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Advantage of structured catalyst system for CO_2 methanation under extremely high flow rate.

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Highlights

- The multi-stacked structured catalyst exhibited high methanation performance.
- The conversion was recovered under high feed rate condition.
- The multi-stacked structured catalyst indicated the powerful process for CO_2 reduction.

1. Introduction

A familiar Sabatier CO_2 methanation ($CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$, $\Delta H^0_{298K} = -165$ kJ·mol^{-1}) is recently employed to catalytically convert a CO_2 greenhouse gas to useful CH_4 gas *via* reacting with renewable H_2 expected from water splitting by electrolysis technology [1]. Fukuhara et al. reported that the Ni/CeO_2 granular catalyst exhibited the highest methanation performance at low temperature beyond other types of catalyst supports [2]. They subsequently fabricated the structured reaction system for CO_2 methanation, enabling the process to operate at high CO_2 feed rate with low pressure drop across the reactor [2]. However, the methanation performance can decrease significantly under high CO_2 feed rate. In this study, a multi-stacked Ni/CeO_2 structured catalyst is designed to overcome such problem of low methanation performance and local hot spots at extremely CO_2 feed. Therefore, advantage property of structured catalyst for CO_2 methanation under extremely fast rate of feeding was investigated.

2. Experimental

A structured catalyst was prepared by the following two 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. **Fig. 1** shows a construction procedure of a multi-stacked type catalyst composed of honeycomb fin-configuration with 18mmϕ x 50mm, 100*cpsi*, surface area 203cm^2. The uncoated segment unit as static mixer was installed between the coated one. Prior to the CO_2 methanation, the catalyst was reduced by H_2 at 500°C for 1 h. Then feed gas (12%CO_2 and 88%H_2, total flow = 60-3000mL/min) was introduced to the reactor.

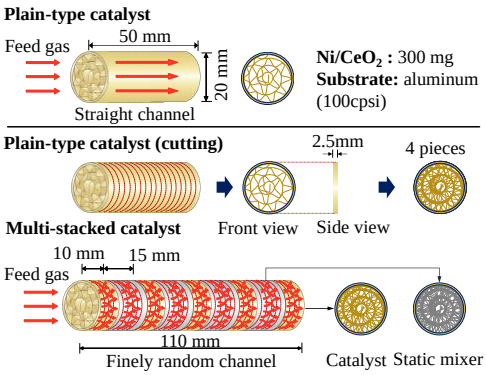

Figure 1. Schematic of structured Ni/CeO_2 catalyst.

3. Results and discussion

Fig. 2 shows the methanation performances over the multi-stacked type catalyst under various setting temperatures and flow rates. As show in **Fig. 2(a)**, at 60 mL/min, CO_2 conversion increased with temperature (5% to 50% at 200 to 250°C) and achieved equilibrium at 100% conversion and selectivity when T > 300°C. At 450°C and higher, the conversion slightly decreased due to its exothermic characteristics. Interestingly, at extremely high flow rate of 3000mL/min, the multi-stacked segment catalyst can maintain high CO_2 conversion over 90% at 288-500°C. This result shows that ultra-rapid CO_2 transformation to produce high CH_4 yield and high CH_4 selectivity (residence time = 275ms, Y_{CH4} = 2861 mol/kg$_{cat}$·h, S_{CH4} = 99.5%, 290°C) were obtained over such structured catalyst system. This confirms the advantage of multi-stacked segment structured catalyst for CO_2 methanation under high flow rate condition at low temperature.

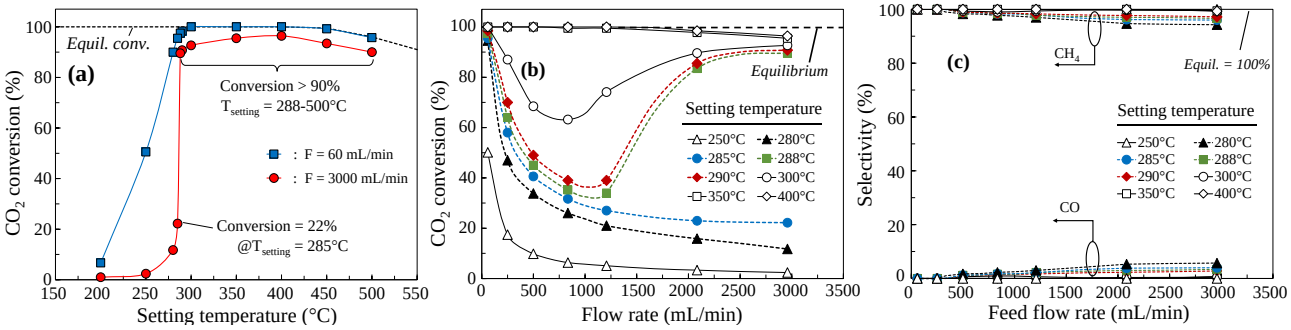

Figure 2. (a) CO_2 conversion at various temperatures, (b) CO_2 conversion, and (c) CH_4 and CO selectivity under various flow rates.

Fig. 2(b) shows CO_2 conversion under various flow rates of feed gas (60-3000mL/min). At low setting temperature of 250-285°C, the conversion decreased sharply to less than 30% as the flow rate increased. Surprisingly, at certain temperature of 288-300°C, the conversions were recovered to high level when the flow rate was higher than 1000mL/min. The multi-stacked configuration increased heat and mass transfer at the reaction filed to further enhance the reaction. Temperature at reaction field was elevated to moderate level in which Ni catalyst still exhibits high activity. In addition, all CH_4 selectivity remained more than 95% as shown in **Fig. 2(c)**.

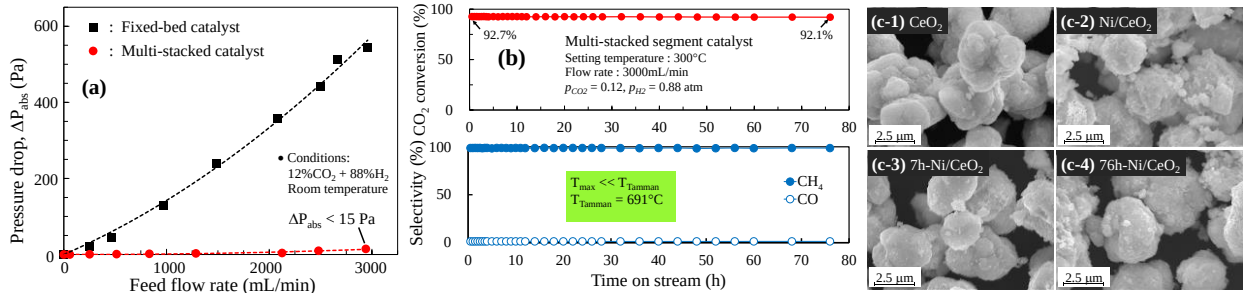

Figure 3. (a) pressure drop across fixed-bed and structured catalysts, (b) durability performance test, and (c) SEM images of catalyst.

Fig. 3(a) shows pressure drops of fixed-bed and structured catalysts. In the fixed-bed catalyst, the pressure increased significantly with flow rate while the structured catalyst shows negligible pressure in the system (<15Pa). This confirms the advantage of structured catalyst for mass processing of CO_2. The durability test of structured catalyst was carried out under severe condition of 3000mL/min, 300°C, for 76h as shown in **Fig. 3(b)**. The catalyst shows high stability with slightly drop in conversion (0.6%) with almost 100%CH_4 selectivity. Morphology of catalyst before and after reaction was remained almost the same as shown in **Fig. 3(c)**. The multi-stacked type catalyst shows a promising reaction system for CO_2 reduction and utilization under extremely high flow rate with high conversion and CH_4 purity, and high durability of catalyst.

4. Conclusions

The multi-stacked catalyst exhibited high methanation performance even under extremely CO_2 feed rate of 3000mL/min. The structured catalyst system can maintain high conversion and high selectivity even at low temperature (X_{CO2} = 0.91, S_{CH4} 99.5%, 290°C). The CO_2 conversion can be recovered to high level at certain temperature under high feed rate. The multi-stacked catalyst shows a powerful process for CO_2 reduction and utilization under extremely high feed rate and low temperature.

References

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Keywords
CO_2 methanation, Ni/CeO_2 structured catalyst, Extremely high flow rate.