TRI-REFORMING OF METHANE: A NOVEL CONCEPT FOR SYNTHESIS OF INDUSTRIALLY USEFUL SYNTHESIS GAS WITH DESIRED H_2/CO RATIOS USING CO_2 IN FLUE GAS OF POWER PLANTS WITHOUT CO_2 SEPARATION

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Introduction

CO_2 conversion and utilization are an important element in chemical research on sustainable development, because CO_2 also represents an important source of carbon for fuels and chemical feedstock in the future [1-3]. The prevailing thinking for CO_2 conversion and utilization begins with the use of pure CO_2, which can be obtained by separation. In general, CO_2 can be separated, recovered and purified from concentrated CO_2 sources by two or more steps based on either absorption or adsorption or membrane separation. Even the recovery of CO_2 from concentrated sources requires substantial energy input [4,5]. According to US DOE, current CO_2 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 CO_2 in the flue gases from electric power plants without CO_2 pre-separation, which can be used for the production of synthesis gas (CO + H_2) with desired H_2/CO ratios for synthesizing clean fuels and chemicals. The tri-reforming concept represents a new way of thinking both for conversion and utilization of CO_2 in flue gas without CO_2 separation, and for production of industrially useful synthesis gas with desired H_2/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 CO_2 sources in the US. If CO_2 is to be separated, as much as 100 megawatts of a typical 500-megawatt coal-fired power plant would be necessary for today's CO_2 capture processes based on the alkanolamines [4-6]. Therefore, it would be highly desirable if the flue gas mixtures can be used for CO_2 conversion but without pre-separation of CO_2. CO_2 conversion and utilization should be an integral part of CO_2 management, although the amount of CO_2 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 CO_2 from flue gases, for the proposed tri-reforming process. Typical flue gases from natural gas-fired power plants may contain 8-10% CO_2, 18-20% H_2O, 2-3% O_2, and 67-72% N_2; typical flue gases from coal-fired boilers may contain 12-14 vol% CO_2, 8-10 vol% H_2O, 3-5 vol % O_2 and 72-77% N_2. 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 CO_2 and H_2O as well as O_2 remain largely unchanged.

Concept of Tri-reforming

Tri-reforming is a synergetic combination of endothermic CO_2 reforming (eq. 1) and steam reforming (eq. 2) and exothermic partial oxidation of methane (eq. 3, eq. 4). CO_2, H_2O and O_2 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:

$CH_4 + CO_2 = 2\ CO + 2\ H_2$	[Endo: $\Delta H° = 247.3$ kJ/mol]	(1)
$CH_4 + H_2O = CO + 3\ H_2$	[Endo: $\Delta H° = 206.3$ kJ/mol]	(2)
$CH_4 + 1/2\ O_2 = CO + 2\ H_2$	[Exo: $\Delta H° = -35.6$ kJ/mol]	(3)
$CH_4 + 2\ O_2 = CO_2 + 2\ H_2O$	[Exo: $\Delta H° = -880$ kJ/mol]	(4)

Reactions for Coke Formation and Destruction:

$CH_4 = C + 2\ H_2$	[Endo: $\Delta H° = 74.9$ kJ/mol]	(5)
$2\ CO = C + CO_2$	[Exo: $\Delta H° = -172.2$ kJ/mol]	(6)
$C + CO_2 = 2\ CO$	[Endo: $\Delta H° = 172.2$ kJ/mol]	(7)
$C + H_2O = CO + H_2$	[Endo: $\Delta H° = 131.4$ kJ/mol]	(8)
$C + O_2 = CO_2$	[Exo: $\Delta H° = -393.7$ kJ/mol]	(9)

Fig. 1 illustrates the tri-reforming concept as a new approach to CO_2 conversion using flue gases for syngas production. The tri-reforming is a synergetic combination of three catalytic reforming reaction processes. Coupling CO_2 reforming and steam reforming can give syngas with desired H_2/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, CO_2 reforming of methane, and autothermal reforming of methane are the representative reaction processes for syngas production from natural gas.

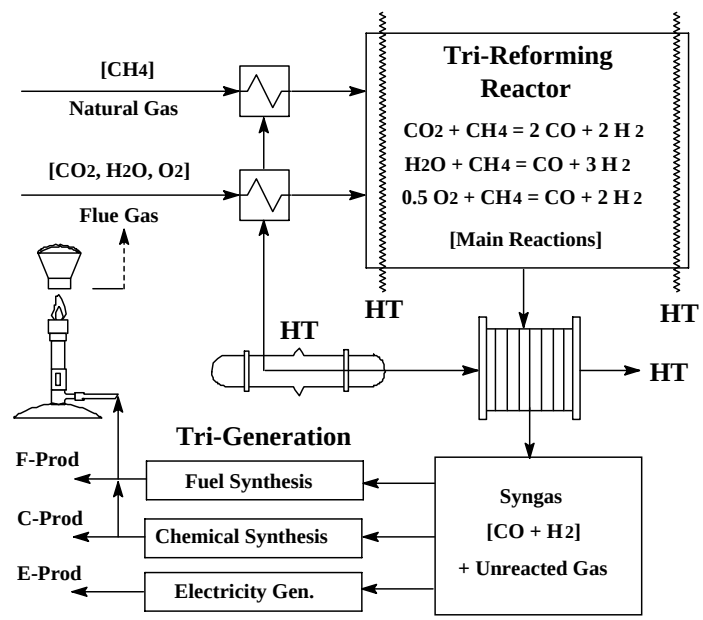

Fig. 1. Process concept for tri-reforming of natural gas using flue gas from fossil fuel-based power plants. HT represents heat transfer or heat exchange including reactor heat up and waste heat utilization .

The combination of dry reforming with steam reforming can accomplish two important missions: to produce syngas with desired H_2/CO ratios and to mitigate the carbon formation problem that is significant for dry reforming. Integrating steam reforming and partial

oxidation with CO_2 reforming could dramatically reduce or eliminate carbon formation on reforming catalyst 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 O_2 in the reaction generates heat in situ that can be used to increase energy efficiency and O_2 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 O_2 that is already present in flue gas.

Thermodynamics of Tri-reforming Reactions

Table 1 shows the equilibrium conversions and the product H_2/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% CH_4 conversion and over 80% CO_2 conversion at 800-850 °C when the ratio of CO_2 and H_2O is close to 1.0, O_2/CH_4= 0.1, and the ratio of $(CO_2+H_2O+O_2)/CH_4$ = 1.05. This is close to the cases with compositions of flue gases.

Table 1. Equilibrium CO_2 and CH_4 conversions and product H_2/CO molar ratios for tri-reforming of CH_4 with CH_4:CO_2:H_2O:O_2 =1:0.475:0.475:0.1 at 850C under 1 atm.

Reaction	Equilibrium		
Temperature °C	CH_4 Conv. (%)	CO_2 conv. (%)	H_2/CO Mol Ratio
850	98.54	84.50	1.71
800	96.00	81.10	1.72
750	90.70	73.33	1.77
700	86.00	55.60	2.14

Is Tri-reforming Feasible?

We have not found any previous publications or reports on reforming using flue gases for CO_2 conversion related to the concept proposed [7-9]. Our computational analysis shows there are benefits of incorporating steam (H_2O) and oxygen (O_2) simultaneously in CO_2 reforming of CH_4 [10,11]. Prior work established that CO_2 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 CO_2 reforming [14-17] or the addition of oxygen to steam reforming of CH_4 [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 H_2 production by simultaneous catalytic combustion and catalytic CO_2-H_2O reforming of methane using mixture of pure gases including CH_4, CO_2, H_2O and O_2 [19]. Choudhary et al. reported their experimental study on simultaneous steam and CO_2 reforming of methane in the presence of O_2 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 H_2. Ross and coworkers have shown that a Pt/ZrO_2 catalyst is active for steam and CO_2 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, ZrO_2, CeO_2-ZrO_2, and Mg-CeO_2-ZrO_2 supports) [10]. Figs. 2, 3 and 4 show the CH_4 conversion, CO_2 conversion, and H_2/CO ratio in the products, respectively, for tri-reforming over Ni/MgO, Ni/ZrO_2, Ni/CeO_2, Ni/CeZrO and Ni/MgO/CeZrO catalysts prepared in our laboratory as well as commercial Ni/Al_2O_3 (ICI Synetix 23-4) catalyst. The feed for tri-reforming had the composition of CH_4:CO_2:H_2O:O_2 (mol ratio) = 1:0.48:0.54:0.1. Almost equal amounts of CO_2 and H_2O in the feed were intentionally selected for the convenience of comparing CO_2 conversions in the presence of an equal amount of H_2O in tri-reforming. The tri-reforming reactions were conducted at 700ºC – 850ºC and 1 atm at the space velocity of ca. 32,000 ml/(h.g cat.). Under all these reaction conditions, CH_4 and CO_2 conversions are very dependent on the type of catalysts used, but O_2 conversion is always 100%. Ni/MgO and Ni/MgO/CeZrO show the highest CO_2 conversion in general (Fig. 3). Ni/MgO/CeZrO, Ni/ZrO_2, and Ni/Al_2O_3 (ICI catalyst) give almost the same CH_4 conversions at 800ºC – 850ºC, while Ni/CeO_2 and Ni/CeZrO have relatively lower CH_4 conversions (Fig. 2).. With the reaction temperature decreasing, CH_4 conversion over Ni/MgO declines much faster than that over other catalysts. At 700ºC, the CH_4 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 CH_4 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 750ºC 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 850ºC. Then the reaction temperatures were gradually decreased to 700ºC.

Among all the catalysts tested, Ni/CeO_2 has the second lowest CH_4 conversion at reaction temperatures above 750ºC. The low CH_4 conversion over Ni/CeO_2 is probably related to the larger Ni particles over Ni-CeO_2 or the occurring of strong metal-support interaction (SMSI) due to the partial reduction of CeO_2 at high temperatures. Surprisingly, Ni/CeZrO has the lowest CH_4 conversion. Although Ni/MgO, Ni/MgO/CeZrO, Ni/Al_2O_3 (ICI catalyst), and Ni/ZrO_2 have similar CH_4 conversions, their CO_2 conversions are quite different. Ni/MgO shows the highest CO_2 conversion at temperatures above 750ºC, followed by Ni/MgO/CeZrO. Ni/CeO_2 and Ni/CeZrO again show the lowest CO_2 conversion.

The H_2/CO ratio in the products depends mainly on the CO_2 and H_2O conversions in tri-reforming. If more H_2O is converted than CO_2, then the H_2/CO ratio in the product would be higher. Similarly, if less H_2O is converted than CO_2, the H_2/CO ratio would be lower. Therefore, the H_2/CO ratio is a good indicator for comparing the ability to convert CO_2 in the presence of H_2O over different catalysts. Ni/MgO gives the lowest H_2/CO ratio, followed by Ni/MgO/CeZrO (shown in Fig. 4). The H_2/CO ratios over Ni/CeO_2, Ni/ZrO_2, and Ni/Al_2O_3 (ICI catalyst) are similar and slightly higher than Ni/MgO/CeZrO. Ni/CeZrO gives the highest H_2/CO ratio. These results strongly suggest that Ni/MgO enhance the CO_2 conversion most in the presence of H_2O and O_2. Among all the tested catalysts, their ability to enhance the conversion of CO_2 follows the order of Ni/MgO > Ni/MgO/CeZrO > Ni/CeO_2 ≈ Ni/ZrO_2 ≈ Ni/Al_2O_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. The enhancement of CO_2 conversion over Ni/MgO might be related to its enhanced CO_2 adsorption ability as evidenced by the CO_2-TPD results (not shown here). However, catalysts supported on CeZrO (e.g., Ni/MgO/CeZrO and Ni/CeZrO) do not show more enhancement of CO_2 conversion than Ni/MgO even though these catalysts demonstrate more and stronger CO_2 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.

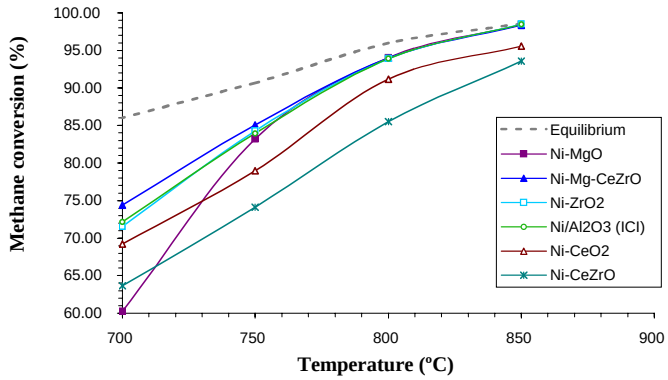

Fig. 2. *CH_4 conversions in the tri-reforming reaction over 100 mg supported Ni catalysts at 1 atm and feed composition of CH_4 : CO_2 : H_2O : O_2 = 1 : 0.48 : 0.54 : 0.1 (CH_4 flow rate = 25 ml/min)*

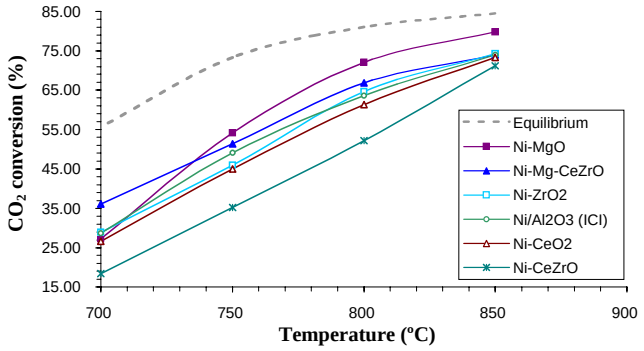

Fig. 3. CO_2 conversions in the tri-reforming reaction over 100 mg supported Ni catalysts at 1 atm and feed composition of CH_4 : CO_2 : H_2O : O_2 = 1 : 0.48 : 0.54 : 0.1 (CH_4 flow rate = 25 ml/min)

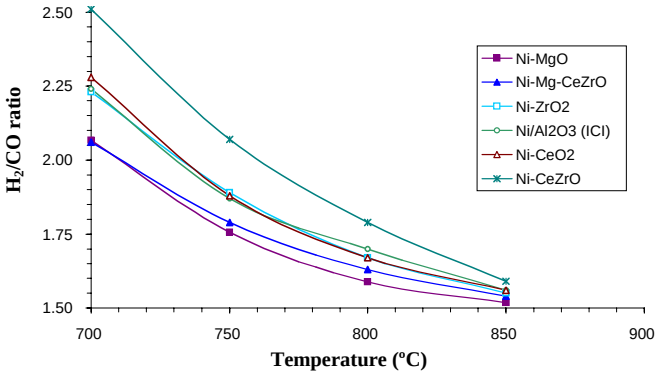

Fig. 4. H_2/CO ratios in the tri-reforming reaction over 100 mg supported Ni catalysts at 1 atm and feed composition of CH_4 : CO_2 : H_2O : O_2 = 1 : 0.48 : 0.54 : 0.1 (CH_4 flow rate = 25 ml/min)

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/ZrO2 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_2O:CH_4:O_2 = 1:1:1:0.1, mol ratio) and from natural gas-fired power plants (CO_2:H_2O: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 °C 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.

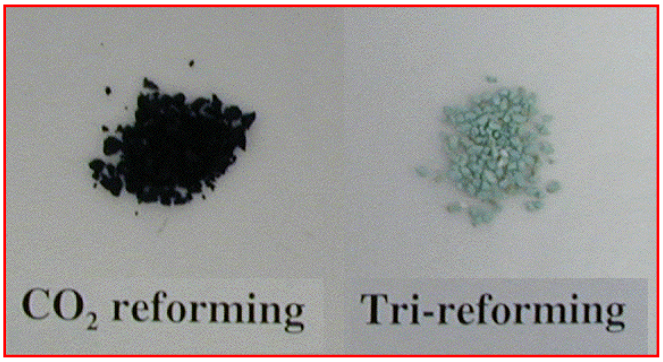

Fig. 5. Appearance of Haldor-Topsoe R67 Ni-based catalyst after 300 min TOS of CO_2-reforming (CO_2:CH_4 = 1:1, used catalyst particles are black in color) and tri-reforming (CO_2:H_2O:O_2:CH_4 = 1:1:0.1:1, used catalyst particles are green in color) at 850 °C.

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 °C 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 > Ni/MgO/CeZrO > Ni/CeO_2 ≈ Ni/ZrO_2 ≈ Ni/Al_2O_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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