

Reducible oxide (CeO₂, ZrO₂, and CeO₂-ZrO₂) promoted Ni-MgO catalysts for carbon dioxide reforming of methane reaction

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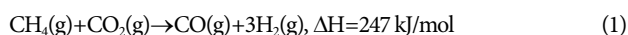
(Received 26 November 2019 • Revised 25 March 2020 • Accepted 26 March 2020)

Abstract—Ni-MgO catalysts have been widely applied for carbon dioxide reforming (CDR) reaction due to their ability of anti-carbon formation. However, activation of Ni-MgO catalyst consumes considerable energy because of its very low reducibility. In this study, ZrO₂, CeO₂, and CeO₂-ZrO₂ promoted Ni-MgO catalysts were prepared via a facile co-precipitation method and applied to the CDR reaction. Among the prepared catalysts, the ZrO₂-promoted Ni-MgO catalyst showed the highest methane conversion. The high catalytic performance of the ZrO₂-promoted Ni-MgO catalyst is mainly due to easier reducibility, high Ni dispersion, and high specific surface area.

Keywords: Carbon Dioxide Reforming of Methane, Reducible Oxide Promoters, Reducibility, Ni Dispersion, Surface Area

INTRODUCTION

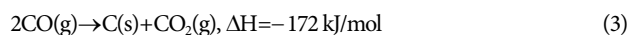
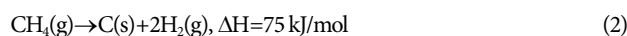
Increasing greenhouse gas emissions due to the excessive use of fossil fuels has led to growing concern about climate change, with the greenhouse gas CO₂ accounting for the largest portion. Therefore, many attempts have been made to reduce the CO₂ concentration in the atmosphere through CO₂ utilization [1,2]. Recently, technologies for the use of CO₂ as a carbon resource, such as the carbon dioxide reforming of methane (CDR, Eq. (1)) and the combined steam and carbon dioxide reforming of methane (CSCRM), have been developed.



The CDR reaction has attracted particular attention due to its environmental advantages and the chemical possibilities of CO₂ utilization, because it can utilize both CO₂ and CH₄, which are the mainly emitted greenhouse gases [2-4]. Moreover, the synthesis gas produced through CDR reaction shows a suitable ratio of H₂/CO (about 1.0), which can be utilized as the basis for the Fischer-Tropsch synthesis of long-chain hydrocarbons, DME (dimethyl ether), acetic acid, and oxo-alcohols without adjusting the H₂/CO ratio of produced syngas through the additional chemical processes [5,6].

However, the CDR reaction has some drawbacks related to catalyst deactivation, as coke deposition problems can occur due to the high reaction temperature required to activate the stable gases (CH₄ and CO₂). At such high temperature, the CH₄ decomposition (Eq. (2)) reaction is accelerated. Furthermore, the CDR reaction is highly endothermic; therefore, the temperature may partially decrease in the reactor, and this phenomenon induces the Boudouard reaction (Eq. (3)). These side reactions lead to serious coking problems

on the reforming catalyst. Moreover, the high temperature of the reaction can promote sintering of the active metals or support materials. Thus, the major issues to the commercialization of the CDR process are coke formation and sintering [7-10].



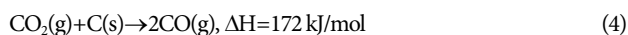
To prevent these problems, many studies dealing with the active metal, support, and promoter have been conducted. Precious metals (Ir, Rh, Ru, Pt, and Pd) have been found to show much greater resistance to carbon formation than non-precious metals [11-15]. However, their high cost is a drawback. In case of the CDR reaction, it has not yet been developed for industrial scale. It is usually combined with SRM, which is known as CSCRM. In that case, catalysts using Ni as an active metal have been chosen because of their good catalytic performance, which is comparable to that of precious-metal-based catalysts, and their affordable price. However, they are easily deactivated by carbon formation and/or Ni sintering during the CDR reaction [16]. Therefore, the development of a catalyst which has high activity and stability as well as resistance to carbon formation and sintering of the Ni metal is necessary. It has been reported that coke formation occurs easier when the particle size of active metal is larger [3,17,18]. The size of the active metal particles can be controlled effectively using metal oxide supports, which strongly interact with the active metal [19]. Such metal-to-support interactions can be enhanced through the formation of a solid solution of the metal and support. Among the various oxide support materials, MgO is known to easily form a solid solution with NiO due to the similar lattice parameters of the two oxides [20-22]. NiO-MgO solid solution also forms nano-structured catalysts, which usually show better catalytic performance in CDR reaction. Additionally, MgO affects the adsorption of CO₂ and coke resistance by controlling the basicity of the catalyst. Increasing the

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basicity results in an increase in the adsorbed CO₂ (acidic), which leads to the following reaction, called reverse Boudouard reaction (Eq. (4)). As a result, Ni and MgO are frequently used together in CDR reaction catalysts [19,21,22]. However, Ni-MgO catalysts should be reduced at high temperature for a long time due to its very low reducibility [23].



ZrO₂, CeO₂, and CeO₂-ZrO₂ have attracted interest as promising support or promoter materials due to its superior reducible characteristics during recent decades [24]. Wang et al. reported that the addition of CeO₂ to a catalyst as a promoter increased its catalytic activity and stability while suppressing carbon deposition. This suppressing effect was due to the highly dispersed Ni atoms on the catalyst surface [25]. Zhang et al. reported that the strong interaction between Ni and CeO₂ and the confinement effect of the mesoporous structure suppressed the aggregation of Ni particles in NiCe/SBA-16 catalysts [26]. Debek et al. demonstrated that a Zr-promoted catalyst showed narrower porosity and higher surface area than a promoter-free or Ce-promoted catalyst [27]. Yao et al. found that the introduction of Zr as a promoter to a Ni/SiO₂ catalyst increased the reducibility of the catalysts [28]. Liu et al. reported that the structural stability and the Ni dispersion of catalysts were increased with the addition of Zr. Additionally, the excellent catalytic activity and long-term stability of these catalysts resulted from the strong anchoring effect of Zr and the partial activation of CO₂ by Zr [29]. Faria et al. reported that the high oxygen mobility of CeO₂-ZrO₂ effectively prevented the oxidation of metallic Ni⁰ particles by CO₂ from the feed during the reaction. In addition, it also prevented carbon deposition on the catalyst [30]. Shanmugam et al. reported that the incorporation of CeO₂ and ZrO₂ promoters effectively controlled the Ni particle size via the strong interaction between the promoter and Ni [31].

The purpose of this work was to investigate the effect of the CeO₂-ZrO₂ ratio on the physicochemical properties and catalytic performance ZrO₂, CeO₂, and CeO₂-ZrO₂ promoted Ni-MgO catalysts in the CDR reaction. We prepared ZrO₂, CeO₂, and CeO₂-ZrO₂ promoted Ni-MgO catalysts via a facile and economic co-precipitation method [32] and applied them in the CDR reaction. The effects of the CeO₂-ZrO₂ ratio on the physicochemical properties of the catalysts were studied by various characterization methods and were related to the catalytic performance in the CDR reaction. We also attempted to determine the optimum CeO₂-ZrO₂ ratio of the ZrO₂, CeO₂, and CeO₂-ZrO₂ promoted Ni-MgO catalysts to achieve excellent catalytic performance.

EXPERIMENTAL

1. Catalyst Preparation

Ni-MgO-CeO₂ (NMC), Ni-MgO-Ce_{0.8}Zr_{0.2}O₂ (NMCZ), Ni-MgO-Ce_{0.2}Zr_{0.8}O₂ (NMZC), and Ni-MgO-ZrO₂ (NMZ) catalysts were synthesized using co-precipitation. The loading amount of active metal (Ni) was fixed at 15 wt%, and that of the support MgO was fixed at 50 wt%. Ni(NO₃)₂·6H₂O (97%, Junsei), Mg(NO₃)₂·6H₂O (99%,

Aldrich), Ce(NO₃)₃·6H₂O (99%, Aldrich), and zirconyl nitrate solution (20 wt% ZrO₂ basis, MEL Chemicals) were used as precursors. All the precursors were mixed in one-pot with deionized water. Following the dissolution of precursors, this precursor solution was heated to 80 °C by a heating mantle. 15 wt% KOH solution was added to the precursor solution with 60 mL/min for the precipitation step. After aging for three days, the precipitates were thoroughly washed with distilled water for the removal of impurities and dried in ambient condition for 24 h. Then the as-dried catalysts were dried again in oven at 110 °C for 6 h to remove the moisture. Finally, the calcination step was carried out in air at 800 °C for 6 h.

2. Catalyst Characterization

The Brunauer-Emmett-Teller (BET) specific surface area of the calcined samples was analyzed via nitrogen adsorption/desorption technique using an ASAP 2010 (Micromeritics) accelerated surface area and porosimetry instrument. Before the measurement, the prepared catalysts were thermal treated at 110 °C for 12 h under vacuum condition. X-ray diffraction (XRD) patterns of catalysts were measured by Rigaku Ultima IV diffractometer operated at 40 kV and 40 mA with Ni filtered Cu-K α radiation. A 2 θ step of 0.02°/s was used for a wide-range scan (range=20-80°). All the samples were pre-reduced at 800 °C for 3 h in 5% H₂/N₂ before the XRD analysis to collect the data when it participated to the CDR reaction. The crystallite size of Ni⁰ was calculated by Scherrer's equation (Eq. (6)).

$$\text{Ni}^0 \text{ crystallite size (nm)} = \frac{K \times \lambda}{\beta \times \cos \theta} \quad (6)$$

where K means the dimensionless shape factor (0.89), λ is X-ray wavelength (0.154 nm), β is the line broadening at half the maximum intensity (FWHM), and θ is the Bragg angle.

H₂-chemisorption was conducted using an Autochem 2920 (Micromeritics). The pre-reduction of calcined samples was also performed in 5 vol% H₂/Ar at 800 °C for 3 h. After the pre-reduction step, the amount of H₂ chemisorbed on active metals was measured by the H₂ pulse technique at 50 °C. The numeric value of Ni dispersion was calculated by the following equation, based on the assumption that the stoichiometric value of hydrogen atom over the Ni metal on the catalyst surface is 1 (H/Ni_{surface}=1).

$$D (\%) = \frac{V_s \times SF \times M_{Ni}}{W_s \times W_f \times V_{m, STP}} \times 100 \quad (7)$$

The H₂-temperature programmed reduction (TPR) analysis was performed at a heating rate of 10 °C/min in the temperature range of 50-1,000 °C. In this case, calcined samples were analyzed. 10 vol% H₂/Ar flow was fed during the analysis to provide the reducing atmosphere. The additional TPR experiment was performed in the temperature range of 50-800 °C in the same condition to calculate the reduction degree of each catalysts. The reduction degree was calculated employing the following equation from the integration of the peak area under the TPR profile at 800 °C and 1,000 °C, respectively.

$$\begin{aligned} \text{Reduction degree (\%)} \\ = \frac{\text{H}_2 \text{ consumption amount (800 } ^\circ\text{C)}}{\text{H}_2 \text{ consumption amount (1,000 } ^\circ\text{C)}} \times 100 \end{aligned} \quad (8)$$

Table 1. Characteristics of NMC, NMCZ, NMZC, and NMZ catalysts

Catalyst	BET surface area (m ² /g) ^a	Crystallite size of Ni ⁰ (nm) ^b	Ni dispersion reduced at 800 °C (%) ^c	Reduction degree (%) ^d	Total desorbed CO ₂ (CO ₂ cm ³ /g _{cat}) ^e
NMC	82.0	4.5	1.8	72	4.6
NMCZ	102.7	9.8	2.4	87	4.6
NMZC	104.2	13.1	2.7	90	2.9
NMZ	104.3	12.1	2.7	100	2.7

^aEstimated from N₂ adsorption at −196 °C.^bCalculated from XRD patterns.^cCalculated from H₂ chemisorption.^dReduction degree=H₂ consumption amount (800 °C)/H₂ consumption amount (1,000 °C).^eEstimated from CO₂-TPD.

CO₂-temperature programmed desorption (TPD) of the reduced samples was also conducted in an Autochem 2920 (Micromeritics). The pre-reduction of calcined samples was also in 5 vol% H₂/Ar at 800 °C for 3 h. After the pre-reduction step, each sample was exposed to 250 °C with He gas for 1 h and then cooled. Next, CO₂ was adsorbed at 100 °C for 20 min. Then by purging with He for 2 h, weakly adsorbed CO₂ was removed. As desorption step, the sample was heated from 50 to 800 °C at a heating rate of 10 °C/min in a He flow. The desorbed CO₂ amount was calculated by thermal conductivity detector (TCD), and the total desorbed CO₂ amount was calculated by the integration of the TPD patterns. The amount of carbon deposited on used catalysts was determined by thermogravimetry analyzer (TGA, SDT Q600 V20.9 Build 20). The thermogravimetry analysis of the collected catalysts after CDR reaction for 12 h was at a heating rate of 10 °C/min under an air flow at a flow rate of 100 ml/min. The carbon formation of spent catalysts was checked also by scanning electron microscope (SEM, JEOL-7800F) at 10.0 kV.

3. Catalytic Reaction

Catalytic performance tests were performed in a quartz reactor (inner diameter: 4 mm). Reactor temperature was real-time monitored and controlled by temperature control box (ss-TFCB-N-2, SamSon Hi Tech). Before the catalytic test, pre-reduction was performed at 800 °C for 3 h under 5% H₂/N₂ condition. The feed gas consisted of CH₄, CO₂, and N₂ in a 1 : 1 : 1 ratio; each gas was controlled using an independent mass flow controller. The N₂ acted as an internal standard gas [33]. The effluent gases were connected to a moisture trap to remove the remaining H₂O. The composition of product gases was monitored by an online micro-gas chromatograph (Agilent 3000). 12 mg of the catalyst was loaded into the quartz reactor, and a stability test was performed at 800 °C with a gas hourly space velocity (GHSV) of 720,000 h^{−1} for 10 h. CH₄ and CO₂ conversion was calculated using the following equations:

$$\text{CH}_4 \text{ conversion (\%)} = \frac{[\text{CH}_4]_{\text{in}} - [\text{CH}_4]_{\text{out}}}{[\text{CH}_4]_{\text{in}}} \times 100 \quad (9)$$

$$\text{CO}_2 \text{ conversion (\%)} = \frac{[\text{CO}_2]_{\text{in}} - [\text{CO}_2]_{\text{out}}}{[\text{CO}_2]_{\text{in}}} \times 100 \quad (10)$$

$$\text{H}_2 \text{ selectivity (\%)} = \frac{\text{H}_2 \text{ out}}{2 \times (\text{CH}_{4,\text{in}} - \text{CH}_{4,\text{out}})} \times 100 \quad (11)$$

$$\text{CO selectivity (\%)} = \frac{\text{CO}_{\text{out}}}{(\text{CH}_{4,\text{in}} - \text{CH}_{4,\text{out}}) + (\text{CO}_{2,\text{in}} - \text{CO}_{2,\text{out}})} \times 100 \quad (12)$$

$$\text{H}_2/\text{CO ratio} = \frac{[\text{H}_2]_{\text{out}}}{[\text{CO}]_{\text{out}}} \quad (13)$$

where the [X]_{in} and [X]_{out} are the inlet and outlet concentration of X. In the same way, the X_{in} and X_{out} are the inlet and outlet amount of X.

RESULTS AND DISCUSSION

1. Catalyst Characterization

Table 1 summarizes the characteristics of the NMC, NMCZ, NMZC, and NMZ catalysts. The NMZ catalyst shows the highest surface area (104.3 m²/g), whereas the NMC catalyst the lowest value (82.0 m²/g). The surface area of the NM-Ce_(1-x)Zr_(x)O₂ catalysts decreases when the Ce content increases. As a result, NMZC catalyst shows the surface area of 104.2 m²/g and NMCZ catalyst shows the surface area of 102.7 m²/g.

The Ni dispersion of the prepared catalysts was calculated from the pulse H₂-chemisorption results. The Ni dispersion values of the NMC, NMCZ, NMZC, and NMZ catalysts are also listed in Table 1. The NMZ and NMZC catalysts both exhibit an Ni dispersion value of 2.7%. The NMC catalyst showed the lowest Ni dispersion value (1.8%). The Ni dispersion value of the NMC, NMCZ, NMZC, and NMZ catalysts decreases in the following order: NMZ (2.7%) = NMZC (2.7%) > NMCZ (2.4%) > NMC (1.8%).

The XRD patterns of the prepared catalysts are shown in Fig. 1. The diffractograms of the NMC, NMCZ, and NMZC catalysts show peaks assigned to CeO₂ characteristic peaks [JCPDS No. #34-0394], which shifted to higher 2θ value with increasing ZrO₂ content [34]. The atomic size of Zr⁴⁺ (0.84 Å) is smaller than that of Ce⁴⁺ (0.97 Å); thus, Zr⁴⁺ atoms can enter the CeO₂ lattice, and a solid solution CeO₂-ZrO₂ mixed oxide is formed by the partial substitution of Ce⁴⁺ with Zr⁴⁺ [35,36]. The spectrum of the NMZ catalyst exhibits diffraction peak arising from ZrO₂ crystallites [JCPDS No. #27-0997].

The characteristic diffraction peaks of NiO [JCPDS No. #47-1049] and MgO [JCPDS No. #65-0476] crystallites are detected in all the prepared catalysts. The peaks which are assigned to Ni⁰ (active phase) [JCPDS No. #04-0850] are also observed at 44.5,

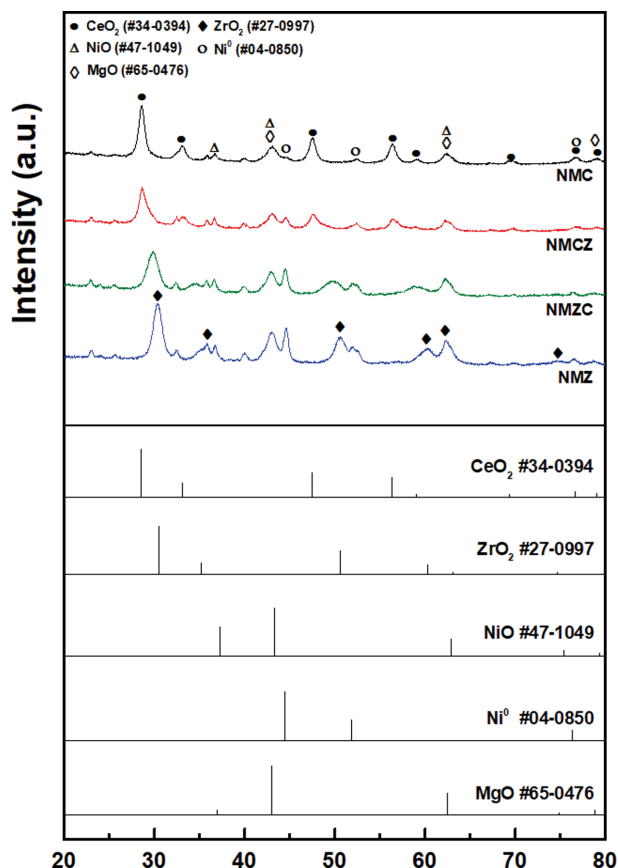


Fig. 1. XRD patterns of NMC, NMCZ, NMZC, and NMZ catalysts.

51.8, 76.4° [25,27]. The crystallite size of Ni^0 is shown in Table 1. It was calculated from Ni^0 (1 1 1) peaks using the Scherrer's equation (Eq. (6)). Interestingly, ZrO_2 -rich catalysts exhibited larger Ni^0 crystallite size than that of CeO_2 -rich catalysts despite of higher Ni dispersion. Additionally, the Ni^0 peaks of the NMZ and NMZC catalysts are clearer than those of the NMCZ and NMC catalysts, because the crystallinity of Ni^0 increases with increasing ZrO_2 weight percentage.

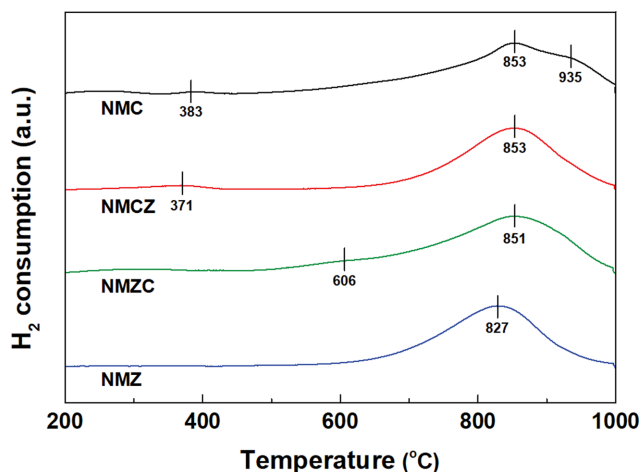


Fig. 2. TPR patterns of NMC, NMCZ, NMZC, and NMZ catalysts.

The redox property of catalysts typically has a crucial impact on their catalytic activity in the reforming reaction [25,27]. Fig. 2 exhibits the TPR patterns of the NMC, NMCZ, NMZC, and NMZ catalysts. Each catalyst has different characteristic peaks depending on its applied material and composition. All prepared catalysts were characterized by a small reduction peak at low temperature range and huge reduction peak at high temperature range except NMZ. It is well known that characteristic peaks which arise at low temperature range are induced by the reduction of relatively free NiO species which are weakly interacting with the support or promoter [37]. The characteristic peaks which arise at high temperature range are attributed to the reduction of complex NiO species strongly interacting with the support or promoter [38]. The reduction peaks observed in relatively low temperature range (383, 371, 606 °C) originate from the reduction of relatively free NiO species which are weakly interacting with MgO . Additionally, surface ceria which is in catalyst sub-layer and interacting with NiO and/or MgO can be partially reduced in this temperature range [34]. The clear peak observed around 850 °C is related to the reduction of complex NiO species which are strongly interacting with MgO , for which the composition is 50 wt% in this system. In the case of NMC catalyst, a shoulder peak was observed (935 °C) which is mainly related to the reduction of complex NiO strongly interacting with CeO_2 . Partial reduction of bulk CeO_2 may also affect this peak [34]. The NMZ catalyst did not show a reduction peak related to the free NiO species due to the high dispersion of Ni [39]. Among the prepared catalysts, the ZrO_2 -rich catalyst showed easier reducibility of the complex NiO species, indicating that the addition of ZrO_2 enhances the reducibility of the catalyst. These results indicate that the NMZ catalyst can be more easily reduced than the other prepared catalysts and should have higher catalytic activity.

Fig. 3 shows the CO_2 -TPD patterns of the reduced NMC, NMCZ, NMZC, and NMZ catalysts. The total desorbed CO_2 amount estimated from CO_2 -TPD of the reduced samples is also listed in Table 1. The CeO_2 -rich catalysts showed higher total desorbed CO_2 amount compared to the ZrO_2 -rich catalysts due to the formation of new basic sites induced by the introduction of CeO_2 [40-43].

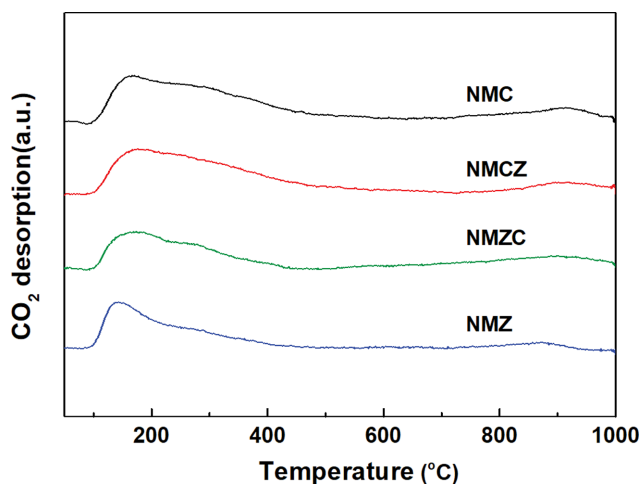


Fig. 3. CO_2 -TPD patterns of reduced NMC, NMCZ, NMZC, and NMZ catalysts.

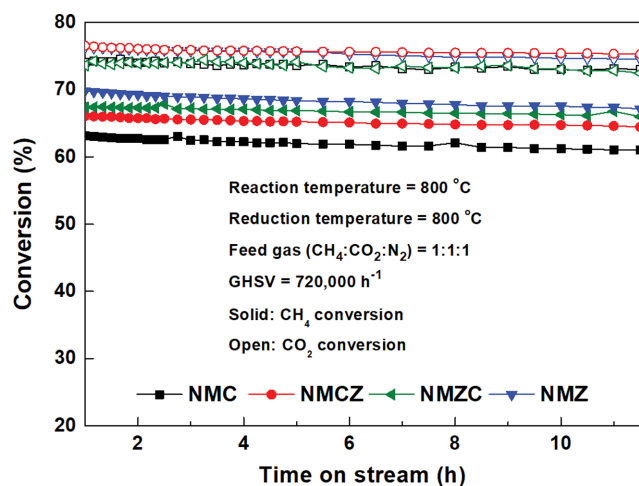


Fig. 4. CH₄ and CO₂ conversion with time on stream over NMC, NMCZ, NMZC, and NMZ catalysts (Reaction conditions: T=800 °C, CH₄:CO₂:N₂=1:1:1, GHSV=720,000 h⁻¹).

2. Catalytic Performance

In the beginning of our study, we checked the performance of Ni-MgO catalyst without reducible oxides and it had deactivated rapidly due to the coke formation (Fig. S1). As a result, we focused on the reducible oxide promoted Ni-MgO catalysts. Fig. 4 depicts the CH₄ and CO₂ conversion with the time on stream (TOS) over the NMC, NMCZ, NMZC, and NMZ catalysts. The NMZ catalyst shows the highest CH₄ conversion, whereas the NMC catalyst shows the lowest CH₄ conversion. The reaction results are summarized in Table 2. In the case of CO₂ conversion, all of the catalysts show higher value compared to the CH₄ conversion due to the side reactions including reverse Boudouard reaction (Eq. (4)) and reverse water-gas shift reaction (Eq. (5)). Especially, CeO₂-rich catalyst exhibits higher increase rate of CO₂ conversion value than that of ZrO₂-rich catalysts due to the higher basicity, which increases the adsorption of acidic CO₂ at the surface of the catalyst. Despite the extremely high GHSV of 720,000 h⁻¹, all the prepared catalysts show stable catalytic activity during 10 h. The used samples were analyzed by TGA and SEM technique to confirm the formation of coke during the CDR reaction. Fig. S2 shows the TGA result, which indicates that reducible oxide promoted Ni-MgO catalysts showed similar coke resistance ability, while the Ni-MgO catalyst without reducible oxide promoter showed a large amount of weight loss due to the oxidation of coke. SEM images are shown in Fig.

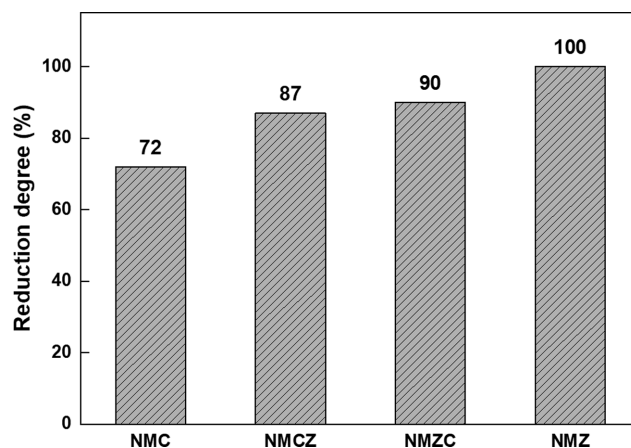


Fig. 5. Reduction degrees of NMC, NMCZ, NMZC, and NMZ catalysts.

S3, which also reveals that there is no formed coke in the catalyst surface, except in the Ni-MgO catalyst without reducible oxide promoter. Both results reveal that all prepared catalysts show similar coke resistance ability due to the promotional effect of reducible oxide, maintaining their catalytic activity except the bare Ni-MgO catalyst. The initial degree of CH₄ conversion was different for each of the prepared catalysts, but the stability of the catalysts was very similar. The differences in the initial CH₄ conversion originated from their physicochemical properties, such as reducibility of the catalysts, specific surface area, and Ni dispersion. In this work, the trend of initial CH₄ conversion matches with the number of Ni⁰ active sites, which considers the Ni dispersion and reduction degree. This result alludes to the importance of the reduction degree in Ni-MgO based catalyst system. On the other hand, the pre-reduction of the catalysts was conducted at 800 °C, considering the operating temperature of CDR in this study (800 °C). As shown in the TPR results, a reduction temperature of 800 °C was insufficient to reduce the complex NiO species in the NMZC, NMCZ, and NMC catalysts. Reduction degree calculations can be used to obtain a quantitative analysis of the reducibility of a catalyst [8,9].

The estimated values of the reduction degrees are shown in Fig. 5. The estimated value of NMZ catalyst was 100% owing to its easier reducibility. Thus, the high catalytic activity of the NMZ catalyst was due to the full conversion of the complex NiO species into Ni⁰. The NMZC, NMCZ, and NMC catalysts exhibited reduction degrees of 90, 87, and 72%, respectively. Therefore, a fraction

Table 2. Reaction results of NMC, NMCZ, NMZC, and NMZ catalyst

Catalyst	Conversion (%) ^a		Selectivity (%) ^a		H ₂ /CO ratio ^a	Ni ⁰ active sites (gmol/g _{cat}) ^b
	CH ₄	CO ₂	H ₂	CO		
NMC	62.4	74.7 (↑20.0%)	88.3	104.3	0.78	3.93×10 ⁻⁷
NMCZ	65.6	77.2 (↑17.7%)	89.8	105.1	0.79	6.35×10 ⁻⁷
NMZC	66.9	73.7 (↑10.2%)	90.1	97.8	0.88	7.43×10 ⁻⁷
NMZ	68.9	76.5 (↑11.0%)	91.3	98.1	0.89	8.12×10 ⁻⁷

^aT=800 °C, CH₄:CO₂:N₂=1:1:1, GHSV=720,000 h⁻¹.

^bNi⁰ active sites=g_{cat}×Ni loading×reduction degree×dispersion/Ni atomic weight.

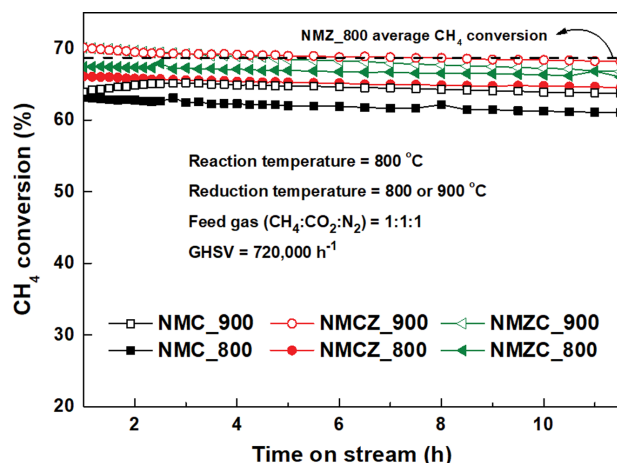


Fig. 6. CH_4 conversion with time on stream over NMC, NMCZ, and NMZC catalysts reduced at 800 °C and 900 °C (Reaction conditions: $T=800^\circ\text{C}$, $\text{CH}_4:\text{CO}_2:\text{N}_2=1:1:1$, $\text{GHSV}=720,000\text{ h}^{-1}$).

of the complex NiO species remained as an inactive oxide form.

To confirm the correlation between the calculated reduction degree values and catalytic activity results, we repeatedly tested NMC, NMCZ, and NMZC catalysts in the same reaction condition, while changing the reduction temperature to 900 °C. Fig. 6 shows the CDR reaction result as a function of time on stream after the reduction at 900 °C, which all the catalysts show higher catalytic activity compared to the catalysts reduced at 800 °C. The reduction of NMZ catalyst at 900 °C was not conducted because the reduction degree value had already reached 100% at the reduction temperature of 800 °C.

Fig. 7 includes the result of BET surface area, reduction degree values, and the average CH_4 conversion value after the reduction at 900 °C. The NMCZ and NMZC catalyst reached the reduction degree value of 100%, and as a result they also reached the similar catalytic activity with NMZ reduced at 800 °C. However, the NMC catalyst still did not reach the reduction degree value of 100% due to the strong interaction between the NiO-MgO- CeO_2 . Because of this reason, the catalytic activity also increased only 1.9%, and could not reach the value of NMZ. All catalysts pre-reduced at increased temperature (900 °C) showed lower value of BET surface area and Ni dispersion due to the thermal sintering. Considering the decrease of BET surface area, the long-term stability of the catalyst may decrease after increasing the reduction temperature. In addition, increasing the reduction temperature from 800 °C to 900 °C requires extensive energy [44]. However, their conversion is almost the same with the NMZ reduced at 800 °C, indicating that the conver-

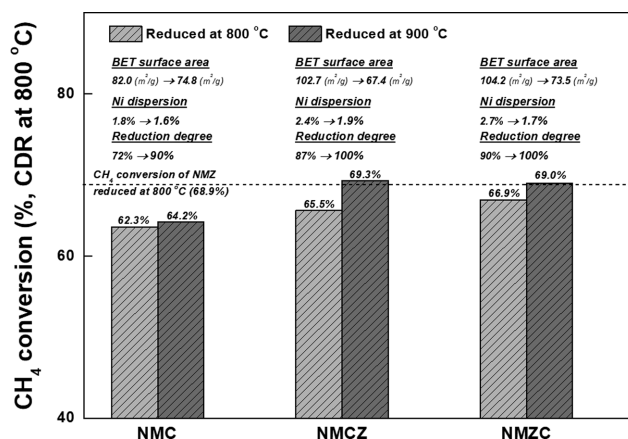


Fig. 7. Effects of reduction temperature on the BET surface area, reduction degree, and performance of NMC, NMCZ, and NMZC catalysts.

sion of CH_4 is directly related to the reduction degree of the NiO. As a result, we determined that ZrO_2 was the optimum promoter for the Ni-MgO catalyst for the CDR reaction, considering both catalytic activity and thermal energy efficiency for increasing the reduction temperature. Table 3 provides a comparison of reported data on the information of reaction conditions and the value of catalytic activity in CDR using Ni-MgO based catalysts [45–47]. According to the table, the developed catalyst shows superior catalytic activity even at a high GHSV.

CONCLUSIONS

ZrO_2 , CeO_2 , and $\text{CeO}_2\text{-ZrO}_2$ promoted Ni-MgO catalysts were prepared and applied for use in CDR reaction at extremely high GHSV of 720,000 h^{-1} . All prepared catalysts showed similar coke resistance ability due to the promotional effect of reducible oxides, thereby maintaining their catalytic activity for the CDR reaction. By comparing the reduction degree of the catalyst in different pre-reduction temperature, ZrO_2 -promoted Ni-MgO catalyst was selected as the optimum catalyst considering the catalytic performance and thermal energy efficiency for activating the catalyst. The superior performance of NMZ catalyst in CDR reaction was due to the easier reducibility, high Ni dispersion, and high specific surface area.

ACKNOWLEDGEMENTS

This work was supported by Next Generation Carbon Upcy-

Table 3. Comparison of reported data and our results

Catalyst description	Reactant gas ($\text{CH}_4:\text{CO}_2$ ratio)	Reaction temperature (°C)	Conversion (%)		GHSV (h^{-1})	Ref. No.
			CH_4	CO_2		
Ni-MgO- ZrO_2	1:1	800	69	77	720,000	This work
Ni- CeO_2/MgO	2:1	700	45	90	12,000	[45]
Ni-MgO	1:1	700	59	65	24,000	[46]
Ni-MgO	1:1	850	46	55	168,000	[47]

cling Project (Project No. 2017M1A2A2044372) through the National Research Foundation (NRF) funded by the Ministry of Science and ICT, Republic of Korea.

SUPPORTING INFORMATION

Additional information as noted in the text. This information is available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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Supporting Information

Reducible oxide (CeO_2 , ZrO_2 , and CeO_2 - ZrO_2) promoted Ni-MgO catalysts for carbon dioxide reforming of methane reaction

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(Received 26 November 2019 • Revised 25 March 2020 • Accepted 26 March 2020)

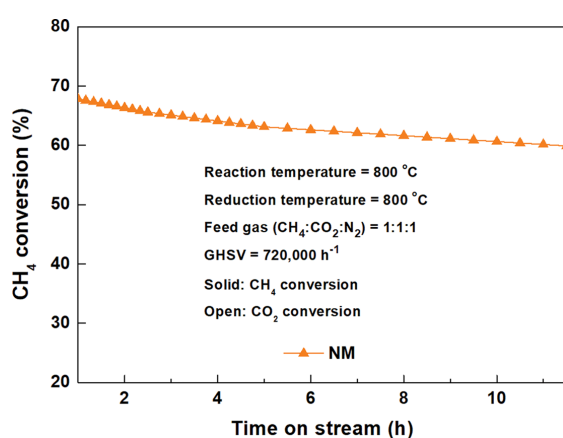


Fig. S1. CH₄ conversion with time on stream over NM catalyst (Reaction conditions: T=800 °C, CH₄:CO₂:N₂=1:1:1, GHSV=720,000 h⁻¹).

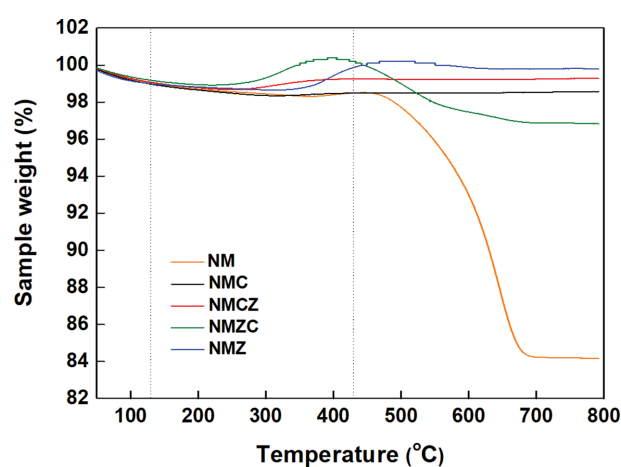


Fig. S2. TGA results of NM, NMC, NMCZ, NMZC, and NMZ catalysts.

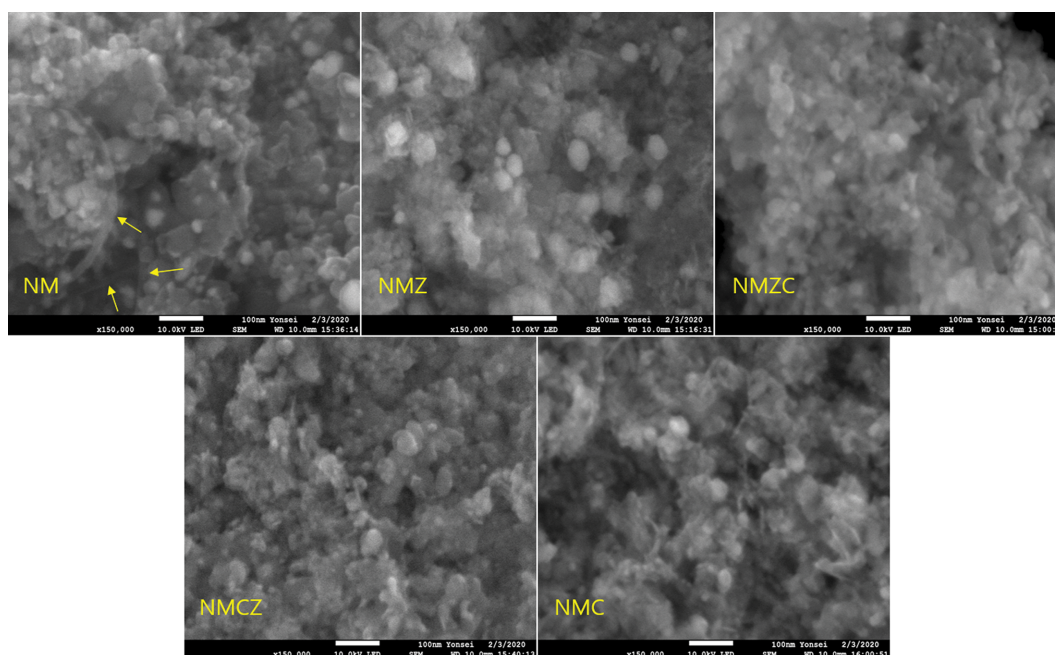


Fig. S3. SEM image of NM, NMC, NMCZ, NMZC, and NMZ catalysts after reaction.