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Development of a powerful CO_2 methanation process using a structured Ni/CeO_2 catalyst

Sakhon Ratchahat[a], Masao Sudoh[a], Yuji Suzuki[b], Wataru Kawasaki[b], Ryo Watanabe[b], Choji Fukuhara[b,*]

[a] *Amano Institute of Technology, 7955-98 Hosoe-cho Kiga, Kita-ku, Hamamatsu, Shizuoka 431-1305, Japan*
[b] *Department of Applied Chemistry and Biochemical Engineering, Graduate School of Engineering, Shizuoka University, 3-5-1 Johoku, Naka-ku, Hamamatsu, Shizuoka 432-8561, Japan*

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ABSTRACT

The purpose of this study is to develop a powerful CO_2 methanation process using a variety of structured Ni/CeO_2 catalysts. Various configurations of metallic honeycomb-type catalysts, which are plain, stacked, segment, and multi-stacked were constructed and tested under various reaction conditions; i.e. inlet temperature, feed flow rate and CO_2 partial pressure. Effects of the developed configurations including stack and gap distance were examined. The random-flow channels of stacked type and the gap distance of segment type could improve the catalytic activity, resulting in high CO_2 conversion. Under industrial-like high feed rate condition and pure feed gas component, a moderate hot spot over the multi-stacked catalyst was observed and reported for the first time. The moderate hot spot reboosted the conversion to a high level even at high feed flow rate condition of 3000 mL/min (contact time of 235 ms). As a result, high CO_2 conversion > 90%, high CH_4 selectivity > 99.5%, and high stability with dropped conversion < 0.6%, could be maintained over 76 h test at setting temperature of 300 °C, flow rate of 3000 mL/min and feed ratio of $p_{CO_2}/p_{H_2} = 0.12/0.88$. The stability of the Ni/CeO_2 catalyst under the moderate hot spot condition was revealed by BET, SEM and XRD analyses.

1. Introduction

CO_2 methanation, the so-called Sabatier reaction, is the hydrogenation of CO_2 for production of CH_4 as shown in Eq. (1) [1]. Nowadays CO_2 methanation has gained great attention in the aspect of CO_2 reduction/utilization and hydrogen energy carrier [2–5]. The reaction is highly promising for reducing CO_2 greenhouse gas by reacting with renewable H_2 obtained from water electrolysis using solar and wind energy [6]. The CH_4 product gas is versatile since it could be either used as synthetic natural gas (SNG) for direct supply to the existing natural gas networks, or employed as intermediates for production of higher carbon chemicals [5]. Research and development have been focusing on (i) development of highly active/selective catalysts [7], and (ii) construction of efficient system for handling a large amount of CO_2 [8]. In catalyst development, most methanation catalysts are nickel and/or precious metals (Ru and Rh) supported onto metal oxide or zeolite [7]. The nickel exhibits the most economical price and high activity, while the CeO_2 shows the most promising support in terms of large CO_2 coverage and CO_2 activation-dissociation due to the agile migration of oxygen species [8–10].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O\ (\triangle H^{\circ}_{298\ K} = -165\ kJ/mol) \qquad (1)$$

A powerful methanation process for handling a large amount of CO_2 and efficient heat exchange/removal would be required in order to meet the industrial-scale requirement for such highly exothermic CO_2 methanation process. In a conventional fixed-bed reactor with low conductive heat transfer of catalyst bed, the highly exothermic heat accumulates and causes the severe hot spot on catalyst, leading to the catalyst deactivation and runaway at temperature higher than 700 °C reported by Schlereth [11]. Managing heat in the fixed-bed reactor can be difficult due to the tendency of hot spot formation. They investigated many parameters concerning all process and design variables to find the condition of a moderate hot spot for high yields and stability. Nevertheless, no operation point with a moderate hot spot is found. The formation of a hot spot provokes a runaway even at a tube diameter of 10 mm [11]. Under high feed rate condition, a large pressure drop also

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* Corresponding author at: Applied Chemistry and Biochemical Engineering Course, Department of Engineering, Graduate School of Integrated Science and Technology, Shizuoka University, 3-5-1 Johoku Naka-ku Hamamatsu 432-8561, Japan.
E-mail addresses: sakhon_chula@hotmail.com (S. Ratchahat), sudoh@zai-amano.or.jp (M. Sudoh), suzuki.yuji.16@shizuoka.ac.jp (Y. Suzuki), kawasaki.wataru.15@shizuoka.ac.jp (W. Kawasaki), trwatan@ipc.shizuoka.ac.jp (R. Watanabe), tcfukuh@ipc.shizuoka.ac.jp (C. Fukuhara).

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Nomenclatures

A	apparent 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	volume flow rate of feed gas [m^3/s],
$\hat{H}_{in}$, $\hat{H}_{in}$	molar specific enthalpy [J/mol],
ΔH_i	reaction heat [W],
J	flux of feed gas [$mol/m^2 \cdot s$],
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],
$n_{i,in}$, $n_{i,out}$	mole per unit time [mol/s],
S	product selectivity [−],
ΔT_m	mean temperature difference of wall and center [K],
U	overall heat transfer coefficient [$W/m^2 \cdot K$],
X	conversion [−],
Z	direction along the catalyst length [m]

inevitably developed in the fixed-bed reactor. A metallic structured catalyst has been introduced to overcome these challenges [8,12]. Many types of structured catalyst including metallic foam [13], micro channel [14], and macro-structured support (mesh type) [15], have been widely investigated for CO_2 methanation reaction.

Recently we have been reported the novel nickel-based structured catalyst for CO_2 methanation [8]. The structured catalyst was constructed by a simple and effective method of wash-coating Ni/CeO_2 granular catalyst on aluminum honeycomb-type substrate. The structured Ni/CeO_2 catalyst demonstrated not only the rapid CO_2 transformation due to the highly active Ni/CeO_2 catalyst, but also the efficient heat exchange of exothermic heat through the highly conductive honeycomb substrate. This pioneer research work shows the promising way to transform CO_2 into CH_4 with efficient heat management and mass processing. A further study on a variety of structured catalyst configuration will provide a vital understanding on the process development and optimization. Moreover, the investigation on performance of structured catalyst under high feed rate condition is crucial for constructing a powerful methanation process.

In this study, we therefore aim to develop a powerful methanation process using a structured Ni/CeO_2 catalyst. Four configurations of honeycomb-type structures, namely, plain, stacked, segment, and multi-stacked types were employed to examine their effects on methanation performance. The plain-type catalyst consists of straight-flow channel, while the stacked-type catalyst has a random-flow channel. Segment-type catalyst has the divided flow-path unit with gap distance. The gap distance is a gap space between a catalyst stack. Effects of these configuration and gap distance were elucidated. The last configuration is assembly of numerous stacks (44 stacks of 2.5 mm-length honeycomb) to form the multi-stacked catalyst. The catalyst was coated alternatively with the uncoated parts, being as a static mixer. The multi-stacked catalyst was tested under high feed rate condition of 3000 mL/min and below. A moderate hot spot was observed over such configuration. The moderate hot spot behavior was explained according to the temperature profiles in the monolith measured during reaction.

2. Experimental

2.1. Preparation of granular Ni/CeO_2 catalyst component for structuring

In order to fabricate a structured Ni/CeO_2 catalyst, first a nickel-based granular catalyst component was prepared by a wet impregnation method. Cerium oxide (JRC-CEO-2) provided by Catalysis Society of Japan was employed as support material. The CeO_2 support has mesopore structure with average pore size of 6.8 nm, BET surface area of 126.4 m^2/g and pore volume of 0.22 cm^3/g. Distilled water was put into the support and then well-stirred for 12 h under vacuum condition at room temperature. Then a solution of $Ni(NO_3) \cdot 6H_2O$ was added to the support suspension and kept under stirring condition for 2 h. The mixture was subsequently evaporated completely at 80 °C while stirring. After drying, the obtained powder was calcined at 10 °C/min to 500 °C, and kept at this temperature for 3 h before naturally cooled down to room temperature. The Ni-based granular catalyst with dark brown color was obtained. Nickel loading on the support is fixed at a

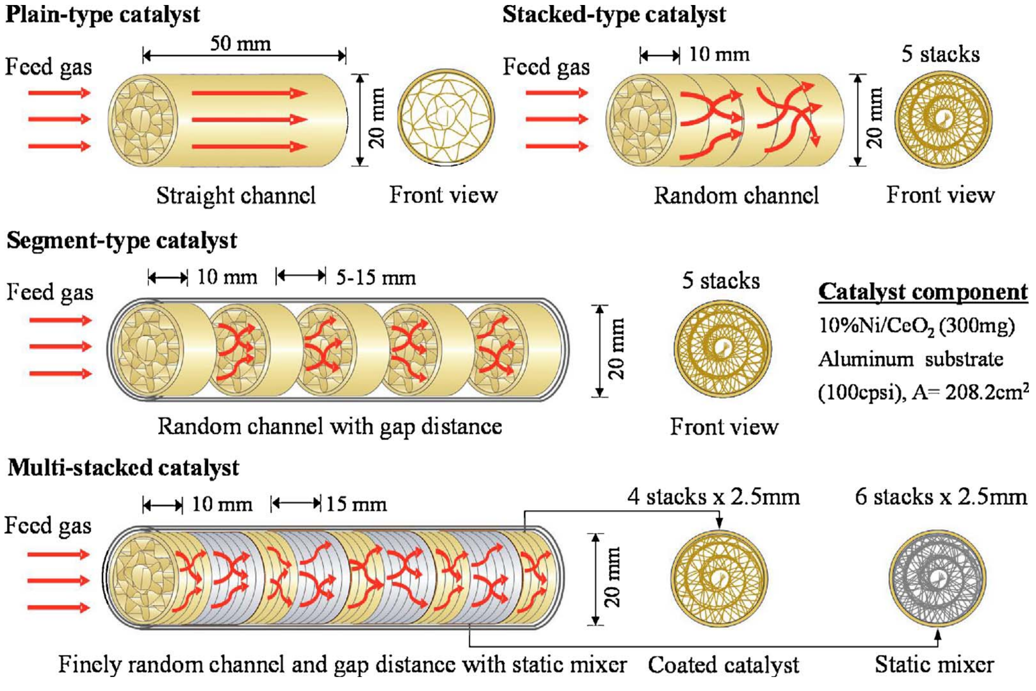

Fig. 1. Schematic of honeycomb-type catalysts: plain, stacked, segment and multi-stacked catalysts.