

A simplified mathematical modeling for thermo-catalytic decomposition of methane over carbon black catalyst in a fluidized bed reactor

Eun Hwa Jang*, Myung Wu Woo*, Seung Chul Lee**, Ki June Yoon**, and Gui Young Han**,*

*Department of Chemical Engineering, Sunchon National University, Sunchon 540-742, Korea

**Department of Chemical Engineering Sungkyunkwan University, Suwon 440-746, Korea

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Abstract—A mathematical model for thermo-catalytic decomposition of methane over carbon black catalysts in a fluidized bed was proposed. The simplified isothermal, uniform flow model was considered and implemented into a computer code to predict the reactor performance. The experiment of methane decomposition into hydrogen and carbon was carried out in a fluidized bed of I.D of 0.055 m and height of 1.0 m. The range of reaction temperature was 850-900 °C, gas velocity was 1.0-3.0 U_{mf} , and catalyst loading was 50-200 g. The reaction parameters for model equation were determined from the curve fittings and the comparison of experimental data with simulation results showed good agreement for fluidized bed reactor system. From the simulation results, the fluidized bed performance with different operating conditions were obtained, and this simple model can be used to predict the performance of a larger scale fluidized bed reactor and also in determining the optimum operating conditions.

Key words: Mathematical Modeling, Thermo-catalytic Decomposition of Methane, Fluidized Bed

INTRODUCTION

Thermo-catalytic decomposition of methane is an environmentally attractive approach to the production of hydrogen with reduced CO₂ emission [1,2]. Direct decomposition of methane requires high temperature (more than 1,400 °C); therefore, much research on the development of efficient catalysts for the process has been conducted since early 1960's. Recently, in order to decrease the reaction temperature of methane decomposition, the catalytic decomposition of methane has been focused on as a new research field [1]. In our earlier work [2,3], reaction characteristics and the mechanism of active site of carbon catalyst were studied. In the previous studies, several researches were conducted on the modeling of methane catalytic decomposition in fluidized bed reactor [4,5]. However, Ammendola et al. [4] proposed a model which was focused on the carbon deposition and elutriation rate and they used the fixed bed kinetic data. Muradov et al. [5] employed the two-phase model of fluidized bed with activated carbon as the catalyst. In their experiment the expanded bed height was less than 1.0 cm. This result of a small scale fluidized bed may not represent the realistic phenomena in a large scale fluidized bed reactor system. The thermocatalytic decomposition of methane with carbon black catalyst in a fluidized bed system is a quite recent research area and needs larger scale data. Therefore, at this point, we may need a simpler and lumped parameter model to understand the basic kinetic data and parameter effect on the reactor performance in a fluidized bed reactor. For this purpose, a simplified mathematical model of fluidized bed reactor was proposed to account for the effect of parameters on the performance of fluidized bed reactor.

EXPERIMENTAL

A schematic diagram of fluidized bed reactor used in this experiment is shown in Fig. 1. The fluidized bed reactor was made of quartz with I.D. of 0.055 m and 1.0 m in height. The initial loading of activated carbon and carbon black catalysts used in the experiment was 100 g. The methane flow rate was controlled by mass flow controller. A feed stream of methane which was preheated to

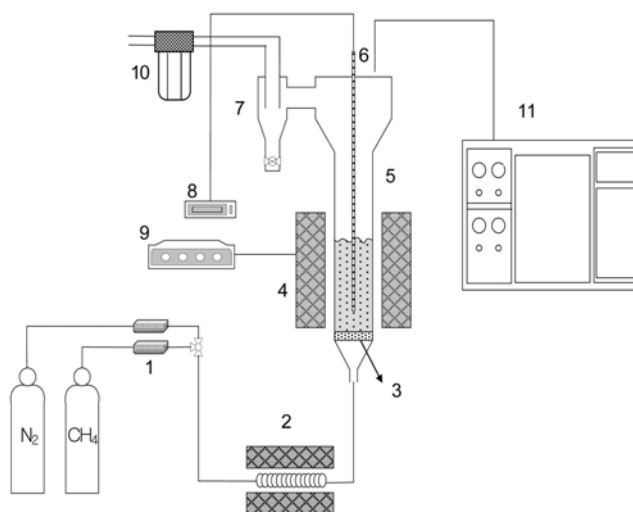


Fig. 1. Schematic diagram of fluidized bed reactor.

- | | |
|--------------------------|---------------------------|
| 1. Mass flow controller | 7. Cyclone |
| 2. Preheater | 8. Data logger |
| 3. Distributor | 9. Temperature controller |
| 4. Furnace | 10. Bag filter |
| 5. Fluidized bed reactor | 11. G/C |
| 6. Thermocouple | |

*To whom correspondence should be addressed.

E-mail: gyhan@skku.ac.kr

400 °C entered the reactor from the bottom and contacted with the fluidized bed of carbon catalysts at the operating temperature in the reaction zone, where thermo-catalytic decomposition of methane occurred. Temperature was monitored by a thermocouple in the middle of the bed. The flow of hydrogen containing gas exited from the top of the reactor via cyclone and bag filter. The reaction products were analyzed by gas chromatography (TCD detector).

MATHEMATICAL MODEL FOR THE METHANE DECOMPOSITION

The correct prediction of the kinetics of this reaction system provided valuable information to determine the optimal conditions for commercial scale plant operations. In this study, the fluidized bed reactor was assumed to be an isothermal and uniform flow reactor. The time dependent continuity equation is expressed as follows:

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D \nabla c_i + c_i \mathbf{u}) = r_i \quad (1)$$

$$\text{I.C. } c_i = 0$$

$$\text{B.C. } c_i|_{z=0} = c_{i0}, -D_i \nabla c_i|_{z=H_{\text{bed}}} = 0$$

There are many factors affecting the height of the fluidized bed, such as weight of the catalyst loading, fluid velocity, reaction temperature and reaction times. The variation of the catalyst activity with reaction time also influences the bed height of the reaction system. Considering all of these factors, we concluded the following equation to describe the bed height.

$$H_{\text{bed}} = (2.65 + 0.275 \times W_{\text{catalyst}}) \times \{1 + (0.0175 + 0.011 \times U_{mf})t\} \times \{1 + (-0.59 \times 5.25 \times 10^{-5} \times T_{\text{rxn}})t\} \quad (2)$$

The resulting coupled partial differential equations were solved and the composition of the reactant and products was determined by using the above bed height correlation equation. To verify the reliability of the proposed model, experimental data were obtained in a fluidized bed of I.D. of 0.055 m and bed height of 1.0 m. The operating temperature of 850–900 °C, and gas velocity of 1.0–3.0 U_{mf} , and the amount of catalyst loading of 50–200 g was used [2].

RESULTS AND DISCUSSION

1. Effect of Catalyst Deactivation

The deactivation rate of the employed carbon catalyst due to car-

Table 1. Estimated parameters for methane thermo-catalytic decomposition reaction

Catalyst	Temperature	Gas velocity	Catalyst loading	Param_ a	Param_ c
N-330	850 °C	1 U_{mf}	100 g	17.0	1.0
		2 U_{mf}		13.5	0.6
		3 U_{mf}		11.0	0.4
	875 °C	1 U_{mf}	100 g	25.0	1.0
	900 °C	1 U_{mf}	50 g	25.0	0.5
			100 g	33.0	1.0
			150 g	39.0	1.5
			200 g	48.0	2.0

Effect of the reaction temperature

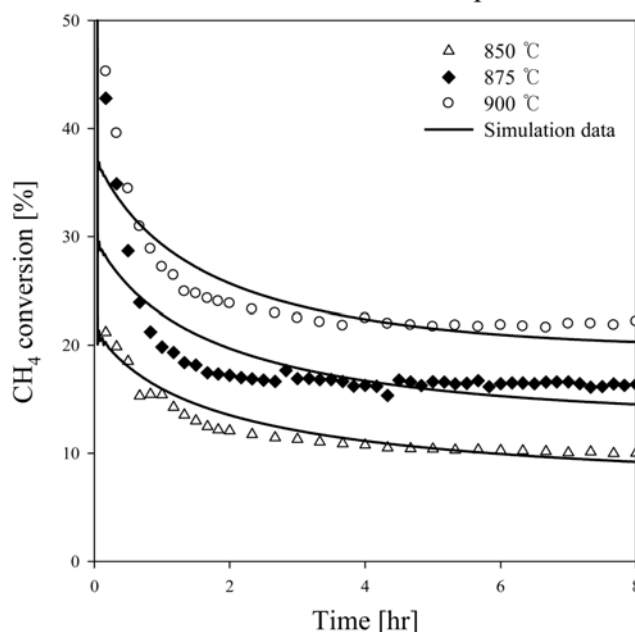


Fig. 2. Simulation results with experimental data for different reaction temperature (catalyst: HI20, gas velocity: 1 U_{mf} , catalyst loading: 100 g).

bon deposition on the active site was found to be in the form of the power law from the experimental data. Therefore, the deactivation rate of k was proposed as Eq. (3) and the reaction parameters a and c were determined from the curve fitting of experimental data. Table 1 shows the estimated parameters for methane catalytic decomposition reaction.

$$k = \frac{a}{\sqrt{1+ct}} \quad (3)$$

2. Effect of Reaction Temperature

Fig. 2 shows a comparison of simulation result and the experimental data at different reaction temperatures. At the beginning of reaction, there was some disagreement of simulation results. However, as the reaction proceeded for a long time the simulation results predicted the reaction rate very well. From the variation of reaction rate with time, it seemed that at the beginning of the reaction higher reaction rates were obtained due to many numbers of fresh active sites, and as the fresh active sites are saturated with produced carbon from the methane decomposition, the reaction reached quasi-steady-state. As can be seen in Fig. 2, the methane conversion was strongly dependent on reaction temperature, and the experimentally determined activation energy for this reaction in a fluidized bed was about 200 KJ/mol.

3. Effect of Gas Velocity

In a fluidized bed operation, the gas velocity is considered as a major operating variable. This is because the gas velocity changed the flow regime of gas-solid contacting and the dynamics of gas bubble. Fig. 3 shows the effect of gas velocity on the methane conversion. As expected, the reaction rates decreased in the form of power law in all ranges of fluidizing gas velocity. At a gas velocity of 1.0 U_{mf} , a higher conversion of methane was obtained, and as

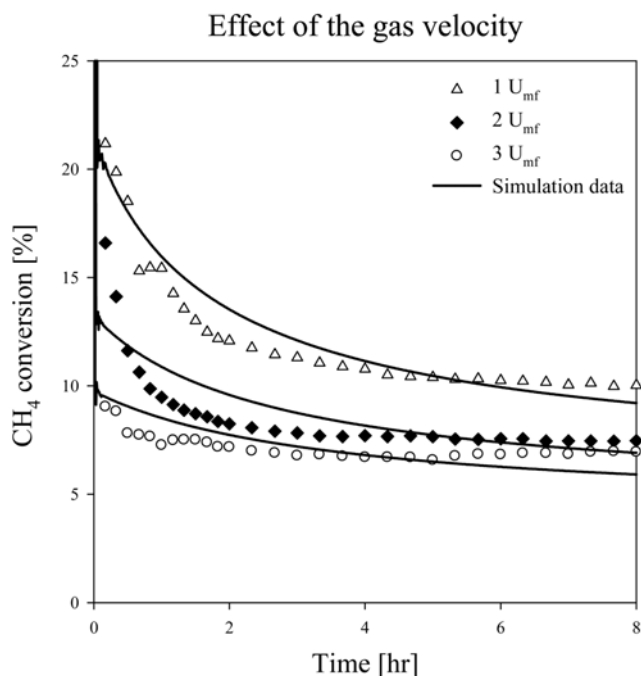


Fig. 3. Simulation results with experimental data for different flow rates (catalyst: HI170, temperature: 850 °C, catalyst loading: 100 g).

the gas velocity was increased, the methane conversion decreased. As the gas velocity increased, the retention time for reaction in the fluidized bed was decreased, and thus conversion decreased. However, at the gas velocity of 2.0 U_{mf} and 3.0 U_{mf}, the effect of gas ve-

locity on the methane conversion was less significant compared to 1.0 U_{mf}. It seems that at 3.0 U_{mf}, even though the retention time was decreased, the higher gas velocity caused vigorous mixing between methane and carbon black catalyst, thus increasing the contacting efficiency of reactants.

4. Effect of Amount of Catalyst Loading

The effect of amounts of catalyst loading on the methane conversion was examined. As shown in Fig. 4, the retention time of gas in a fluidized bed increased with the bed height, and the methane conversion was increased. However, as the catalyst loading increased from 50 g to 200 g, a linear increase of methane conversion was not obtained. It is believed that the employed carbon black was Geldart C type particles and is known to be difficult to fluidize well. Therefore, as the bed height increased, it was more difficult to make a uniform distribution of the reactant gas in the bed of carbon black.

CONCLUSION

A mathematical model for thermocatalytic decomposition of methane over carbon black catalyst in a fluidized bed was proposed. The experiment was performed in a fluidized bed of I.D of 0.055 m and height of 1.0 m. The experimental variables were bed temperature, gas velocity and the amount of catalyst. The comparison of experimental data with simulation results showed good agreement and the reaction parameters were determined from curve fitting. From the simulation results, the fluidized bed performance with different operating conditions was obtained, and this simple model can be used to predict the performance of a larger scale fluidized bed reactor and in determining the optimum operating conditions.

NOMENCLATURE

C_i	: methane conc. [mol/m ³]
D	: diffusivity [m ² /hr]
r_i	: reaction rate [mol/m ³ hr]
H_{head}	: bed height [m]
$W_{catalyst}$	: weight of catalyst [g]
U_{mf}	: minimum fluidization velocity [m/sec]
T_{rxn}	: temperature [K]
t	: time [hr]
k	: deactivation rate [1/hr]
a, c	: reaction parameter [1/hr]

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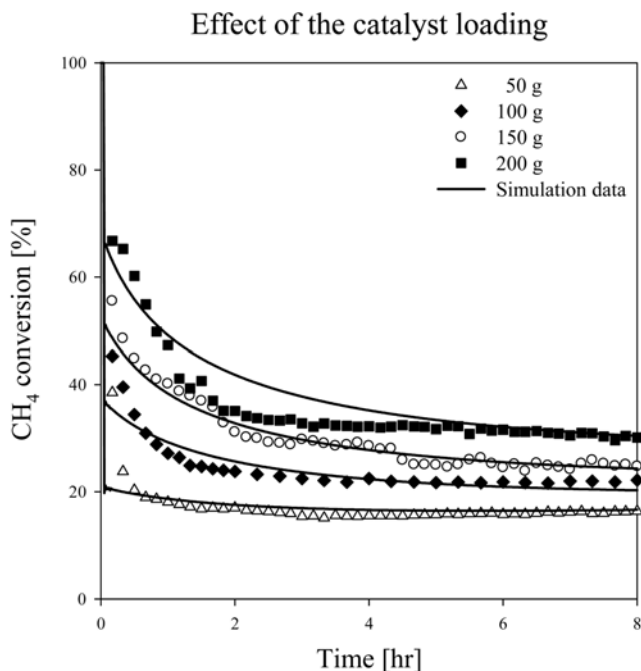


Fig. 4. Simulation results with experimental data for different catalyst loading (catalyst: HI170, temperature: 900 °C, gas velocity: 1 U_{mf}).