1. Introduction
The CO₂ methanation is the hydrogenation of CO₂ for production of CH₄ in Eq.1. The CO₂ methanation has also gained great attention in the aspect of CO₂ utilization and hydrogen production. Fukuhara et al. have introduced the structured reaction system for CO₂ methanation, enabling the process to operate at high gas feed rate with low pressure drop across the reactor. Furthermore, they reported that the structured Ni/CeO₂ catalyst indicated a high methanation performance.

In this study, various type structured catalysts which are 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 to promote the heat and mass transfer in the methanation system. These promotion effects were investigated and estimated to show the higher structured catalyst performance.

CO₂ + 4H₂ → CH₄ + 2H₂O, ΔH²⁹⁸ = −165 kJ·mol⁻¹ (1)

2. Experimental
The preparation procedure of a structured catalyst was composed of the following two processes; (i) preparing the nickel-based granular catalyst, (ii) coating such nickel-based catalyst (300mg) on an aluminum fin-substrate by wash-coating. The nickel-based granular catalyst was a Ni(10wt%)/CeO₂ catalyst prepared by evaporation to dryness. Three types of the fin configuration with 18mm x 50mm-length of catalyst pack, 100 cpsi, surface area 203 cm² were used as shown in Fig. 1.

CO₂ methanation was performed in a flow-type reactor. Prior to the reaction, the prepared catalyst was reduced by H₂ stream at 500°C for 1 h. Then feeds gas (CO₂:H₂/He = 1/4/5 molar ratio, total flow = 70-300ml/min) was introduced to the reactor.

The reaction temperature was ranged from 200-500°C. The outlet gas was analysed by GC-TCD.

3. Results and Discussion
3.1 Methanation properties
Fig. 2 shows the methanation properties of each type structured catalyst. An increase in CO₂ conversion was due to the benefits of random-flow channel and the segmented gap of segment-type catalyst, compared to the plain-type catalyst with straight-flow channel only. In addition, the longer gap distance from 5 to 15 mm, the higher conversions were obtained. It was attributed to the improved heat and mass transfer properties. Moreover, the CH₄ selectivity of all structured catalysts achieved the equilibrium values at all temperatures.

![Fig. 2 (a) CO₂ conversion and (b) product selectivity of various type structured Ni/CeO₂ catalysts](image)

3.2 Estimation of heat and mass transfer properties
Heat balance in the reaction zone was described by Eq. 2. U is an overall heat transfer coefficient. ΔTm is a mean temperature difference which is averaged from inlet to outlet, between wall and center of radius. Heat transfer property of the structured catalyst was estimated by U values in this equation.

\[ \frac{UAΔT_m}{∑ \sum (\dot{n}_{i,\text{in}} \dot{n}_{i,\text{in}}) + \dot{n}_{\text{CO}_2,\text{in}} ∑ S_i(−ΔH_i))} \]

(2)

Based on the gas phase reaction and the gas film theory, a relation between mass transfer rate and reaction rate is represented by Eq. 3. By rearranging and assumption of first-order reaction, the relation of K, kᵣ, and kₑ is obtained in Eq. 4.

\[ J = KC_m = k_c(C_m - C_w) = k_cC_w^m \]

(3)

\[ \frac{1}{k} = \frac{1}{k_r} + \frac{1}{k_c} \]

(4)

Mass transfer property was estimated through K value in this time. The mass balance of unit cell of the...
structured catalyst is formulated in Eq. 5. The $K$ values can be obtained by an integration of Eq. 5 with boundary conditions of $C_z = C_0$ at $z = 0$, and $C_z = C_{out}$ at $z = L$.

$$F(C_z - dC_z) - FC_0 = KC_z(2πd)(a + dz) = 0$$

$$K = \frac{F}{\pi d_1 L} \ln\left(\frac{C_{out}}{C_0}\right) = \frac{F}{A} \ln(1 - X) \quad (6)$$

### 3.3 Transfer properties at various temperatures

Fig. 3 shows the estimated $U$ and $K$ values of the stacked and the segment-type catalysts increased significantly, compared to the plain-type catalyst. The $y$-axis is a normalized $U$ and $K$ value with the $U$ and $K$ of the plain-type catalyst. At 250°C, the $U$ value increased 2 times ascribed to the random-flow channel of stacked type catalyst, resulting in the well mixing feed gas in the radial direction. Addition of gap between each stack of segment-type catalyst further increased $U$ value. For the gap of 10mm, the $U$ value increased almost 4 times at 250°C. From Fig. 3(b), the promotion effect on mass transfer property was also observed as the $K$ value increased almost 2 times of the segment-type catalyst (gap=15mm) at 250°C. As a result, the structured catalysts could promote the heat and mass transfer properties of CO2 methanation.

**Fig. 3** (a) $U$ values, and (b) $K$ values of different structured catalysts at various temperatures

### 3.4 Transfer properties at various flow rates

Fig. 4 shows that the CO2 conversions of each type structured catalyst decreased at higher feed rates. Interestingly, the degree of decreased conversion became smaller for the stacked type catalyst and the segment-type catalyst due to the promotion effect of heat and mass transfer properties.

**Fig. 4** CO2 conversion at various feed rates

Fig. 5 shows the $U$ and $K$ values of each type structured catalyst at various flow rates. It was found that the $U$ values were almost constant and it was independent of flow rate. In contrast, $K$ values 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. 5** (a) $U$ values, and (b) $K$ values of different structured catalysts at various flow rates

### 4. Conclusions

The structured catalysts exhibited high performance for CO2 methanation at low temperature. The random-flow channel and the segmented gap enhanced the heat and mass transfer properties, resulting in the highest conversion of the segment-type catalyst.

### Nomenclatures

$A$ : apparent surface area of honeycomb cell 
$m^2$
$C_{b,w}$ : concentration of bulk and at wall 
$mol/m^3$
$d_h$ : hydraulic diameter 
$m$
$F$ : volume flow rate of feed gas 
$m^3/s$
$\dot{H}_{in}, \dot{H}_{out}$ : molar specific enthalpy 
$J/mol$
$\Delta H_r$ : reaction heat 
$W$
$J$ : flux of feed gas 
$mol/m^2 s$
$K$ : overall reaction rate constant 
$m/s$
$k_c$ : mass transfer coefficient 
$m/s$
$k_r$ : reaction rate constant 
$m/s$
$L$ : catalyst length 
$m$
$\dot{n}$ : mole per unit time 
$mol/s$
$S$ : product selectivity 
$\%$
$\Delta T_w$ : mean temperature difference between wall and center of radius 
$K$
$U$ : overall heat transfer coefficient 
$W/(m^2 K)$
$X$ : conversion 
$\%$
$Z$ : direction along the structured catalyst length 
$m$

### References