Estimation of heat and mass transfer of structured catalyst system for CO_2 methanation.

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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 CO_2 conversion.

1. Introduction

The CO_2 methanation is the hydrogenation of CO_2 to produce CH_4 ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, $\Delta H^0_{298K} = -165$ kJ·mol^{-1}) [1]. Fukuhara et al. have introduced the Ni/CeO_2 structured catalyst for CO_2 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 CO_2.

2. Experimental

A structured catalyst was prepared by the following processes; (i) preparing a Ni(10wt%)/CeO_2 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 203cm^2 were used. Prior to the CO_2 methanation, the catalyst was reduced by H_2 at 500°C for 1 h. Then feed gas (CO_2/H_2/He = 1/4/5 molar ratio) was introduced to the reactor under feeding flow rate of 70-300mL/min.

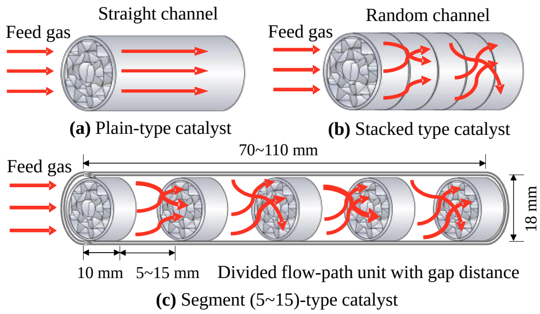

Figure 1. Schematic of various structured catalysts.

3. Results and discussion

Fig. 2 shows methanation property of various structured catalysts. As shown in **Fig. 2(a)**, CO_2 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 CH_4 selectivity achieved the equilibrium at all temperatures.

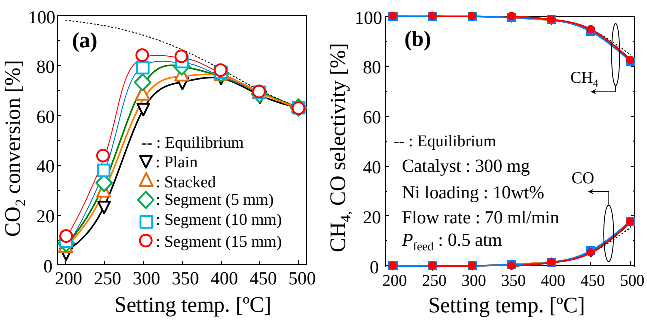

Figure 2. (a) CO_2 conversion and (b) CH_4 and CO selectivity.

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_c) 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 $C_z = C_0$ at z = 0, and $C_z = C_{out}$ at z = L.

$$UA\Delta T_m = \sum_i(\dot{n}_{i,in}\hat{H}_{i,in}) - \sum_i(\dot{n}_{i,out}\hat{H}_{i,out}) + \dot{n}_{CO2,in}X\sum_i\{S_i(-\Delta H_i)\} \ldots(\mathbf{1}),\ J = KC_m = k_c(C_m - C_w) = k_r C_w{}^n \ldots(\mathbf{2}),$$

$$\frac{1}{K} = \frac{1}{k_r} + \frac{1}{k_c} \ldots(\mathbf{3}),\ F(C_z - dC_z) - FC_z - KC_z \cdot \pi d_h((z+dz) - z) = 0 \ldots(\mathbf{4}),\ K = -\frac{F}{\pi d_h L}ln(C_{out}/C_0) = -\frac{F}{A}ln(1-X) \ldots(\mathbf{5})$$

[A : surface area of honeycomb cell [m^2], C_m,C_w :concentration of bulk and at wall [mol/m^3], d_h :hydraulic diameter [m], F: gas flow rate [m^3/s], $\hat{H}_{in}$, $\hat{H}_{in}$: specific enthalpy [J/mol], ΔH_i : reaction heat [W], J: flux of feed gas [mol/m^2·s], L:catalyst length [m], $\dot{n}_{i,in}$, $\dot{n}_{i,out}$:mole flow [mol/s], S : product selectivity [−], ΔT_m:mean temp. difference of wall and center [K], X:conversion [−], Z:direction along the catalyst length [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.

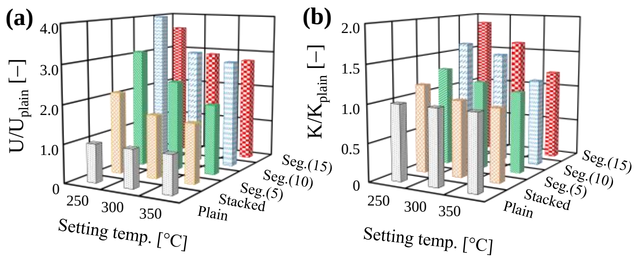

Figure 3. (a) U and (b) K values of different structured catalysts.

Fig. 4(a) shows the 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.

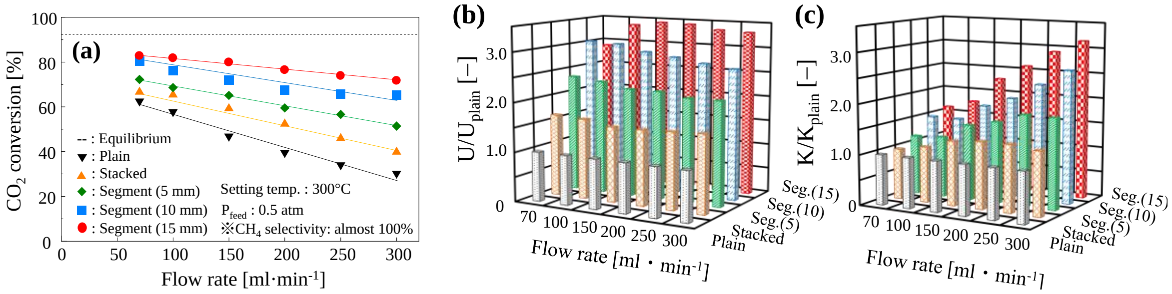

Figure 4. (a) CO_2 conversion, (b) U values, and (c) K values of different structured catalysts at various flow rates.

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 CO_2 reduction and utilization even under high feeding flow rate.

References

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Keywords
CO_2 methanation, Ni/CeO_2 catalyst, Structured catalyst, Heat and mass transfer.