

Microreactor for Catalytic Partial Oxidation of Methane

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Abstract

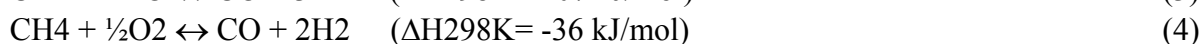
Fixed-bed reactors for partial oxidation of methane to produce synthetic gas bear a hot-spot problem. To avoid this problem, an alternative reactor, which is called shell and tube type microreactor, has been developed in this work. Combustion and reforming reactions are integrated in this reactor. The microreactor used in this work consists of a 1 cm outside-diameter, 0.8 cm inside-diameter and 11 cm length tube, and a 1.8 cm inside-diameter shell. The tube is made of dense alumina and the shell of quartz. Two different methods dip and spray coating were performed to coat the tube side with LaNi_xO_y catalyst. Gaseous reactants burn in the tube side to produce flue gases which in turn flow countercurrently and react in the shell side to yield reforming products. The methane conversion reaches 97% at 700°C with the catalyst spray-coated tube, while the catalyst dip-coated tube reaches only 7.78%. Turnover frequencies (TOF) using the catalyst sprayed and dip-coated tubes are 5.75 x 10⁻⁵ and 2.24 x 10⁻⁵ mol/gram cat.s, respectively. The hydrogen to carbon monoxide ratios produced are greater than the stoichiometric ratio, which are probably caused by carbon deposit through methane cracking and Boudouard reactions.

Keywords: micro reactor, catalytic partial oxidation, coating.

1.0 Introduction

Synthesis gas, which consists primarily of carbon monoxide and hydrogen, is produced through steam reforming, carbon dioxide reforming and partial oxidation. The H₂/CO ratio produced by the high-endothermal steam and CO₂ reforming is not suitable to use as the feedstocks of methanol production and Fischer-Tropsch synthetic fuels [1]. Partial oxidation of methane is an interesting process to avoid the drawback born by the two reactions [2]. The other advantages of partial oxidation of methane are the reaction is slightly exothermal and the resident time is fast.

Fixed-bed reactors for partial oxidation of methane bear a drawback, i.e. hot spots mostly in the reactor entry. This is related to the reaction mechanisms of partial oxidation of methane, direct as depicted in Eqs. 1-3, or indirect as showed in Eq. 4 below,



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The exothermal total oxidation takes place at the entry of the reactor. It is followed by the endothermal CO₂ and steam reforming taking place at reactor parts being far away from the entry.

In its better design a reactor for partial oxidation of methane delivers heat released by total oxidation in such way that heat is utilized by steam and CO₂ reforming; for example shell and tube micro reactor [3]. Total oxidation takes place in the tube side, and steam and CO₂ reforming occur in the shell side of the reactor utilizing heat released by the reaction in the tube side.

This paper will discuss the development of shell and tube micro reactor for catalytic partial oxidation of methane.

2.0 Materials & Method

2.1 Reactor system

The shell and tube microreactor (Figure 1) was made of dense alumina for the tubes, quartz for the shell, and stainless steel for the unions. The catalyst length in the inside and outside of the tubes is 11 cm; the outside and inside diameter of the tubes are 1 cm and 0.8 cm, respectively; and the inside diameter of the shell is 1.8 cm. The reactant flow rate was 300 ml/min with the CH₄/O₂ ratio of 2.3. Gas leaving the reactor passed through a water trap to condense water contained in the gas. A bubble soap was mounted to meter the gas flow rate. Gas composition was analyzed by a TDC-typed gas chromatography with active carbon column.

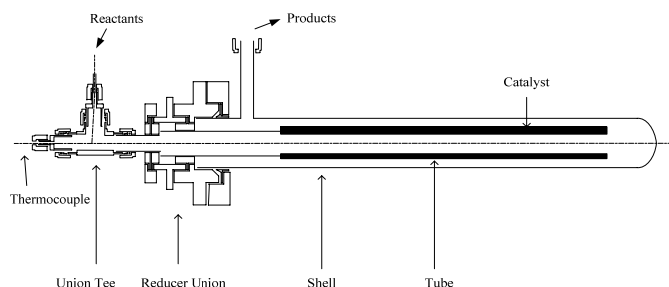


Figure 1 Natural fiber reinforced composite application in automotives.

2.2 Catalyst preparation and coating

LaNi_xO_y catalyst was prepared using sol-gel technique [4]. Precursor La(NO₃)₃.6H₂O was mixed with Ni(NO₃)₂.6H₂O with the Ni/La molar ratio of 10. The mixture was then solved in

water. Maleic acid was added gradually into the resulting nitric solution until the maleic acid/total nitric molar ratio of one was achieved. The solution was then stirred at 70°C.

Coating of the catalyst on the tube was performed through dip-coating and spray-pyrolisis methods. In dip-coating method the tube was immersed in catalyst sol. The catalyst-deposited tubes were heated to evaporate the solvent. The catalyst was then calcinated at 900 °C for 3 hours. In spray-pyrolisis method, the catalyst sol was calcinated at 900 °C then crushed into small size of powder and solved in isopropyl alcohol (0.2 gram/mL). The catalyst solution was sprayed on the tube surface which has been heated. The catalyst deposit was sintered in accordance with sintering temperatures (900 and 1250 °C) for 4 hours [5]. Two catalysts prepared by this method were distinguished. The first one was sintered at 900°C (in the whole text content is called as spray-900 catalyst) and the second at 1250°C (spray-1250 catalyst).

3.0 Results and Discussion

3.1 Impact of coating method

Tests in the blank reactor at 700 °C shows that no product gases was observed (Figure 2). The catalyst prepared by dip-coating method converted 7.7% of methane. The low conversion of methane is caused by very low loading of catalyst in the tube (0.06 g in the outside and 0.02 g in the inside of the tube). The spray-900 and spray-1250 catalysts gave high methane conversions (more than 97%) due to the higher loading of the catalyst in the outside (0.4 g) and the inside (0.2 g) of the tube.

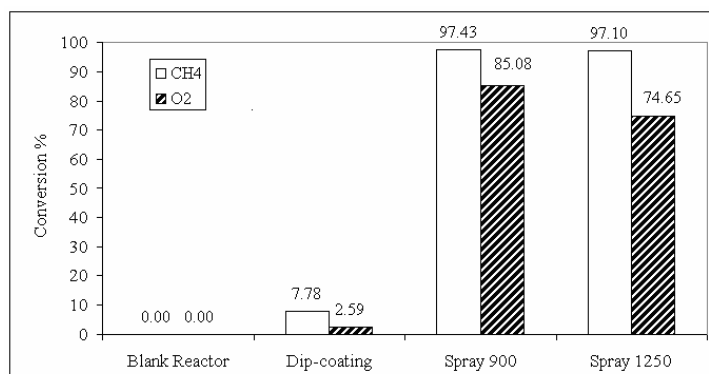


Figure 2 Methane Conversions at 700°C for each types of catalysts.

Figure 3 shows the turn over frequency (TOF) of the three different catalysts at 700°C represent the reaction performance per weight of catalyst. The TOF with the spray-pyrolisis catalysts possesses better performance ($5.75 \cdot 10^{-5}$ and $5.73 \cdot 10^{-5}$ mol/g cat. s) than dip-coating catalyst ($2.24 \cdot 10^{-5}$ mol/g cat. s). The BET characterization of the catalysts depicts that the surface area of the spray-900 catalyst is larger than that of the spray-1250 catalyst.

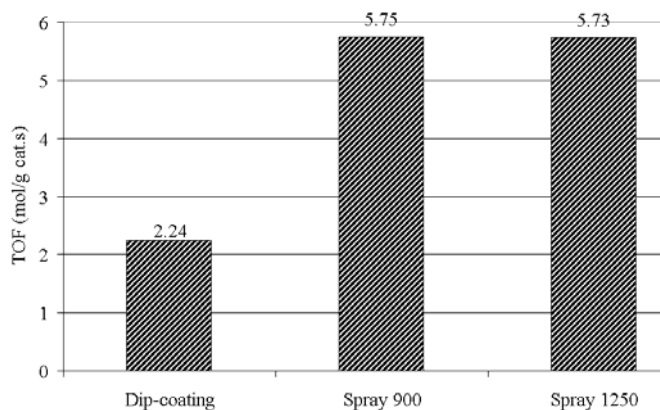


Figure 3 TOF at 700°C.

3.2 Impact of temperature

Impact of reaction temperatures on conversion is shown in Figure 4. It shows that the decrease in temperatures will decrease the conversion of methane. At higher temperature (700°C) the methane conversion is approximately the same for the spray-900 catalyst and spray-1250 catalyst (~97%). The reaction is probably thermal-controlled at higher temperature. The difference of methane conversion significantly occurs at lower temperatures (600°C and 500°C), in which the methane conversion of the spray-900 catalysts is larger than that of the spray-1250 catalyst.

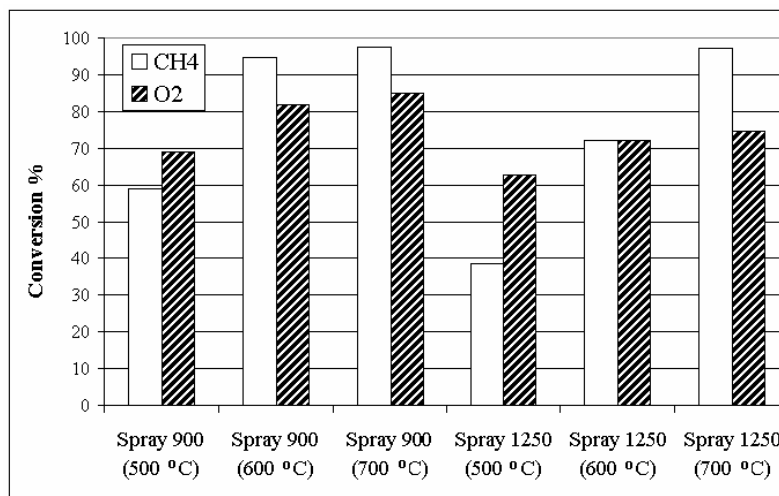


Figure 4 Impact of temperature on reactant conversion.

The selectivities of CO, CO₂, and H₂ for the spray-pyrolysis catalysts are shown in Figure 5. The H₂ selectivity increases, while the CO₂ selectivity decreases with increasing temperatures. It can be explained that the Gibbs's free-energy of methane combustion is more negative than those of steam and CO₂ reforming within the temperature range of 500°C – 700°C. The CO selectivity is relatively constant, although reforming reactions proceed more spontaneously at higher temperatures. This is possibly affected by the carbon deposition.

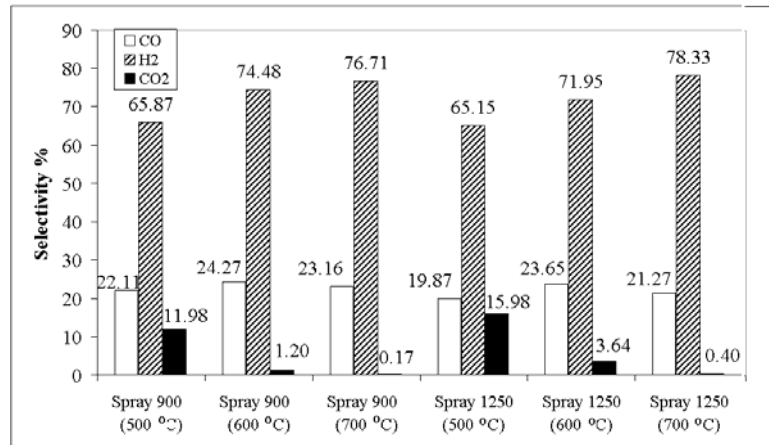


Figure 5 Impact of temperature on products selectivities.

Figure 6 exhibits that the H₂/CO ratios are always greater than 2, which are possibly caused by the existence of methane cracking and Boudouard reactions. The occurrence of carbon deposition was proved by the appearance of CO₂ when it was flushed by oxygen.

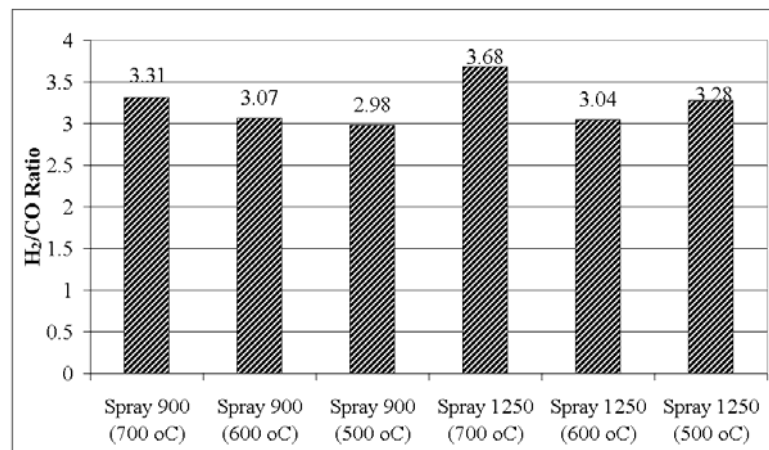


Figure 6 Impact of temperature on hydrogen to carbon monoxide ratio.

4.0 Conclusion

From the discussion above we conclude that:

- 1 The spray-pyrolysis method yields higher loadings of catalysts than the dip-coating method does, leading to better performance of partial oxidation of methane, with the methane conversion being 97%, and the TOF being 5.75 10⁻⁵ mol/g cat.s.
- 2 The sintering temperature of 900°C gives better performance than that of 1250°C does, due to the higher surface area of the 900°C-calcined catalyst.
- 3 The spray-900 catalyst converts more methane than the spray-1250 does at lower temperatures (500 and 600°C). At the higher temperature they convert almost the same amount of methane.
- 4 The hydrogen to carbon monoxide ratios produced are greater than the stoichiometric ratio, which are probably caused by carbon deposit through methane cracking and Boudouard reactions.

References

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