Estimation of heat and mass transfer of structured catalyst system for CO₂ methanation.

Choji Fukuhara¹*, Yuji Suzuki¹, Ryo Watanabe¹, Masao Sudo², Sakhon Ratchahat²


*Corresponding author: fukuhara.choji@shizuoka.ac.jp

Highlights
- The structured catalyst exhibited high methanation performance at low temperature.
- The stacked and segment improved heat and mass transfer in the reaction field.
- The structured catalyst system represented the powerful potential for CO₂ conversion.

1. Introduction

The CO₂ methanation is the hydrogenation of CO₂ to produce CH₄ (CO₂ + 4H₂ → CH₄ + 2H₂O, ΔH°298K = −165 kJ·mol⁻¹) [1]. Fukuhara et al. have introduced the Ni/CeO₂ structured catalyst for CO₂ methanation under high flow rate with effective heat exchange and low pressure drop [2]. In this study, heat and mass transfer property for methanation were investigated over various types of structured catalysts from the viewpoint of chemical reaction engineering. A plain-type with straight-flow channel, a stacked type with random-flow channel, and segment-type having the divided flow-path unit with gap distance were employed in this study. The proposed reaction system had a powerful potential for reduction and utilization of CO₂.

2. Experimental

A structured catalyst was prepared by the following processes; (i) preparing a Ni(10wt%)/CeO₂ granular catalyst by impregnation [2], (ii) coating such granular catalyst (300mg) on an aluminum fin-substrate by wash-coating. As shown in Fig. 1, three types of substrate with 18mmφ x 50mm, 100 cpsi, surface area 203cm² were used. Prior to the CO₂ methanation, the catalyst was reduced by H₂ at 500°C for 1 h. Then feed gas (CO₂/H₂/He = 1/4/5 molar ratio) was introduced to the reactor under feeding flow rate of 70-300mL/min.

3. Results and discussion

Fig. 2 shows methanation property of various structured catalysts. As shown in Fig. 2(a), CO₂ conversion at 250-350°C increased due to the random-flow channel and the segmented gap, compared to the straight-flow channel of the plain-type catalyst. In addition, the longer gap distance (5 to 15 mm), the higher conversions were obtained. It was attributed to the improved heat and mass transfer properties. Moreover, in Fig. 2(b) all CH₄ selectivity achieved the equilibrium at all temperatures.

Heat balance in the reaction zone is described by overall heat transfer coefficient (U) in Eq. 1. Heat transfer property was estimated through U values. Based on the gas phase reaction and the gas film theory, a relation of mass transfer rate and reaction rate is represented by Eq. 2.
By rearranging and assuming 1st order reaction, the relation of overall reaction rate constant \((K)\), reaction rate constant \((k_r)\), and mass transfer coefficient \((k_i)\) is obtained in Eq. 3. In this study, mass transfer property was estimated through \(K\) values. The mass balance of unit cell of the structured catalyst is formulated in Eq. 4. The \(K\) values in Eq. 5 can be obtained by an integration of Eq. 4 with boundary conditions of \([C_i = C_\text{b} at z = 0, and \(C_w = C_\text{out} at z = L\].

\[
UAT_m = \sum_i (\dot{n}_{i,\text{in}}R_{i,\text{in}}) - \sum_i (\dot{n}_{i,\text{out}}R_{i,\text{out}}) + \dot{n}_{\text{CO}_2,\text{in}}X \sum_i (S_i (-\Delta H_i)) \quad \ldots \quad (1)
\]

\[
J = KC_m = k_r(C_m - C_w) = k_iC_w^n \quad \ldots \quad (2)
\]

\[
\frac{1}{K} = \frac{1}{k_i} + \frac{1}{k_r} \quad \ldots \quad (3)
\]

\[
F(C_\text{in} - dC) - F(C_i - KCG) \cdot \pi d_i (z + dz) - z) = 0 \quad \ldots \quad (4)
\]

\[
K = \frac{F}{\pi d_i L} \ln(C_\text{out}/C_\text{in}) = \frac{F}{A} \ln(1 - X) \quad \ldots \quad (5)
\]

\(A\): surface area of honeycomb cell \([\text{m}^2], C_i, C_w\): concentration of bulk and at wall \([\text{mol/m}^3], d_i\): hydraulic diameter \([\text{m}], F\): gas flow rate \([\text{m}^3/\text{s}], \)

\(\dot{H}_in, \dot{H}_c\): specific enthalpy \([\text{J/mol}], \Delta H\): reaction heat \([\text{J}], J\): flux of feed gas \([\text{mol/m}^3/\text{s}], L\): catalyst length \([\text{m}], \dot{n}_{i,\text{in}}, \dot{n}_{\text{out}}\): mole flow \([\text{mol/s}], S\): product selectivity \([\%], AT_m\): mean temp. difference of wall and center \([\text{K}], X\): conversion \([\%], Z\): direction along the catalyst length \([\text{m}]\)

**Fig. 3** shows the estimated \(U\) and \(K\) values of the structured catalysts under the performance shown in Fig. 2. The \(U\) and \(K\) values which are normalized with those of the plain-type catalyst increased significantly. The random-flow channel and the gap space improved the well mixing feed gas. In Fig. 3(b), the \(K\) value increased almost 2 times of the segment-type catalyst (gap=15mm) at 250°C.

**Fig. 4(a)** shows the \(\text{CO}_2\) conversions at higher feed rates using various structured catalysts. The decrease in conversion became smaller for the stacked and the segment-type catalysts. Especially, the segment-type catalyst with 15mm gap distance maintained high conversion even at 300mL/min. In Fig. 4(b), the \(U\) values were almost constant. In contrast, \(K\) values in Fig. 4(c) were improved with the increased feed rate. This indicates the profound performance of the structured catalyst on the methanation, especially for the segment-type catalyst.

**Fig. 4**. (a) \(U\) values, and (c) \(K\) values of different structured catalysts at various flow rates.

**4. Conclusions**

The estimated heat and mass transfer properties of structured catalysts show that high methanation performance was ascribed to the random-flow channel and the segmented gap. The structured reaction system indicated the powerful potential for \(\text{CO}_2\) reduction and utilization even under high feeding flow rate.

**References**


**Keywords**

\(\text{CO}_2\) methanation, Ni/\(\text{CeO}_2\) catalyst, Structured catalyst, Heat and mass transfer.