TRI-REFORMING OF METHANE: A NOVEL CONCEPT FOR SYNTHESIS OF INDUSTRIALLY USEFUL SYNTHESIS GAS WITH DESIRED H2/CO RATIOS USING CO2 IN FLUE GAS OF POWER PLANTS WITHOUT CO2 SEPARATION

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Introduction

CO2 conversion and utilization are an important element in chemical research on sustainable development, because CO2 also represents an important source of carbon for fuels and chemical feedstock in the future [1-3]. The prevailing thinking for CO2 conversion and utilization begins with the use of pure CO2, which can be obtained by separation. In general, CO2 can be separated, recovered and purified from concentrated CO2 sources by two or more steps based on either adsorption or absorption or membrane separation. Even the recovery of CO2 from concentrated sources requires substantial energy input [4,5]. According to US DOE, current CO2 separation processes alone require significant amount of energy which reduces a power plant's net electricity output by as much as 20% [6].

This paper discusses a new process concept that has been recently proposed [7-9] for effective conversion of CO2 in the flue gases from electric power plants without CO2 pre-separation, which can be used for the production of synthesis gas (CO + H2) with desired H2/CO ratios for synthesizing clean fuels and chemicals. The tri-reforming concept represents a new way of thinking both for conversion and utilization of CO2 in flue gas without CO2 separation, and for production of industrially useful synthesis gas with desired H2/CO ratios using flue gas and natural gas. Experimental results with Ni catalysts will be reported.

Why Using Flue Gas?

Flue gases from fossil fuel-based electricity-generating units are the major concentrated CO2 sources in the US. If CO2 is to be separated, as much as 100 megawatts of a typical 500-megawatt coal-fired power plant would be necessary for today's CO2 capture processes based on the alkanolamines [4-6]. Therefore, it would be highly desirable if the flue gas mixtures can be used for CO2 conversion but without pre-separation of CO2. CO2 conversion and utilization should be an integral part of CO2 management, although the amount of CO2 that can be used for making industrial chemicals is small compared to the quantity of flue gas.

Based on our research, there appears to be a unique advantage of directly using flue gases, rather than using pre-separated and purified CO2 from flue gases, for the proposed tri-reforming process. Typical flue gases from natural gas-fired power plants may contain 8-10% CO2, 18-20% H2O, 2-3% O2, and 67-72% N2; typical flue gases from coal-fired boilers may contain 12-14 mol% CO2, 8-10 mol% H2O, 3.5 vol % O2 and 72-77% N2. The typical furnace outlet temperature of flue gases is usually around 1200°C which will decreases gradually along the pathway of heat transfer, while the temperature of the flue gases going to stack is around 150°C. Pollution control technologies can remove the SOx, NOx and particulate matter effectively, but CO2 and H2O as well as O2 remain largely unchanged.

Concept of Tri-reforming

Tri-reforming is a synergetic combination of endothermic CO2 reforming (eq. 1) and steam reforming (eq. 2) and exothermic partial oxidation of methane (eq. 3, eq. 4). CO2, H2O and O2 in the waste flue gas from fossil-fuel-based power plants will be utilized as co-reactants for tri-reforming of natural gas for the production of synthesis gas.

Tri-reforming of Natural Gas:

\[
\begin{align*}
\text{CH}_4 + \text{CO}_2 & = 2 \text{ CO} + 2 \text{ H}_2 \quad \text{[Endo: } \Delta H^\circ = 247.3 \text{ kJ/mol]} \\
\text{CH}_4 + \text{H}_2\text{O} & = \text{CO} + 3 \text{ H}_2 \quad \text{[Endo: } \Delta H^\circ = 206.3 \text{ kJ/mol]} \\
\text{CH} + 1/2 \text{O}_2 & = \text{CO} + 2 \text{ H}_2 \quad \text{[Exo: } \Delta H^\circ = -35.6 \text{ kJ/mol]} \\
\text{CH}_4 + 2 \text{ O}_2 & = \text{CO}_2 + 2 \text{ H}_2\text{O} \quad \text{[Exo: } \Delta H^\circ = -880 \text{ kJ/mol]} \\
\end{align*}
\]

Reactions for Coke Formation and Destruction:

\[
\begin{align*}
\text{CH}_4 & = \text{C} + 2 \text{ H}_2 \quad \text{[Endo: } \Delta H^\circ = 74.9 \text{ kJ/mol]} \\
2 \text{ CO} & = \text{C} + \text{ CO}_2 \quad \text{[Exo: } \Delta H^\circ = -122.2 \text{ kJ/mol]} \\
\text{C} + \text{CO}_2 & = 2 \text{ CO} \quad \text{[Endo: } \Delta H^\circ = 172.2 \text{ kJ/mol]} \\
\text{C} + \text{H}_2\text{O} & = \text{CO} + \text{ H}_2 \quad \text{[Endo: } \Delta H^\circ = 131.4 \text{ kJ/mol]} \\
\text{C} + \text{ O}_2 & = \text{CO}_2 \quad \text{[Exo: } \Delta H^\circ = -593.7 \text{ kJ/mol]} \\
\end{align*}
\]

Fig. 1 illustrates the tri-reforming concept as a new approach to CO2 conversion using flue gases for syngas production. The tri-reforming is a synergetic combination of three catalytic reforming reaction processes. Coupling CO2 reforming and steam reforming can give syngas with desired H2/CO ratios for methanol (MeOH) and Fischer-Tropsch (F-T) synthesis. Synthesis gas (syngas) can be made using natural gas, coal, naphtha, and other carbon-based feedstocks by various processes. Steam reforming of methane, partial oxidation of methane, CO2 reforming of methane, and autothermal reforming of methane are the representative reaction processes for syngas production from natural gas.

![Fig. 1. Process concept for tri-reforming of natural gas using flue gas from fossil fuel-based power plants. HT represents heat transfer or heat exchange including reactor heat up and waste heat utilization.](image-url)

The combination of dry reforming with steam reforming can accomplish two important missions: to produce syngas with desired H2/CO ratios and to mitigate the carbon formation problem that is significant for dry reforming. Integrating steam reforming and partial
oxidation with CO₂ reforming could dramatically reduce or eliminate carbon formation on reforming catalysts thus increase catalyst life and process efficiency. Therefore, the proposed tri-reforming can solve two important problems that are encountered in individual processing. The incorporation of O₂ in the reaction generates heat in situ that can be used to increase energy efficiency and O₂ also reduces or eliminates the carbon formation on the reforming catalyst. The tri-reforming can thus be achieved with natural gas and flue gases using the ‘waste heat’ in the power plant and the heat generated in situ from oxidation with the O₂ that is already present in flue gas.

Thermodynamics of Tri-reforming Reactions

Table 1 shows the equilibrium conversions and the product H₂/CO molar ratios calculated using HSC program [10,11] for tri-reforming under atmospheric pressure. It is possible to perform tri-reforming with over 95% CH₄ conversion and over 80% CO₂ conversion at 800–850 °C when the ratio of CO₂ and H₂O is close to 1.0, O₂/CH₄ = 0.1, and the ratio of (CO₂ + H₂O + O₂)/CH₄ = 1.05. This is close to the cases with compositions of flue gases.

Table 1. Equilibrium CO₂ and CH₄ conversions and product H₂/CO molar ratios for tri-reforming of CH₄ with CH₄:CO₂:H₂O=1:0.475:0.475:0.1 at 850°C under 1 atm.

<table>
<thead>
<tr>
<th>Reaction Temperature °C</th>
<th>CH₄ Conv. (%)</th>
<th>CO₂ conv. (%)</th>
<th>H₂/CO Mol Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>98.54</td>
<td>84.50</td>
<td>1.71</td>
</tr>
<tr>
<td>800</td>
<td>96.60</td>
<td>81.10</td>
<td>1.72</td>
</tr>
<tr>
<td>750</td>
<td>90.70</td>
<td>73.33</td>
<td>1.77</td>
</tr>
<tr>
<td>700</td>
<td>86.60</td>
<td>55.60</td>
<td>2.14</td>
</tr>
</tbody>
</table>

Is Tri-reforming Feasible?

We have not found any previous publications or reports on reforming using flue gases for CO₂ conversion related to the concept proposed [7-9]. Our computational analysis shows there are benefits of incorporating steam (H₂O) and oxygen (O₂) simultaneously in CO₂ reforming of CH₄ [10,11]. Prior work established that CO₂ reforming encounters carbon formation problem, even with noble metal catalysts, particularly under elevated pressure [11-13]. Some recent laboratory studies with pure gases have shown that the addition of oxygen to CO₂ reforming [14-17] or the addition of oxygen to steam reforming of CH₄ [18] can have some beneficial effects in terms of improved energy efficiency or synergetic effects in processing and in mitigation of coking. Inui and coworkers have studied energy-efficient H₂ production by simultaneous catalytic combustion and catalytic CO₂-H₂O reforming of methane using mixture of pure gases including CH₄, CO₂, H₂O and O₂ [19]. Choudhary et al. reported their experimental study on simultaneous steam and CO₂ reforming of methane in the presence of O₂ at atmospheric pressure over Ni/CaO [20,21] or Ni/MgO-SA [22]; they have shown that it is possible to convert methane into syngas with high conversion and high selectivity for both CO and H₂. Ross and coworkers have shown that a Pt/ZrO₂ catalyst is active for steam and CO₂ reforming combined with partial oxidation of methane [23]. Therefore, tri-reforming seems feasible, and we also conducted laboratory studies [7-10].

Catalytic Tri-reforming Reactions

We also conducted catalytic tri-reforming experiments in a fixed-bed reactor using various catalysts prepared at Penn State University (by wet impregnation onto MgO, ZrO₂, CeO₂-ZrO₂, and Mg-CeO₂-ZrO₂ supports) [10]. Figs. 2, 3 and 4 show the CH₄ conversion, CO₂ conversion, and H₂/CO ratio in the products, respectively, for tri-reforming over Ni/MgO, Ni/ZrO₂, Ni/CeO₂, Ni/CeZrO and Ni/MgO/CeZrO catalysts prepared in our laboratory as well as commercial Ni/Al₂O₃ (ICI Synetix 23-4) catalyst. The feed for tri-reforming had the composition of CH₄:CO₂:H₂O:O₂ (mol ratio) = 1.0:0.48:0.54:0.1. Almost equal amounts of CO₂ and H₂O in the feed were intentionally selected for the convenience of comparing CO₂ conversions in the presence of an equal amount of H₂O in tri-reforming. The tri-reforming reactions were conducted at 700°C – 850°C and 1 atm at the space velocity of ca. 32,000 ml/(h·g cat.). Under all these reaction conditions, CH₄ and CO₂ conversions are very dependent on the type of catalysts used, but O₂ conversion is always 100%. Ni/MgO and Ni/MgO/CeZrO show the highest CO₂ conversion in general (Fig. 3). Ni/MgO/CeZrO, Ni/ZrO₂, and Ni/Al₂O₃ (ICI catalyst) give almost the same CH₄ conversions at 800°C – 850°C, while Ni/CeO₂ and Ni/CeZrO have relatively lower CH₄ conversions (Fig. 2). With the reaction temperature decreasing, CH₄ conversion over Ni/MgO declines much faster than that over other catalysts. At 700°C, the CH₄ conversion over Ni/MgO is the lowest among all the tested catalysts. We speculate that the deactivation of Ni/MgO at lower temperatures cause the fast decline of CH₄ conversion over Ni/MgO and the deactivation is caused by the re-oxidation of Ni. This speculation is justified by the facts that NiO in the NiO/MgO catalyst is not reducible at temperature below 750°C and no carbon formation is observed on the used Ni/MgO catalyst. In addition, metal sintering may not be the reason for deactivation because all the catalytic performance tests were first carried out at 850°C. Then the reaction temperatures were gradually decreased to 700°C.

Among all the catalysts tested, Ni/CeO₂ has the second lowest CH₄ conversion at reaction temperatures above 750°C. The low CH₄ conversion over Ni/CeO₂ is probably related to the larger Ni particles over Ni-CeO₂ or the occurring of strong metal-support interaction (SMSI) due to the partial reduction of CeO₂ at high temperatures. Surprisingly, Ni/CeZrO has the lowest CH₄ conversion. Although Ni/MgO, Ni/MgO/CeZrO, Ni/Al₂O₃ (ICI catalyst), and Ni/ZrO₂ have similar CH₄ conversions, their CO₂ conversions are quite different. Ni/MgO shows the highest CO₂ conversion at temperatures above 750°C, followed by Ni/MgO/CeZrO. Ni/CeO₂ and Ni/CeZrO again show the lowest CO₂ conversion.

The H₂/CO ratio in the products depends mainly on the CO₂ and H₂O conversions in tri-reforming. If more H₂O is converted than CO₂, then the H₂/CO ratio in the product would be higher. Similarly, if less H₂O is converted than CO₂, the H₂/CO ratio would be lower. Therefore, the H₂/CO ratio is a good indicator for comparing the ability to convert CO₂ in the presence of H₂O over different catalysts. Ni/MgO gives the lowest H₂/CO ratio, followed by Ni/MgO/CeZrO (shown in Fig. 4). The H₂/CO ratios over Ni/CeO₂, Ni/ZrO₂, and Ni/Al₂O₃ (ICI catalyst) are similar and slightly higher than Ni/MgO/CeZrO. Ni/CeZrO gives the highest H₂/CO ratio. These results strongly suggest that Ni/MgO enhance the CO₂ conversion most in the presence of H₂O and O₂. Among all the tested catalysts, their ability to enhance the conversion of CO₂ follows the order of Ni/MgO > Ni/MgO/CeZrO > Ni/CeO₂ ≈ Ni/ZrO₂ ≈ Ni/Al₂O₃ (ICI) > Ni/CeZrO.

The different ability to convert CO₂ over different catalysts in tri-reforming is related to the properties of the catalysts. The enhancement of CO₂ conversion over Ni/MgO might be related to its enhanced CO₂ adsorption ability as evidenced by the CO₂-TPD results (not shown here). However, catalysts supported on CeZrO (e.g., Ni/MgO/CeZrO and Ni/CeZrO) do not show more enhancement of CO₂ conversion than Ni/MgO even though these catalysts demonstrate more and stronger CO₂ adsorption than...
Ni/MgO as indicated by the large CO$_2$ desorption peaks at 710-717ºC. To further elucidate the enhancement of CO$_2$ conversion over Ni/MgO in tri-reforming, a kinetic study was carried out, the result of which will be reported in the future.

Elimination of Carbon Formation by Tri-reforming Compared to CO$_2$ Reforming

We conducted temperature-programmed oxidation of the used catalysts from the above tri-reforming experiments and found that except for Ni/ZrO$_2$ catalyst, all the other catalysts (corresponding to the experiments shown in Figs. 2 and 3) showed no sign of carbon formation after the tri-reforming experiments. We have also tested a commercially available Haldor-Topsoe R67 Ni-based catalyst for tri-reforming in a fixed-bed flow reactor using gas mixtures that simulate the cases with flue gases from coal-fired power plants (CO$_2$:H$_2$O:CH$_4$:O$_2$ = 1:1:1:0.1, mol ratio) and from natural gas-fired power plants (CO$_2$:H$_2$O:CH$_4$:O$_2$ = 1:2:1:0.1, mol ratio) [28]. For CO$_2$ reforming of CH$_4$, carbon formation is an important problem [12,13,24-27]. Temperature-programmed oxidation (TPO) results show that the used Haldor-Topsoe R67 catalyst after 300 min time-on-stream for CO$_2$ reforming at 850 ºC and 1 atm contained 21.8 wt% carbon [28]. On the other hand, the same catalyst employed in tri-reforming showed no sign of carbon formation after 300 min TOS, as the used catalyst appears to be greenish power (versus the black sample from CO$_2$ reforming). Fig. 5 shows the photographs of the used catalysts after CO$_2$ reforming and tri-reforming. Therefore, our results show that tri-reforming can be performed with stable operation, and no carbon formation and no appreciable deactivation of catalyst were observed under the tri-reforming conditions.

Does Tri-reforming Consume More Energy Than Steam or CO$_2$ Reforming?

A comparative energy analysis by calculation indicated that tri-reforming is more desired for producing syngas with H$_2$/CO ratios of 1.5-2.0 compared to CO$_2$ reforming and steam reforming of methane, in terms of less amount of energy required and less net amount of CO$_2$ emitted in the whole process for producing synthesis gas with H$_2$/CO ratio of 2.0 [8]. The tri-reforming process could be applied, in principle, to the natural gas-based power plants and coal-based power plants.

Conclusions

Catalytic tri-reforming of methane can be achieved successfully with high CH$_4$ conversion (>97%) and high CO$_2$ conversion (>80%) for producing syngas with desired H$_2$/CO ratios of 1.5-2.0 over supported nickel catalysts at 800-850 ºC under atmospheric pressure.
without the problem of carbon formation on the catalyst.

The CO$_2$ and CH$_4$ conversion as well as H$_2$/CO ratios of the products from tri-reforming also depend on the type and nature of catalysts.

An important observation is that CO$_2$ conversion can be maximized by tailoring catalyst composition and preparation method. In other words, certain catalysts with proper feature can give much higher CO$_2$ conversion than other catalysts under the same reaction conditions with the same reactants feed.

Among all the catalysts tested for tri-reforming, their ability to enhance the conversion of CO$_2$ follows the order of Ni/MgO/CeZrO > Ni/MgO/CeZrO $\approx$ Ni/Al$_2$O$_3$ (ICI) $>$ Ni/CeZrO. The different ability to convert CO$_2$ over different catalysts in tri-reforming is related to the properties of the catalysts.

Results of catalytic performance tests over Ni/MgO/CeZrO catalysts at 850ºC and 1 atm at different feed compositions confirm the predictions based on the thermodynamic analysis for equilibrium conversions in tri-reforming of methane.

Further studies on improving catalysts are necessary for understanding the factors affecting CO$_2$ conversion and CH$_4$ in the presence of steam and oxygen during tri-reforming.

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References