



## Research article

New Ni-based quaternary disk-shaped catalysts for low-temperature CO<sub>2</sub> methanation: Fabrication, characterization, and performanceDea Hyun Moon<sup>a</sup>, Sang Moon Lee<sup>b</sup>, Jeong Yoon Ahn<sup>a</sup>, Dinh Duc Nguyen<sup>b</sup>, Sung Su Kim<sup>b</sup>, Soon Woong Chang<sup>b,\*</sup><sup>a</sup> Department of Environmental Energy Engineering, Graduate School of Kyonggi University, 94 San, Iui-dong, Youngtong-ku, Suwon-si, Gyeonggi-do, 16227, Republic of Korea<sup>b</sup> Department of Environmental Energy Engineering, Kyonggi University, 94 San, Iui-dong, Youngtong-gu, Suwon-si, Gyeonggi-do, 16227, Republic of Korea

## ARTICLE INFO

## Article history:

Received 28 September 2017

Received in revised form

26 March 2018

Accepted 6 April 2018

## Keywords:

Carbon dioxide  
CO<sub>2</sub> methanation  
Methane  
Ni catalyst  
Ni oxide  
Calcined catalyst

## ABSTRACT

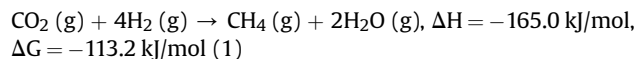
Ni-based quaternary disk catalysts were manufactured for low-temperature CO<sub>2</sub> methanation reactions, and the reaction activity was examined with respect to the thermal treatment conditions. By applying varying reduction and combustion treatments, the same catalysts were compared, and the Ni oxidation conditions and physical features were confirmed through X-Ray diffraction, scanning electron microscopy, and energy dispersive X-ray analyses. In addition, oxygen adsorption/desorption changes were measured by temperature-programmed reduction after pre-treating with oxygen and hydrogen. The reduction treatment catalyst showed a conversion of 20% at 280 °C, and the 70% calcined catalyst did not form a NiO crystalloid. The activation of the catalyst increased because of NiO movement on the catalyst surface, which enabled easy transformation to metallic Ni. The prepared catalyst is a highly reactive, yet stable, candidate for practical catalytic CO<sub>2</sub> methanation.

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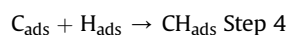
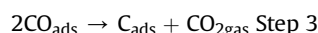
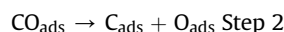
## 1. Introduction

Increasing atmospheric CO<sub>2</sub> concentrations have led to a worldwide greenhouse effect (Ghaib et al., 2016; Karimi et al., 2018). CO<sub>2</sub> constitutes a large portion of greenhouse gases and is one of the major causes of the greenhouse effect and climate change; therefore, diverse processes, such as separation, storage, and utilization of CO<sub>2</sub>, are required to prevent global warming and reduce CO<sub>2</sub> levels in the atmosphere (Goli et al., 2016; Hwang et al., 2013). CO<sub>2</sub> treatments are mainly divided into carbon capture storage (CCS) and carbon capture utilization (CCU) technologies. CCS technologies capture and store exhausted CO<sub>2</sub>; however, their development has been ignored because there are severe challenges associated with safe storage of CO<sub>2</sub> (Morales Mora et al., 2016; Stangeland et al., 2017). CCU technologies convert CO<sub>2</sub> using physical, chemical, and biological methods, and offer the advantage

of generating a new source of energy (Olajire, 2013; Xu et al., 2017). Some examples of CCU technologies include CO<sub>2</sub> biofixation, mineral carbonation, and chemical conversion. The CO<sub>2</sub> methanation reaction is a chemical conversion method that reduces CO<sub>2</sub> and converts it to an energy source, making it a very desirable method. The methanation reaction is described as follows (Xu et al., 2016b).

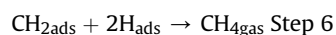
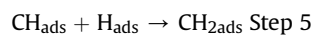


According to Graça et al. (2014), the CO<sub>2</sub> methanation reaction is followed by a six-step mechanism, as follows.



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CO<sub>2</sub> adsorbs on the surface of the catalyst and dissociates to CO and O during the CO<sub>2</sub> methanation reaction. CO is later adsorbed and reacts according to steps 2 and 3. The CO dissociation in step 2 is irreversible because of the rapid removal of surface O by hydrogenation, while the CO dissociation in step 3 is attributed to disproportion (Choe et al., 2005). Steps 4 and 5 occur after the rate-determining steps. Finally, the last reaction, which forms CH<sub>4</sub>, proceeds by hydrogen reacting with CH<sub>2ads</sub>.

The CO<sub>2</sub> methanation reaction is a typical exothermic reaction, that generates two major products, CH<sub>4</sub> and H<sub>2</sub>O, by reacting with four hydrogen molecules at low temperatures (below 400 °C) with an equilibrium turnover rate. In addition, as the reverse water-gas shift reaction progresses at high temperatures (above 450 °C), CO selectivity is increased. Therefore, to facilitate a desirable methanation reaction, the reaction should occur at low temperatures (below 400 °C). In addition, a catalyst is required to obtain the appropriate reaction speed and selectivity (Goodman, 2013; Jwa et al., 2013).

Metal catalysts (e.g., Ni, Fe (Schoder et al., 2013), Co (Zhou et al., 2013), Cu, Ru (Janke et al., 2014), Rh (Karelovic and Ruiz, 2013; Sharma et al., 2011), Pd (Karelovic and Ruiz, 2013; Sharma et al., 2011), and Pt (Kim et al., 2010)) combined with various metal oxides, SiO<sub>2</sub> (Da Silva et al., 2012), Al<sub>2</sub>O<sub>3</sub> (Razzaq et al., 2013), ZrO<sub>2</sub> (Swalus et al., 2012; Zhao et al., 2016), TiO<sub>2</sub> (Ren et al., 2015), and CeO<sub>2</sub> (Xu et al., 2016a), are mainly used for the methanation reaction. Among these, Ni has been frequently used because of its excellent functional properties and low price (Liu et al., 2010). However, Ni shows a low catalytic activity and carbon deposition at low temperatures, motivating ongoing research on various additives (Aldana et al., 2013; Goodman, 2013).

To date, most researchers have focused on powdered additives, and research on molded catalyst materials has rarely been reported, while honeycomb catalysts (Graça et al., 2014; Liu et al., 2012) and Ni tube catalysts using electroless plating have only been partially reported. Despite the excellent activity of the catalyst, an additional applicable catalyst molding material is required (Fukuhara et al., 2013, 2017). However, disk catalysts, which were manufactured in this study, could be prepared using a simple mechanical stirring method. Therefore, the manufacturing method is simple and can be used for mass production. For various disk-type catalyst materials, the manufacturing process is simple when only the molding is modified, and their commercialization is relatively easy because they are not affected by their form or size. Therefore, we produced a catalyst that can be quickly commercialized. We selected Ni because of its high activity and low cost, and Ce and yttria-stabilized zirconia (YSZ) was added to enhance mechanical strength and prevent sintering.

In the present study: i) new Ni-based quaternary disk-shaped catalysts were manufactured for the purpose of testing low-temperature CO<sub>2</sub> methanation; ii) the physicochemical properties of the prepared catalytic disks were then analyzed and evaluated through X-Ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) analyses, H<sub>2</sub> temperature-programmed reduction (H<sub>2</sub>-TPR), and the Brunauer-Emmett-Teller (BET); and iii) the catalytic activity of samples used to achieve low-temperature CO<sub>2</sub> methanation were examined by evaluating the reduction-treated and sintered catalysts based on their Ni oxidation state. Furthermore, the effects upon Ni and the NiO formed during the reaction were measured and results compiled in order to carefully and comprehensively analyze and assess all factors effecting the outcome of the tests.

## 2. Materials and methods

### 2.1. Catalyst preparation

Nickel powder (99.7%, Sigma Aldrich Co., USA), YSZ (92%, Sigma Aldrich Co., USA), CeO<sub>2</sub> (99.9%, Sigma Aldrich Co., USA), and TiO<sub>2</sub> (99%, Ishihara Sangyo Kaisha, Ltd., Japan) were used as reagents. A simple mixing method was used to manufacture the catalysts; each weight was measured and the sample was agitated for 1 h at room temperature after the addition of distilled water. An evaporator (EYELA SB-1100, Changshin Scientific Co., Korea) was used at 70 °C to remove moisture from the sample, and the sample was then dried for 24 h in a dry oven at 110 °C. The dried powder was then molded into a disk form under a pressure of a 44482.2N (10,000 lbf) mold (diameter 2.54 cm). The molded catalysts were heat-treated at 950 °C with a heating rate of 2 °C/min, and the final catalyst was obtained. The completed final catalyst and disk reaction module are shown in Fig. S1.

### 2.2. Catalyst activity tests

The fixed-type reactor of the experimental system was generally manufactured with stainless steel. One of the disk-type catalysts was fixed inside the disk module. The temperature of the catalyst was measured using a K-type thermocouple (REOTEMP Instrument Corp., USA) inserted into the reactor and touching the catalyst bed. A mass flow controller (MKS 1179A, MKS Instruments, Inc., USA) was used for flow control, and a methanation reactor was pre-heated to 180 °C by the pre-heating line. Tests were performed by maintaining the reactor temperature between 200 and 350 °C. The injected gas was CO<sub>2</sub>:H<sub>2</sub>:N<sub>2</sub> = 1.0:4.0:1.0 (volume ratio), and the total flow was set to 120 mL. Moisture was condensed and removed by installing a cooler (−40 °C) at the rear of the reactor. Analysis of the reaction products was conducted using a gas chromatograph (GC, YL6500 GC system, YL Instruments Co., Ltd., Korea) equipped with a thermal conductivity detector and a 60/80 Carboxen-1000 molecular sieve column. After confirming a constant temperature, the GC measured the gas composition every 15 min for 1 h. The CO<sub>2</sub> conversion was calculated using the following formula:

$$\text{CO}_2\text{conversion}(\%) = \frac{\text{CO}_2(\text{influent}) - \text{CO}_2(\text{effluent})}{\text{CO}_2(\text{influent})} \times 100\% \quad (2)$$

### 2.3. Characterizations

#### 2.3.1. X-ray diffraction

To observe the phase changes of reduced and sintered Ni, X-ray diffraction (XRD) analysis was performed using a D/Max 2500V/PC diffractometer (Rigaku Corporation, Japan). Cu K $\alpha$  ( $\lambda = 1.5056 \text{ \AA}$ ) was used as the radiation source; the X-ray generator operated at 18 kW and the  $2\theta$  scan was performed from 10° to 90°.

#### 2.3.2. Scanning electron microscopy & energy dispersive X-ray

The surface form and element composition of the catalyst were examined using scanning electron microscopy (SEM), and an energy dispersive X-ray (EDX) analyzer combined with field emission a scanning electron microscope (CD-SEM S-8820, Hitachi Co., Japan) was used. Images were obtained at  $\times 5,000$ ,  $\times 8,000$ , and  $\times 15,000$  magnifications; the analysis was then performed by selecting the EDX element composition (O, Ti, Ni, Zr, and Ce).

#### 2.3.3. H<sub>2</sub> temperature-programmed reduction

To measure the oxygen adsorption/desorption effects of the

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