increases. The results (Figures 3-5) of intensity in the XRD pattern of metal catalyst component increases with the loading of metal catalysts component over the alumina support. However, the uniform distribution of metal...
Figure 2. The SEM images of the alumina supported metal catalysts, (a) 1 wt% Ru/Al₂O₃, (b) 5 wt% Ru/Al₂O₃, (c) 1 wt% Rh/Al₂O₃, (d) 4 wt% Rh/Al₂O₃, (e) 2 wt% Pt/Al₂O₃, (f) 4 wt% Pt/Al₂O₃, (g) 4 wt% Mo/Al₂O₃
catalyst component over the alumina support is also an important aspect. The uniform and equal distribution metal catalyst over alumina support was observed in a certain range of metal catalyst loading otherwise metal catalyst component either get coagulated or observed in bulky form. However, the crystalline phase of metal catalyst component is also an important aspect to allow the de-oxygenation reaction of CO$_2$ with hydrogen and methane. The conversion of de-oxygenation reaction of CO$_2$ was increased over the alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and (basicity) magnesium catalysts in the studied temperature range.

The acidities of alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and (basicity) magnesium oxide catalysts were given in Table 1. Although, CO$_2$ is an acidic gas, in a certain proportion it is adsorbed over the surface of the metal catalyst ruthenium, rhodium, platinum, molybdenum, vanadium and (basicity) magnesium components. The alumina supported molybdenum, vanadium and (basicity) magnesium catalysts deoxygenate the CO$_2$ to carbon along with other products. Therefore, alumina supported molybdenum, vanadium and (basicity) magnesium catalysts are highly active for the de-oxygenation reaction of CO$_2$. The conversion of de-oxygenation reaction of CO$_2$ was increased with the increased in
the temperature of reaction mixture on catalyst bed from 500 to 650 °C.

3.2. The de-oxygenation of CO₂ by using hydrogen.

However, the de-oxygenation reaction of CO₂ to methane is an eight-electron exchange process with the significant kinetic limitations. The de-oxygenation of carbon dioxide with hydrogen over catalyst would be given as:

\[
\begin{align*}
\text{CO}_2 + 4\text{H}_2 & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H = -167 \text{ kJ/mol} \\
\text{CO}_2 + \text{H}_2 & \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H = 41 \text{ kJ/mol} \\
\text{CO}_2 + 2\text{H}_2 & \rightarrow \text{C} + 2\text{H}_2\text{O} \quad \Delta H = 82.4 \text{ kJ/mol}
\end{align*}
\]

The de-oxygenation of carbon dioxide by using hydrogen were carried out over 1 wt% Ru/Al₂O₃, 1 wt% Rh/Al₂O₃, 1 wt.% Pt/Al₂O₃, 2 wt% Mo, 7.5 wt% V and 5 wt% Mg catalysts in a temperature range 50 to 650 °C (Figures 6-7). The conversion of CO₂ and selectivity for CO and CH₄ were estimated. The conversion of carbon dioxide was observed 0.1 to 2.6 % in a temperature range from 50 to 300 °C over 1 wt% Ru/Al₂O₃, 1 wt% Rh/Al₂O₃ and 1 wt.% Pt/Al₂O₃ catalysts. The observed selectivity for methane was from 1.2 to 1.4 % over 1 wt% Rh/Al₂O₃. In the temperature range from 50 to 300 °C, the activation energy required to activate the catalyst for the de-oxygenation reaction of CO₂ with hydrogen is not enough. Therefore, the conversion of de-oxygenation reaction of CO₂ was observed low.

The conversion of carbon dioxide was increased after the increasing the temperature 400 °C over 1 wt% Ru/Al₂O₃, 1 wt% Rh/Al₂O₃ and 1 wt.% Pt/Al₂O₃ catalysts. The selectivity to methane was also observed with the increased above 400 °C. The conversion of carbon dioxide and selectivity of carbon monoxide increases from the temperature

Figure 5. The XRD patterns of the alumina supported (a) molybdenum (b) vanadium and (c) magnesium catalysts

Figure 6. De-oxygenation of carbon dioxide by using hydrogen with respect to temperature over the catalysts, 1 wt% Ru/Al₂O₃, 1 wt% Rh/Al₂O₃ and 1 wt% Pt/Al₂O₃

Figure 7. De-oxygenation of carbon dioxide by using hydrogen with respect to temperature over the catalysts, 2 wt% Mo/Al₂O₃, 7.5 wt% V/Al₂O₃ and 5 wt% Mg/Al₂O₃
550 to 650 °C over 2 wt% Mo, 7.5 wt% V and 5 wt% Mg catalysts. 25.4% CO₂ conversion was observed over 1 wt% Pt/Al₂O₃ catalyst while the selectivity to methane was 33.8%. However, above the temperature 400 °C, the catalyst get higher energy of activation, therefore, the conversion of de-oxygenation reaction of CO₂ by hydrogen was observed higher.

3.3. De-oxygenation of CO₂ with variation of H₂/CO₂ mol ratio

From the above reactions, it can be seen that the H₂/CO₂ mol ratio is an important aspect to explore for the de-oxygenation reaction of CO₂ by hydrogen as the de-oxygenation of CO₂ and the product formation depend on the reaction mixture composition of CO₂ and hydrogen. The described in the de-oxygenation reactions of CO₂ by variation of mol ratio of CO₂ to H₂, the different products such as C, CO and CH₄ were formed. An effect of H₂/CO₂ mol ratio in a range from 1.0 to 5 for the de-oxygenation of CO₂ by H₂ was studied over 1 wt.% Ru/Al₂O₃, 1 wt.% Rh/Al₂O₃, 1 wt.% Pt/Al₂O₃, 2 wt% Mo, 7.5 wt% V and 5 wt% Mg at the 550 °C. De-oxygenation of CO₂ by H₂ showed the converted 12.1 % carbon dioxide with selectivity 12.5 % to methane over 1 wt.% Ru/Al₂O₃ catalyst at (H₂/CO₂) = 2 mol ratio (Figures 8-9). However, over 1 wt.% Pt/Al₂O₃) catalyst at the 550 °C, 9 % conversion of CO₂ with 14.6 % selectivity to methane was observed. The results showed that the conversion of carbon dioxide at 2 mol ratios was observed higher along with selectivity to carbon monoxide over 2 wt% Mo/Al₂O₃ catalyst. Over 7.5 wt%

<p>| Table 1. Acidity/basicity of Ru/Al₂O₃, Rh/Al₂O₃, Pt/Al₂O₃, Mo/Al₂O₃, V/Al₂O₃ and Mg/Al₂O₃ catalysts |</p>
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<th>Basicity mmol g⁻¹</th>
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</table>

Figure 8: De-oxygenation of carbon dioxide by using hydrogen with variation of H₂/CO₂ mol ratio over the 1 wt% Ru/Al₂O₃, 1 wt% Rh/Al₂O₃ and 1 wt% Pt/Al₂O₃ catalysts at 550 °C

Figure 9: De-oxygenation of carbon dioxide by using hydrogen with variation of H₂/CO₂ mol ratio over the 2 wt% Mo/Al₂O₃, 7.5 wt% V/Al₃O₅ and 5 wt% Mg/Al₂O₃ catalysts

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The reforming of CO at 550 °C. De-oxygenation of carbon dioxide by using hydrogen at 550 °C with variation of loading of Ru, Rh and Pt catalyst over alumina support is an important aspect to explore. The uniform distribution of total amount of supported ruthenium, rhodium, platinum, carbon dioxide and selectivity to carbon monoxide decreases with the increased in mol ratio above 3.

### 3.4. De-oxygenation of CO$_2$ with variation of catalyst loading

The uniform distribution of total amount of metal catalyst component over the alumina support is an important aspect to explore. The uniform and equal distribution metal catalyst amount over alumina support was observed in a certain range of metal catalyst loading otherwise metal catalyst component either get coagulated or observed in bulky form. De-oxygenation reaction of CO$_2$ by using H$_2$ was explored over alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalysts. Ruthenium, rhodium and platinum loadings over alumina were varied from 0.5 to 5 wt%. The molybdenum, vanadium and magnesium loadings over alumina were varied from 1.0 to 10 wt%. In the Figures 10-11, the results were given of conversion of carbon dioxide and selectivity to methane or carbon monoxide. The conversion of carbon dioxide and selectivity to methane was observed in the range 0.4 to 17 % and 0.2 to 18 %, respectively over ruthenium, rhodium and platinum catalysts. The conversions of carbon dioxide and selectivity to carbon monoxide were increased with the increased in the molybdenum, vanadium and magnesium loading from 1.0 to 10.0 wt%. For 10 wt% Mg/Al$_2$O$_3$, conversion of carbon dioxide and selectivity to carbon monoxide were 12.23 % and 20.73 % respectively.

### 3.5. De-oxygenation of CO$_2$ by methane

A reforming reaction of CO$_2$ with methane could be given as:

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{H}_2 + 2 \text{CO}
\]
The reforming of CO\(_2\) by CH\(_4\) at different mol ratios of CH\(_4\)/CO\(_2\), catalysts = 2 wt% Mo/Al\(_2\)O\(_3\), 7.5 wt% V/Al\(_2\)O\(_3\) and 5.0 wt% Mg/Al\(_2\)O\(_3\), amount of catalyst = 0.2 g, temperature = 550 °C, CO\(_2\) = 10 ml/min, He = 10 ml/min and methane variable

<table>
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<tr>
<th>Sr. No.</th>
<th>CH/CO(_2) mol ratio</th>
<th>CO(_2) conversion, %</th>
<th>CH(_4) conversion, %</th>
<th>CO selectivity, %</th>
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</table>

CO\(_2\) + CH\(_4\) → 2CO + 2H\(_2\)  \(\Delta H = 247\) kJ/mol

The de-oxygenation reactions of CO\(_2\) by methane could be given as follows:

CO\(_2\) + CH\(_4\) → 2C + 2H\(_2\)  \(\Delta H = 262.6\) kJ/mol

The product formation of de-oxygenation reaction of CO\(_2\) by methane depends on the composition of CO\(_2\) and methane over the catalyst bed. The results of reforming of CO\(_2\) by methane were given in Tables 2-3 over 2.5 wt% Ru/Al\(_2\)O\(_3\), 1.0 wt% Rh/Al\(_2\)O\(_3\), 1.0 wt% Pt/Al\(_2\)O\(_3\), 2.0 wt% Mo/Al\(_2\)O\(_3\), 7.5 wt% V/Al\(_2\)O\(_3\) and 5.0 wt% Mg/Al\(_2\)O\(_3\) catalysts at different mol ratios of CH\(_4\)/CO\(_2\). However, 5.3 to 8.6 % CO\(_2\) conversion, 5.3 to 8.6 % CH\(_4\) conversion and 4.7 to 5.3 % selectivity to CO were observed over 2.5 wt% Ru/Al\(_2\)O\(_3\) catalyst. Moreover, 0.2 to 2.5 % CO\(_2\) conversion, 0.2 to 2.4 % CH\(_4\) conversion and 0.1 to 1.3 % selectivity to CO were observed over 1.0 wt% Rh/Al\(_2\)O\(_3\) catalyst. In addition to this, 5.8 to 8.8 % CO\(_2\) conversion, CH\(_4\) 5.9 to 8.9 % conversion and 4.6 to 6.3 % selectivity to CO were observed over 1.0 wt% Pt/Al\(_2\)O\(_3\) catalyst. Moreover, over 2.0 wt% Mo/Al\(_2\)O\(_3\) catalyst, 0.83 to 2.66 % CO\(_2\) conversion, 0.04 to 3.0 % CH\(_4\) conversion and 0.08 to 0.63 % selectivity to CO were observed. Furthermore, 0.42 to 2.21 % CO\(_2\) conversion, 0.2 to 3.0 % CH\(_4\) conversion and 0.03 to 0.48 % selectivity to CO were observed over 7.5 wt% V/Al\(_2\)O\(_3\) catalyst. In addition to this, the results of 0.23 to 1.12 % CO\(_2\) conversion, 0.12 to 1.24 % CH\(_4\) conversion and 0.005 to 0.20 % selectivity to CO were observed over 5.0 wt% Mg/Al\(_2\)O\(_3\) catalyst. There is no carbon formation over the alumina supported Ru, Rh, Pt and Mg catalysts, however, there was carbon formation over the alumina supported Mo and V catalysts. However, alumina supported platinum catalyst shows good performance for reforming of CO\(_2\) by CH\(_4\).

3.6. De-oxygenation of CO\(_2\) by using H\(_2\) and CH\(_4\)

The composition of reaction mixture during the de-oxygenation reaction of CO\(_2\) over catalyst bed is an important aspect to investigate. De-oxygenation reactions of carbon dioxide by using a mixture of hydrogen and CH\(_4\) over alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalysts were explored. Hydrogen and methane both de-oxygenate the CO\(_2\) over the alumina supported catalyst. Therefore, the combined effect hydrogen and methane for de-oxygenation of CO\(_2\) was explored. In Tables 4-5, 6.8 to 14.4 % CO\(_2\) conversion, 43.2 to 76.2 % CH\(_4\) conversion, 0.2 to 2.5 % CO\(_2\) conversion, 0.2 to 2.4 % CH\(_4\) conversion and 0.1 to 1.3 % selectivity to CO were observed over 1.0 wt% Pt/Al\(_2\)O\(_3\) catalyst.
conversion and 4.2 to 11 % selectivity to CO were observed over 2.5 wt% Ru/Al₂O₃ catalyst. Moreover, 3.8 to 6.4 % CO₂ conversion, 42.3 to 76.2 % CH₄ conversion and 5 to 9.7 % selectivity to CO were observed over 1 wt% Rh/Al₂O₃ catalyst. Furthermore, 8.1 to 13.9 % CO₂ conversion, 42.8 to 79.4 % CH₄ conversion and 9.0 to 23.1 % selectivity to CO were obtained over 1 wt% Pt/Al₂O₃ catalyst. In addition to this, the results observed of conversion of CO₂ and methane without the carbon formation. Moreover, alumina supported platinum catalyst was found to be efficient catalyst for the reactions of CO₂. The further studies of de-oxygenation reactions of CO₂ by using hydrogen and methane over 2.0 wt% Mo/Al₂O₃ catalyst show that the 1.4 to 6.2 % CO₂ conversion, 43.2 to 95.0 % CH₄ conversion and 3.2 to 9.7 % selectivity to CO. For the de-oxygenation reactions of CO₂ over 7.5 wt% V/Al₂O₃ catalyst, 2.8 to 9.6 % CO₂ conversion, 41.2 to 84.7 % CH₄ conversion and 2.1 to 9.6 % selectivity to CO were observed. Furthermore, 5.2 to 11.7 % CO₂ conversion, 41.5 to 92.8 % CH₄ conversion and 6.9 to 19.7 % selectivity to CO were obtained over 5 wt% Mg/Al₂O₃ catalyst.

3.7 De-oxygenation reactions of CO₂ in presence of carbon

The effect of carbon in presence of methane for the de-oxygenation reaction of CO₂ is also important aspect to explore. The de-oxygenation of CO₂ by using carbon could be given as follows:

\[ CO₂ + C \rightarrow 2CO \]
\[ \Delta H = 172.5 \text{ kJ/mol} \]

In the Figure 12, de-oxygenation reactions of CO₂ by using carbon and methane were studied over the 1 wt% Pt/Al₂O₃ catalyst. The results show that the methane conversion was higher in absence of carbon. The conversions of CO₂ and selectivity to CO trends were observed similar as earlier reported in the reforming of CO₂ by methane.

4. Conclusions

The de-oxygenation reactions have been explored of carbon dioxide by using hydrogen, methane and carbon over alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalysts. De-oxygenation reactions of CO₂ were efficient by using hydrogen or methane and hydrogen and methane over alumina supported ruthenium, rhodium, platinum, molybdenum, vanadium and magnesium catalysts. There was carbon formation during the de-oxygenation reactions of CO₂ over Mo and V supported catalysts. However, there is no carbon formation of over alumina supported ruthenium.

---

**Table 4:** De-oxygenation of CO₂ by using methane and hydrogen at different mol ratio of CH₄/CO₂, catalyst = 2.5 wt% Ru/Al₂O₃, 1.0 wt% Rh/Al₂O₃ and 1.0 wt% Pt/Al₂O₃ amount of catalyst = 0.2 g, temperature = 550 °C, H₂ = 20 ml/min and He = 10 ml/min

<table>
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<th>Sr. No.</th>
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<th>CO₂ conversion, %</th>
<th>CH₄ conversion, %</th>
<th>CO selectivity, %</th>
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**Table 5:** De-oxygenation of CO₂ by using methane and hydrogen at different mol ratio of CH₄/CO₂, catalyst = 2.0 wt% Mo/Al₂O₃, 7.5 wt% V/Al₂O₃ and 5.0 wt% Mg/Al₂O₃ amount of catalyst = 0.2 g, temperature = 550 °C, H₂ = 20 ml/min and He = 10 ml/min

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>CH₄/CO₂ mol ratio</th>
<th>CO₂ conversion, %</th>
<th>CH₄ conversion, %</th>
<th>CO selectivity, %</th>
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rhodium, platinum and magnesium catalysts. It was observed that the de-oxygenation of CO₂ by hydrogen, carbon and methane produced carbon, CO and CH₄.

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References