

Development of Monolithic Catalyst System with Co-Ru-Zr for CO₂ (dry) Reforming of Methane : Enhanced Coke Tolerance

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Abstract

To verify the viability of Co, Ru and Zr-based catalyst for CO₂ (dry) reforming reaction, catalysts were fabricated using cordierite, silicon carbide and rota monolithic substrates, and they were compared with the conventional Co-Ru-Zr/SiO₂ catalyst in terms of performance and durability. Cordierite monolith was showed high activity with the least amount of active component. In addition, when Cordierite monolith was coated with Co-Ru-Zr in various ways, most excellent performance was showed at a precursor solution coating method. In particular, when 0.9 wt% Co-Ru-Zr/Cordierite was used for reaction, it was observed that 95% CO₂ conversion was maintained for 300 h at 900 °C.

Keywords : CO₂ reforming, Cobalt-ruthenium-zirconium, Monolith catalysts, Coking, Catalyst durability

1. Introduction

As global warming resulting from greenhouse gas emission has emerged as a serious environmental issue, carbon capture and utilization (CCU) technology is drawing attention as a solution to capture and utilize CO₂ emission [1-3]. CO₂ (dry) reforming of Methane (CDR or DRM in short) is the representative CCU technology that uses two primary greenhouse gases (CO₂ and CH₄) as raw materials to produce synthetic gas which provides a platform substance for a variety of chemical products downstream. In particular, CDR reaction features H₂:CO generation ratio close to 1:1, more effective in synthesizing hydrocarbon, aldehyde, acetic acid, etc. than steam reforming (SM) or partial oxidation (PO) reaction [4,5].

In CDR reactions, transition metal based catalyst, i.e. Ni/Al₂O₃, or platinum group metal (PGM) catalyst containing Ru, Rh, Pd, Pt, etc. is primarily used [6]. Among them, the PGM catalyst shows high activity as well as excellent anti-coking performance, but its scarcity and low cost-competitiveness limits its value in application for commercial processes [7]. Therefore,

many have studied Ni group catalysts that show similar performance to that of the PGM catalyst at low cost[8-12]. However, it was reported that although Ni catalyst showed high activity in CDR reaction, it also revealed serious carbon deposition [12-14].

Recently, it was reported that cobalt catalyst improved resistance to carbon deposition and showed excellent performance at low temperature [15,16]. It was reported that cobalt-added catalyst improved resistance to carbon deposition when compared with catalysts containing only nickel, contributing to the suppression of catalytic deactivation [17]. To optimize cobalt-based catalyst, Hou and Yashima studied the impacts of calcinations temperature, Co content, and reduction conditions on catalytic activity and carbon generation [18]. They reported that in Co/ α -Al₂O₃, Co surface, reforming activity, and coke-forming speed depended heavily on the calcinations temperature and reduction conditions of catalyst. Promoters added to cobalt-based catalyst were also studied. Ruckenstein and Trépanier reported that when a small amount of Ru was added to Co, it promoted dispersion of Co₃O₄ and suppressed oxidation of

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cobalt and carbon deposition of active site, thus improving activity and carbon resistance [19,20]. In addition, it is known that given its high thermal stability, Zr can contribute to catalytic durability, and precursors such as ZrCl₂O containing chloride affect the dispersion and crystal size of cobalt active substance during calcinations or reduction of catalyst [21]. Based on this study, Lee, et al. manufactured Co-Ru-Zr/SiO₂ ("CRZ/S" here in after) and found that it maintained excellent durability in prolonged CO₂ reforming reaction (500 h, 700 °C) [22].

CO₂ and CH₄ (raw materials for CO₂ (dry) reforming reaction) are generally converted at high temperature at or above 700 °C since they are chemically very stable [23]. Therefore, to maximize CO₂ reduction, it is necessary to develop a catalyst that can allow for stable operation of catalyst react or under high-flux reaction conditions, support high thermal stability without pressure decline. Moreover, as carbon deposition compromises catalytic performance and blocks reaction flow due to destruction of catalyst, it is essential to resolve such issues if the technology proposed herein is to be accomplished.

Hence, we coated the catalyst with Co-Ru-Zr using Cordierite, Silicon Carbide (SiC) and Rota monoliths as substrates that are free from pressure decline, featuring excellent thermal/mechanical strength and finding extensive applications in environmental catalysts including automotive catalysts, and evaluated CO₂ reforming performance and durability. Various catalyst coating methods were reviewed to optimize the monolithic catalyst, and, in particular, Co-Ru-Zr coating content was varied to study its impact on catalyst activation and carbon deposition.

2. Experimental

2.1. Catalyst preparation

Table 1 summarizes the physical properties and data of 4 silica beads (S-1, S-2, S-3, S-4) and 3 monolithic substrates (Cordierite (M-1), Silicon Carbide (M-2), Rota (M-3)) used in this study. In addition, for precursors used in fabricating Co-

Ru-Zr catalyst, cobalt (II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, SamchunChem, 97%), ruthenium (III) nitrosyl nitrate (Ru(NO)(NO₃)₃, StreamChem, 99%) and zirconium (IV) chloride oxide octahydrate (ZrCl₂O·8H₂O, Junsei, 99%) were used and dissolved in distilled water to mix Co, Ru, and Zr in the ratio of 74.3%, 0.7%, and 25% respectively.

CoRuZr/SiO₂ catalysts (CRZ/S-1, CRZ/S-2, CRZ/S-3, CRZ/S-4) using silica bead as substrates were manufactured by impregnation method [22]. Namely, precursor solution where the sum of Co, Ru, and Zr and silica bead were mixed in the mass ratio of 1:4 was mixed with silica bead and evaporated in a rotary evaporator at 50 mbar and 45 °C for 12 h. Subsequently, as -prepared specimen was completely dried up at 110 °C for 24 h. The catalysts were calcinated under stagnant air in muffle furnace at 400 °C for 6 h, with temperature raised at the rate of 2 °C min⁻¹.

All monolithic catalysts were manufactured by dipping method. Monolithic substrates were dipped in CRZ precursor solution and dried with air blown to keep catalytic substance from plugging the channel. This process was repeated until the monolithic substrates were coated with desired amount of catalytic substance. In addition, to evaluate performance in reference to the size of monolith, small and big Cordierite monolithic substrates were prepared respectively. The small monolithic substrates were fabricated to be a cylinder that was 10 mm in diameter, 20 mm in height, and 1.57 mL in capacity where as the big monolithic substrates were fabricated to be 25 mm in diameter, 50 mm in height, and 24.53 mL in capacity of it inside an inconel reactor. In addition, to understand the impact of binder, CRZ precursor was dissolved in silica sol or alumina sol and catalyst was manufactured by repeating the same process as above with Cordierite monolithic substrates. Silica sol and alumina sol were used in 1:1 molar ratio to zirconia. Note that the absolute mass of Co, Ru, and Zr catalytic substances excluding the content of added binder was maintained to be the same as the monolithic catalyst manufactured without addition of binder. Table 2

Table 1. Characteristics of silica bead type and monolith substrate

| Substrate type | Denotation | Particle size (mm) ^{a)} or Cell density (cps) ^{b)} | Surface area (m ² g ⁻¹) | Total pore volume (cm ³ g ⁻¹) | Average pore size (nm) | Remarks |
|----------------|------------|--|--|--|------------------------|----------------------------|
| Silica bead | S-1 | 0.25 - 0.50 | 296 | 1.11 | 15 | Sigma Aldrich |
| | S-2 | 1.70 - 3.35 | 743 | 0.39 | 2 | Sigma Aldrich |
| | S-3 | 1.00 - 3.00 | 711 | 0.36 | 2 | Fluka |
| | S-4 | > 2.36 | 294 | 1.04 | 14 | Alfa Aesar |
| Monolith | M-1 | 200 | 1 > | - | - | Corning (Cordierite) |
| | M-2 | 200 | 1 > | - | - | Khancera (Silicon Carbide) |
| | M-3 | 200 | 37 | 0.11 | 152 | (Rota) |

^{a)} Particle size (mm) for bead type substrate, ^{b)} Cell density (cps) for monolithic substrate.

Table 2. Information of CRZ based catalysts

| Substrate type | Denotation | Content of CRZ (wt%) ^{a)} | Remarks |
|----------------|---------------|--|--|
| Silica bead | CRZ/S-1 | 17.7 | Low surface area |
| | CRZ/S-2 | - | High surface area |
| | CRZ/S-3 | 4 | High surface area |
| | CRZ/S-4 | 18 | Low surface area |
| Monolith | CRZ/M-1 | 0.68 0.94 1.6 (1.2/0.01/0.39) ^{b)} 2.7 | CRZ/M-1 prepared with various content of CRZ |
| | CRZ/M-2 | - | |
| | CRZ/M-3 | - | |
| | CRZS(sol)/M-1 | - | CRZ/M-1 prepared with Alumina sol and Silica sol |
| | CRZA(sol)/M-1 | - | |

(-): not measured

^{a)} determined by ICP-AES, ^{b)} Sum of Co, Ru, Zr content (wt%)

summarize the information of substrates and catalysts used in this study.

2.2. Characterization

2.2.1. Physical property

Pore characteristics of various substrates were analyzed (Micromeritics, TriStarII). Approximately 0.2 g of catalyst was filled into quartz tube and out-gassing was performed in vacuum at 300 °C for 8 h for pre-treatment of catalyst. After pre-treatment, N₂ adsorption/desorption isotherm was measured using nitrogen as adsorption gas at liquid nitrogen temperature and pore characteristics were identified from the line. Shape and surface of the monolithic substrates was observed using scanning electron microscope (SEM) (LEO1530).

Catalytic substance that existed on the substrates and catalyst loading were analyzed using Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (Thermo Scientific, iCAP 7400 duo). Specimens, 0.2 g each, were pre-treated at 200 °C for 80 minutes using 3 mL of HNO₃, HCl, and HF respectively (Atonpar, Multiwave3000). Each specimen was massed-up to 100ml following pre-treatment before analysis was initiated.

2.2.2. Redox property

To understand the Redox property of catalysts, temperature-programmed reduction (TPR) was performed (Micromeritics, AutochemII 2920). After being collected after reaction, catalysts were oxidized to 5% O₂/Ar at calcinations temperature of 400 °C, cooled down to room temperature, and purged under 5% H₂/Ar for 30minutes. Catalyst reduction was performed by raising temperature to 900 °C at the rate of 10 °C min⁻¹, and each

feed flow rate was kept at 20 mL min⁻¹ during the pre-treatment and reduction process. Moisture generated in the reduction process was removed by trap loaded in a mixture of isopropyl alcohol and liquid nitrogen, and change in hydrogen density was monitored with thermal conductivity detector (TCD).

2.3. Catalytic activity tests

Performance of the catalyst using 4 types of silica bead-type substrates, small cordierite monolithic substrates, SiC and rota monolithic substrates was evaluated in a packed bed reactor system equipped with a quartz tube reactor that was 10.5 mm in inner diameter and 550 mm in length. Reactor systems, consisted of gas feeding unit, fixed layer reaction unit, and analytics unit for analyzing gas before and after reaction. For input gases, CH₄, CO₂ which were reactants and mixed gas containing N₂ as internal standard substance were used (CH₄:CO₂:N₂ = 40:40 : 20 mol. ratio). During reaction, gas hourly space velocity (GHSV) was kept at 20,000 ml_{feed} g_{catalyst}⁻¹ h⁻¹ (total flow rate: 30 mL min⁻¹) in the cases of catalyst using silica bead as substrates. In addition, GHSV for evaluating small cordierite monolith, SiC and Rota monolithic substrates-based catalysts was 4,200 ml_{feed} ml_{catalyst}⁻¹ h⁻¹ (total flow rate: 110 mL min⁻¹). Prior to performance evaluation, temperature of the catalyst reactor was raised to 900 °C at the rate of 5 °C min⁻¹ under atmospheric pressure and reactant feed conditions, then lowered from 900 to 600 °C in the increment of 100 °C, being held for 120 minutes at each reaction temperature to allow for evaluation of catalytic activity. Performance was evaluated while maintaining the outer wall temperature of the reactor systems. Change in gas density before/after reaction was analyzed by gas chromatography (GC, DONAM, DS-6200) equipped with TCD and 1.8 m Carbosphere packed column. Catalyst performance was expressed in terms of conversion rate and calculated by Equations (1) and (2) where N indicated the number of moles of applicable substance:

$$\text{Conversion of CH}_4 \text{ (\%)} = \frac{(N_{\text{CH}_4, \text{input}} - N_{\text{CH}_4, \text{output}}) / (N_{\text{CH}_4, \text{input}}) \times 100 \quad (1)$$

$$\text{Conversion of CO}_2 \text{ (\%)} = \frac{(N_{\text{CO}_2, \text{input}} - N_{\text{CO}_2, \text{output}}) / (N_{\text{CO}_2, \text{input}}) \times 100 \quad (2)$$

3. Results and Discussion

3.1. Co-Ru-Zr supported on silica beads

3.1.1. Catalytic activity of Co-Ru-Zr supported on variable silica beads

Co-Ru-Zr/SiO₂ ("CRZ/S" here in after) catalyst is already known to feature excellent catalytic performance and durability [22]. To apply to bigger-scale commercial reactors, we evaluated catalytic performance and durability, using big silica beads

as substrates in the place of small silica beads that were used as substrate. S-1 mentioned in Table 1 is a small silica bead substrates used in preceding reference studies, with specific surface area of approximately 300 m² g⁻¹ and average pore size of about 15 nm. Speaking of the pore characteristics of S-2 and S-3 silica beads which are big beads, both substrates showed relatively bigger specific surface area (700 m² g⁻¹ or bigger), smaller pore volume (0.4 cm³ or less), and pore size (about 2 nm) than S-1. On the other hand, S-4 silica bead which is another big bead shows pore characteristics almost similar to those of the small S-1 substrates. Therefore, it was inferred that given the physical properties, S-1 and S-4 loaded with CRZ catalyst, and S-2 and S-3 would show similar catalytic performance.

Figure 1 illustrates the performance of each bead-type catalyst preparation. CRZ/S-1 catalyst loaded with the same silica bead as previously reported substrates showed 90% CO₂ conversion at 800 °C, 20,000 ml_{feed} g_{catalyst}⁻¹ h⁻¹, in which approximately 84%

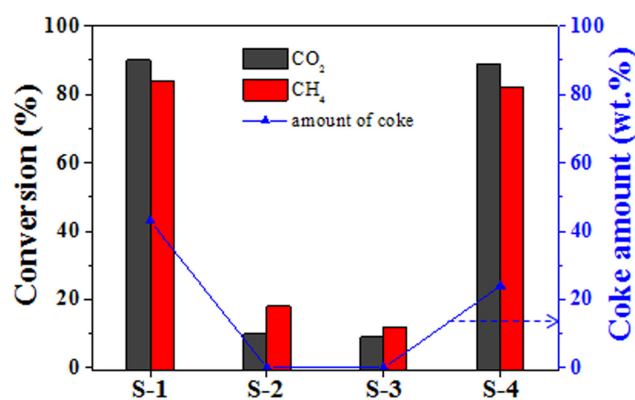


Figure 1. Activity and coke formation over CRZ/S catalysts; (■): conversion of CH₄, (■): conversion of CO₂ and (▲): coke amount. Reaction temperature: 800 °C, Feed composition: 40% CH₄, 40% CO₂, N₂ balance, Total flow: 33 mL min⁻¹ (1 atm), GHSV: 20,000 ml g_{cat}⁻¹ h⁻¹, Prior to activity test, all catalysts were pre-treated at 800 °C in feed stream.

of methane took part in CO₂ conversion. CRZ/S-4 where S-4 associated with similar pore characteristics to those of CRZS-1 was loaded with CRZ also showed similar performance to that of CRZ/S-1, with conversion ratios of 89% for CO₂, and 82% for CH₄. However, CRZ/S-2 and CRZ/S-3, CRZ/S catalysts based on S-2 and S-3 both of which showed significant difference in pore characteristics from S-1 and S-4 showed lower CO₂ conversion than CH₄ conversion as well as considerably lower CO₂ and CH₄ conversion ratios than those of CRZ/S-1 and CRZ/S-4. As illustrated in Table 2, S-3 and S-4 silica beads used as substrates for CRZ/S-3 and CRZ/S-4 showed relative CRZ loading of 4 wt% and 18 wt% respectively, with approximately 4-fold difference in loading. This indicates that catalyst performance has something to do with catalyst loading, but specific impacts of pore characteristics and substrates surface property, etc. on catalyst loading were not addressed in this study.

3.1.2. Stability of Co-Ru-Zr supported on silica with respect to coking

As is the case with other reforming reactions, not only performance but also technology that can alleviate deactivation of catalyst resulting from carbon deposition, etc. in terms of catalyst improvement, change in reaction environment, addition of regenerative mode, etc. are important for CO₂ dry reforming reaction [15]. Although CRZ/S catalyst is known to be effective in preventing carbon deposition [22], As shown in Table 2, CRZ catalytic loading differed per silica bead as well as in activity evaluation which is illustrated in Figure 1. Therefore, difference in carbon deposition can be expected per catalyst and catalyst shape and carbon deposition before and after reaction were studied.

As Figure 2 illustrates, fresh CRZ/S-1 catalyst (a) prior to reaction shows evenly distributed globular shape without being crushed. CRZ/S-2 (b), CRZ/S-3 (c), CRZ/S-4 (d) catalysts using big beads also show even globular shape without being crushed

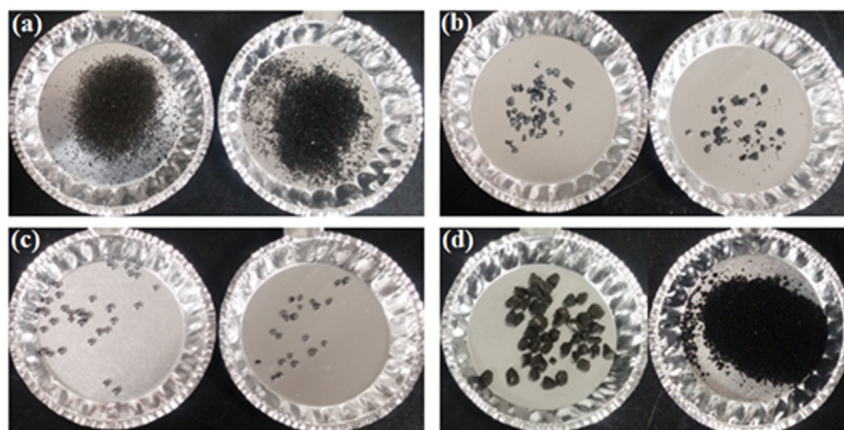


Figure 2. Images of CRZ/S catalysts before and after dry the reaction (a) CRZ/S-1, (b) CRZ/S-2, (c) CRZ/S-3, (d) CRZ/S-4.

irrespective of substrate type when they are fresh. However, considerable amount of fine particles was produced in the CRZ/S-1 (a) recovered after dry reforming reaction. The fine particles believed to have been attributable to damage to substrates or removal of catalyst coating during reaction, and generation of coke in reaction process. In the case of CRZ/S-4 (d) that showed similar characteristics and catalytic performance to those of CRZ/S-1, it was observed that crush in the catalyst was more pronounced than in the case of CRZ/S-1. In particular, it was confirmed that big beads found in the fresh catalyst were not retained at all and turned into almost particle-like form following the reaction. Such catalyst crushing and increase in fine particles including coke, etc. compromised reaction flow and increased inlet pressure of reactor, impacting the equilibrium of dry reforming reaction that is excellent in atmospheric pressure conditions and thus degrading the catalytic performance [24]. Furthermore, if catalyst keeps being crushed and fine particles continue to increase, catalyst reactor will be plugged internally and feed flow blocked, which will require the reaction to be stopped and result in safety risks as well. Therefore, it is believed that CRZ/S-1 and CRZ/S-4 catalysts are compatible with practical reactor systems as long as they do not have to be filled in packed bed form which causes pressure decrease and create pressure differential resulting from catalyst being crushed.

In the cases of CRZ/S-2 (Figure 2(b)) and CRZ/S-3 (Figure 2(c)) catalysts that have lower catalyst loading and poorer performance than CRZ/S-1 and CRZ/S-4 catalysts, the catalyst recovered following reaction showed almost similar shape to that of fresh catalyst. Based on this result, it can be expected that crushed catalyst is related to catalyst performance. The more catalyst is active, the more catalyst is crushed. To identify a cause, we first focused on the products of reaction, as reaction material fed into catalyst bed, temperature and pressure during catalyst evaluation were the same. Gases generated in the reaction include CO, H₂, and H₂O where as solid form is coke deposited in catalyst. Unlike the gaseous products, coke that is produced continuously in reaction is accumulated in the catalyst and the reactor system. Therefore, coke generated in excessive quantity in catalyst particles can cause physical damage to pores and catalyst particles. When the amounts of coke generated in two different catalyst systems were compared, it was known that coke produced during reaction and deposited in catalyst accounted for 43% and 24% of coke mass in CRZ/S-1 and CRZ/S-4-based catalysts respectively. On the other hand, carbon was hardly confirmed in CRZ/S-2 and CRZ/S-3-based catalysts when they were collected following reaction, which is believed to be attributable to low CO₂ and CH₄ conversion in CRZ/S-2 and CRZ/S-3-based catalyst, and reaction selectivity, dispersion form of catalytic substance, and substrate characteristics also seem to

make contribution. However, as the current study is focused on assessing the viability of increasing catalyst size, those factors are not addressed specifically. Performance and characteristic analysis outcomes of the two catalyst systems that showed different characteristics were consolidated to prove that the primary cause of catalyst crushing was carbon deposition and a conclusion was drawn from it that considerations given not only to catalytic substance but also substrate characteristics were important factors of practical reactor design in improving catalyst performance and preventing carbon deposition.

3.2 Co-Ru-Zr monolithic catalysts

3.2.1. Effect of catalyst preparation on catalyst activity

As dry reforming reaction is usually performed in atmospheric pressure and high temperature conditions, it is important to select a catalyst preparation that can prevent pressure from rising during reaction and provide durability at high temperature. The monolith used extensively in automotive emission gas treatment and environmental catalysts can meet the aforementioned requirement. Therefore, CRZ/M-1 catalyst was manufactured using Cordierite substrate which is the representative material of monolithic catalyst. Usual method of coating monolithic substrates with catalyst is to turn fine powder of catalyst into slurry and disperse it in solution for coating [25]. However, it was confirmed that catalyst manufactured by slurry coating under high-temperature CO₂ reforming reaction condition had weak adhesion, resulting in the removal of coating layer during reaction and compromising the catalytic performance (not shown). Therefore, this study used the solution coating method that coated monolith with catalytic precursor mixture solution and dried it to manufacture CRZ(sol)/M-1 and CRZA(sol)/M-1 containing CRZ/M catalyst and binder. Figure 3 illustrates performance evaluation results at $SV = 4,200 \text{ ml}_{\text{feed}} \text{ ml}_{\text{catalyst}}^{-1} \text{ h}^{-1}$ and in the range of 600–900 °C. CRZ/M-1 manufactured without binder showed high CO₂ and CH₄ conversion performance across the entire temperature range used in the evaluation. CO₂ and CH₄ conversion rates at 800 °C declined somewhat when compared with the bead-type catalysts, yet, such conversion rates were still high at 75% and 85% or more respectively. In addition, as noted in the experiment section, GHSV selection criteria are different between bead-type catalysts and monolithic catalysts. Therefore, catalyst content and catalyst bed volume were made the same in bead-type catalysts and monolithic catalysts for performance comparison. CRZ/S-1 based on small silica beads containing the same content of CRZ as monolithic catalyst was taken for reactor and silica beads were added to keep the catalyst content and volume the same in both bead-type and monolithic reactors. Figure 3(a) and inset indicate that at

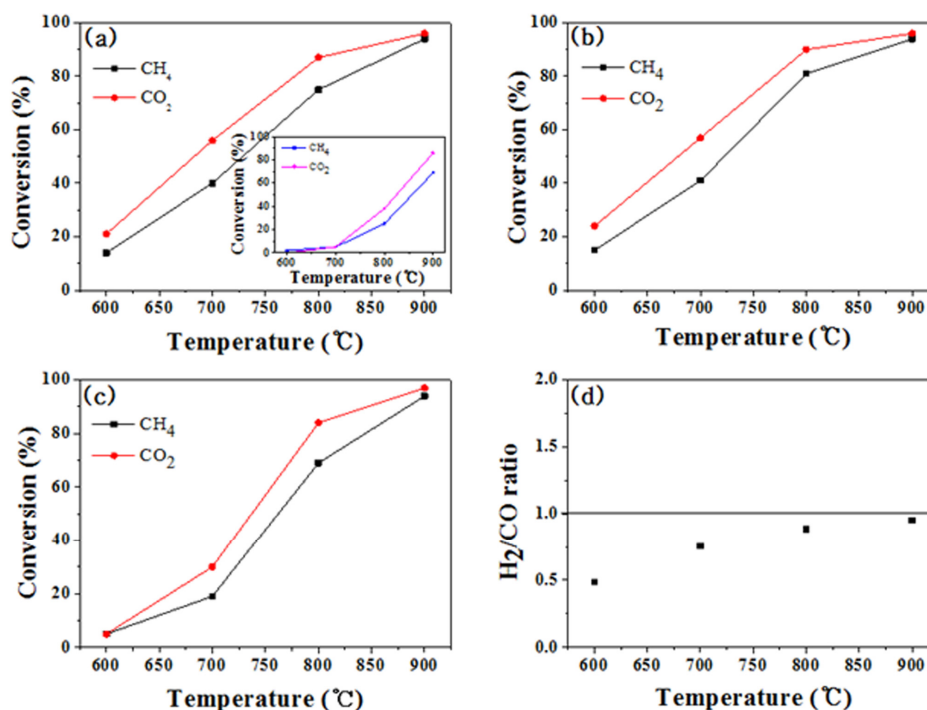


Figure 3. Conversion of CH₄ and CO₂ over monolithic catalysts prepared w/ and w/o binder; (a) CRZ/M-1 (inset:CRZ/S-1w/silica bead), (b) CRZA(sol)/M-1, (c) CRZS(sol)/M-1, (d) H₂/CO ratio of CRZ/M-1. Feed composition: 40% CH₄, 40% CO₂, N₂ balance, Total flow: 110 mL min⁻¹ (1 atm), GHSV:4,200 h⁻¹, Prior to activity test, all catalysts were pre-treated at 900 °C in feed stream.

800 °C, CO₂ conversion rates of CRZ/M-1 and CRZ/S-1 were 83% and 40% respectively, more than double the activity of the same CRZ content. CRZ/M-1 catalyst showed high activity across the entire temperature range. Therefore, it is understood that when spatial velocity is maintained to be the same, catalysts coated with monolithic substrates is more efficient in dry reforming reaction.

CRZA(sol)/M-1 catalyst using alumina sol showed the performance almost the same as that of CRZ/M-1 across the entire range of reaction temperature, which indicates that alumina used in manufacturing the catalyst of this study has no impact on catalyst performance. On the other hand, in the case of CRZS(sol)/M-1 catalyst, CO₂ and CH₄ conversion rate was similar to that of CRZ/M-1 in high temperature range close to thermodynamic equilibrium, but it declined significantly in low temperature area at or under 700 °C, which seems to indicate that the low activity of CRZS(sol)/M-1 catalyst is attributable to the fact that silica reduces activity points exposed on the surface by covering active surface rather than acting as a supporter. Therefore, it was confirmed that CRZ needed to be coated directly in monolithic substrates or with alumina sol mixed to ensure excellent dry reforming performance. However, the CRZ active substance used herein show the same performance as that of CRZA(sol)/M-1 catalyst when it is coated with supporting monolith such as alumina. This indicates that it is possible to manufacture high-quality commercial catalysts

for CO₂ reforming reaction simply by coating monolith with CRZ precursor-mixed solution and thus simplify catalyst manufacturing process at lower cost.

3.2.2. Redox property of bead and monolithic catalysts

H₂-TPR was conducted to compare the characteristics of CRZ/M-1 that showed excellent dry reforming performance with CRZ/S-1 which is a silica bead-based catalyst. As illustrated in Figure 4, CRZ/S catalyst showed two primary reduction peaks at 140 °C and 260 °C in temperature rising process and a shoulder at around 510 °C where small amount of hydrogen was consumed. Hosokawa et al. reported that Ru₂O₃ was reduced to Ru metal in low temperature range around 100 °C, which indicates that hydrogen consumption at 140 °C in Figure 4 is attributable to the reduction of Ru oxide [26]. In addition, Bouarab et al. reported that speaking of Cobalt oxide in Co/SiO₂ catalyst, Co₃O₄ was reduced to CoO, and CoO to metallic cobalt between 280 °C and 500 °C [27]. Therefore, it is expected that high temperature peak at around 260 °C or more is attributable to the reduction of Co oxide. On the other hand, CRZ/M showed an asymmetric peak at 210 °C and a pronounced reduction peak in high temperature range unlike CRZ/S. The low temperature peak is believed to be attributable to the reduction of Co and Ru to bimetallic oxide, and the high temperature peak to the reduction of active substance interacting with ZrO₂. Similarly, Kogelbauer et al. reported change in redox

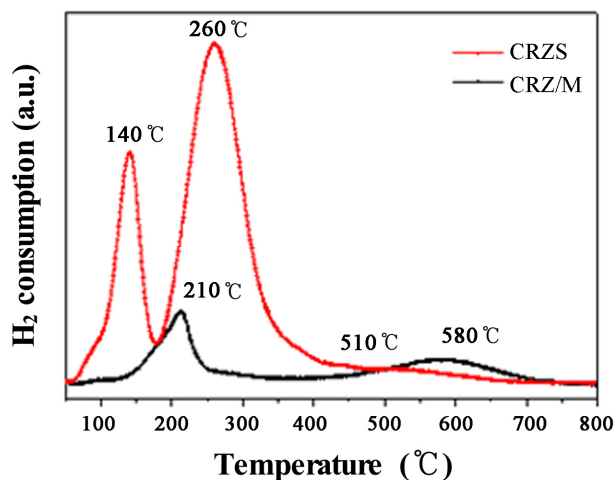


Figure 4. TPR profiles over CRZ/S-1 and CRZ/M-1 catalysts. Pre-treatment: at 400 °C in 5% O₂/Ar for 2 h, Reduction: 10 °C min⁻¹ in 5% H₂/Ar.

Table 3. TPR result of CRZ/S-1 and CRZ/M-1 catalysts

| Catalyst | H ₂ consumption, ccH ₂ /g _{sample} (ccH ₂ /g _{metal}) | | | | | Total |
|----------|---|---------|----------|--------|---------|----------|
| | 140 °C | 210 °C | 260 °C | 510 °C | 580 °C | |
| CRZS | 11(55) | | 34 (172) | 2 (8) | | 47 (235) |
| CRZ/M | - | 6 (353) | | | 5 (312) | 11 (665) |

property resulting from the addition of precious metal Ru to Co/Al₂O₃ catalyst [28]. These TPR results showed that the

redox properties of the two catalysts were different and indicated that their active sites could be different. In particular, Table 3 shows that CRZ/M-1 having low specific loading of catalytic substance has lower H₂ uptake per catalyst weight in comparison with CRZ/S-1, but it consumes about three times more hydrogen per unit mass of active substance than CRZ/S-1. This shows that monolith surface is more advantageous than silica surface in dispersing effective active substance that can participate in reaction and improving redox behavior, and Figure 3(a) and in set effectively confirm difference in performance. However, more specific studies should follow to address the active site of CRZ in specific monoliths. Although CRZ/S-1 and CRZ/M-1 show different redox properties, CRZ/M-1 catalyst also shows excellent dry reforming performance, which necessitated more specific study of CRZ/M-1.

3.2.3. Effect of substrate characteristic on catalyst activity

To evaluate the performance of CRZ monolithic catalyst per monolithic substrates material, Silicon Carbide (SiC) and Rota monolith, widely used in commercial applications, were added and catalysts were manufactured in the same manner as CRZ/M-1. Heat conductivity of SiC monolith is 40 ~ 300 W m⁻¹ k⁻¹, up to 150 times higher than 1.0 ~ 2.0 W m⁻¹ k⁻¹ of Cordierite, with excellent thermal durability. Specific area of Rota monolith is 37 m² g⁻¹, about 40 times higher than 1 > m² g⁻¹ of Cordierite with fabric wall constitution. Performance evaluation results in

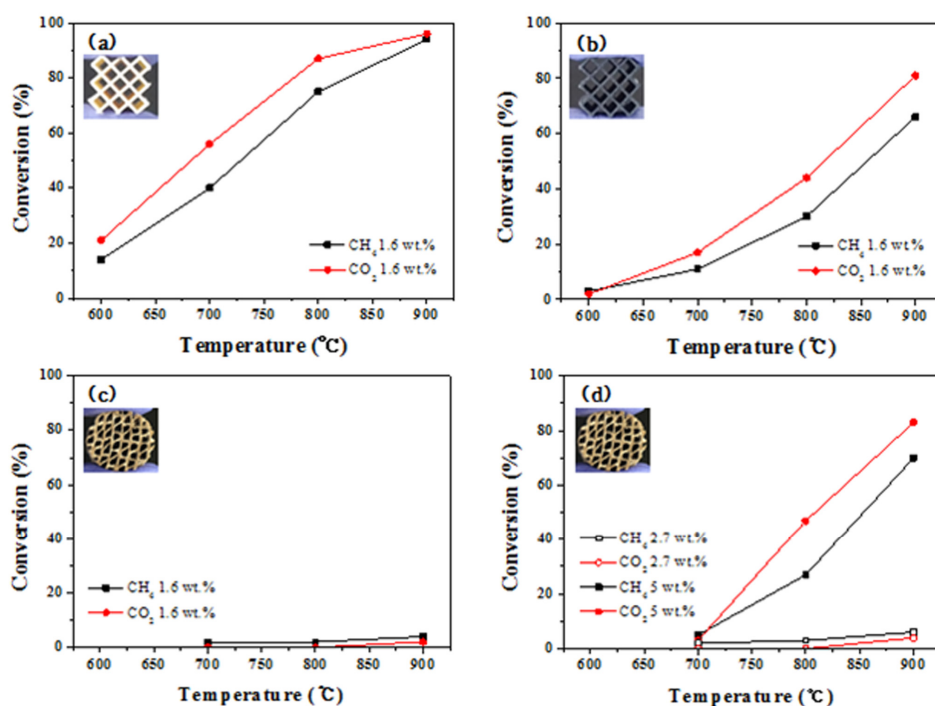


Figure 5. Conversion of CH₄ and CO₂ over monolithic catalysts prepared with three types of monolithic substrates; (a) 1.6 wt% CRZ/M-1, (b) 1.6 wt% CRZ/M-2, (c) 1.6 wt% CRZ/M-3, (d) 2.7~5 wt% CRZ/M-Rota. Feed composition: 40% CH₄, 40% CO₂, N₂ balance, Total flow: 110 mL min⁻¹ (1 atm), GHSV: 4,200 h⁻¹. Prior to activity test, all catalysts were pre-treated at 900 °C in feed stream.

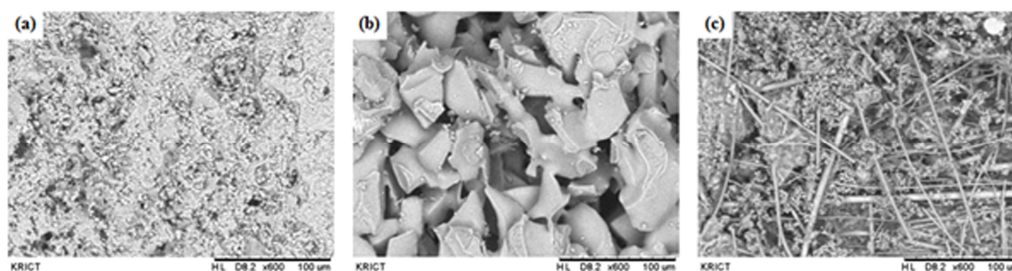


Figure 6. SEM images of three types of monolith substrates w/o catalyst components; (a) M-1, (b) M-2, (c) M-3.

Figure 5 show that catalysts using Cordierite as substrates showed the highest CO₂ and CH₄ conversion rates across the entire reaction temperature range. It was observed that SiC-based catalyst loaded with the same catalytic content, CO₂ conversion rate at 700 °C was 40% lower than that of Cordierite catalyst, and its performance at 900 °C was about 80%. This suggests that CRZ is more active in Cordierite monolith, and heat transfer has minor impact on performance under the given evaluation conditions. On the other hand, Rota monolith loaded with 1.6 wt% of CRZ did not show conversion performance across the entire reaction temperature range unlike Cordierite and SiC-based monolithic catalysts. This is believed to arise from the fact that the Rota substrates consisted of fiber allowed catalytic substance of the same content to penetrate into monolithic channel wall during wash-coating and thus reduce the exposed catalyst surface where reaction materials could react. As a matter of fact, Table 1 and Figure 6 show that when compared with Cordierite and SiC substrates, Rota substrates has drastically wider specific area and substrates surface exists in fiber form as observed in SEM. Therefore, the catalytic performance was confirmed by coating Rota substrates with excessive catalyst and Figure 5(d) showed catalytic performance appeared when CRZ content was 2.7 wt% or more. In the case of 5 wt% CRZ/M-3 where the content of catalyst was three times higher than other catalysts, CO₂ and CH₄ conversion rate became si-

milar to that of 1.6 wt% CRZ/M-2 in 800–900 °C, but low temperature performance at 700 °C or below was hardly confirmed. Therefore, it is concluded that Cordierite, loaded with the same content of catalyst, serves as the most excellent substrates for dry reforming reaction.

3.2.4. Optimization of monolithic catalyst system

Monolithic catalyst using Cordierite substrates shows excellent reforming performance and, in effect, Cordierite monolith products find extensive applications in environmental catalyst products including automotive catalysts. Therefore, more specific study was conducted to optimize Cordierite-based catalyst and evaluate its durability. In the above sections addressing performance evaluation of big beads, it was confirmed that dry reforming reaction performance and carbon deposition varied as catalyst loading increased. This suggests that even in monolithic catalysts, catalytic substance loading has close bearing on performance and carbon deposition. Therefore, in this study, we loaded ceramic monolithic substrates with CRZ catalyst of varying content to investigate CO₂ reforming reaction performance and carbon deposition behavior. CRZ loading was confirmed in ICP results and illustrated in Table 2.

To evaluate the performance of catalyst manufactured, spatial speed was fixed at 4,200 ml_{feed} ml_{catalyst}⁻¹ h⁻¹, evaluation criteria used for small reactor, and CO₂ and CH₄ conversion rate was con-

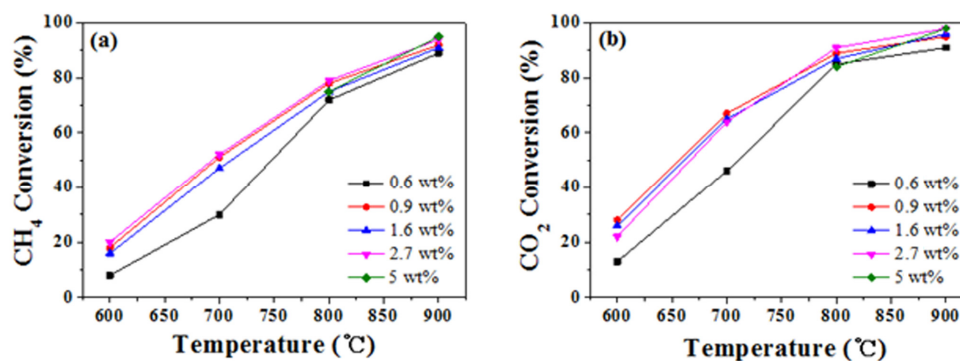


Figure 7. Conversion of CH₄ and CO₂ as a function of reaction temperature over 0.6–5 wt% CRZ/M-1; (a) CH₄ conversion, (b) CO₂ conversion. Feed composition: 40% CH₄, 40% CO₂, N₂ balance, Total flow: 110 mL min⁻¹ (1 atm), GHSV: 4,200 h⁻¹, Prior to activity test, all catalysts were pre-treated at 900 °C in feed stream.

firmed, with varying reaction temperature. As Figure 7 illustrates, catalysts coated with 0.9 wt% or more of CRZ show similar catalytic activity, irrespective of catalyst coating amount. On the other hand, in the case of 0.6 wt% CRZ/M-1 where CRZ content was low, CO₂ and CH₄ conversion rate decreased at 700 or below. This is believed to be attributable simply to the difference in exposed catalyst area that participate in catalytic reaction. What was noted in the performance evaluation was that at catalyst content of 1.6 wt% or below, performance evaluation progressed smoothly across the entire temperature range whereas in the case of catalysts having high content of CRZ, pressure inside the reactor increased in low temperature range of 800 °C or under, blocking the flow of reaction gas. Therefore, catalyst shape before and after reaction was observed.

As Figure 8 illustrates, it was confirmed that the more CRZ content increased, the larger the dark area of carbon deposition became on the monolithic catalyst surface following reaction. In particular, catalyst crush for massive carbon deposition started from the catalyst loaded with 2.7 wt% CRZ, and the layer of carbon particle deposition appeared in the catalyst bed inside the reactor. Among the catalysts subject to evaluation, in the case of 5 wt% CRZ/M-1 catalyst where CRZ content was the highest, the catalyst was completely crushed following reaction without the monolithic shape not retained, and the layer of carbon particle inside the reactor was found to have grown noticeably when visually inspected. This is the same phenomenon as the crushing of big bead catalyst illustrated in Figure 3, which suggests that carbon deposition reduces the mechanical strength of catalytic substrates and increase in carbon deposition has close bearing on the amount of active substance. According to the reports published to date, carbon deposition

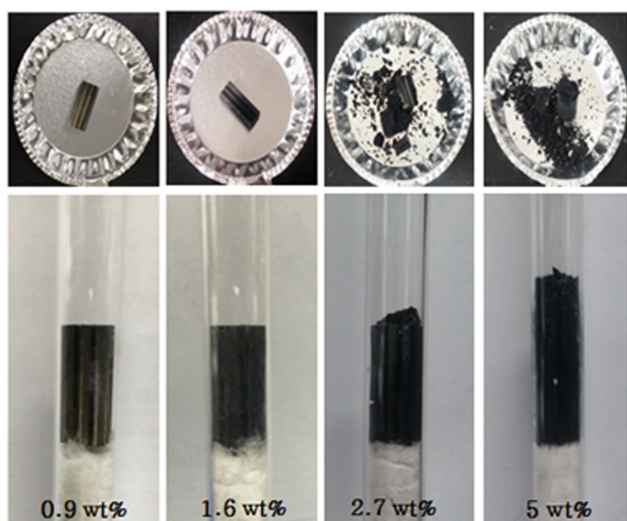


Figure 8. Image of the CRZ/M-1 catalysts with different CRZ contents after the reaction.

increases as the crystal size of active substance increases [20, 29,30]. When active catalytic substance is loaded onto a surface where there is hardly any pore as in the case of monolith, the degree of dispersion of active substance decreases and the size of particle is increased as loading is increased. On the other hand, when the loading of catalyst decreases, the number of exposed catalysts that can participate in reaction decreases. In addition, catalysts loaded with CRZ of 0.9 wt% or more show similar CH₄ and CO₂ conversions, which may indicate that gaseous reaction material or product has just a little impact on the crushing of catalyst. Hence, it can be concluded from the findings of this study that the content of CRZ catalyst that can maintain in performance and prevent carbon deposition at the same time is about 0.9 wt%, which suggests that only one-twentieth of CRZ can ensure high dry reforming performance and durability in comparison with CRZ/S bead-type catalyst.

For catalytic application, not only the performance of developed catalyst but also its long-term durability should be verified. Accordingly, 0.9 wt% CRZ/M-1 catalyst that is the optimum catalyst developed in this study was put into reaction at spatial speed of $4,200 \text{ ml}_{\text{feed}} \text{ ml}_{\text{catalyst}}^{-1} \text{ h}^{-1}$, 900 °C and the reaction gas used the same CH₄:CO₂:N₂=40:40:20 mol ratio as in the previous study. After a reaction for 300 h, CO₂ conversion rate was 96% and CH₄ conversion rate 92% as illustrated in Figure 9, which proved that the reactor operated without significant decrease in activity during the life cycle evaluation period. It was confirmed in post-reaction in set images that the catalyst retained its initial shape without being crushed and carbon deposition was also minimal. Therefore, it was concluded that in dry reforming reaction using monolithic reactor, catalyst

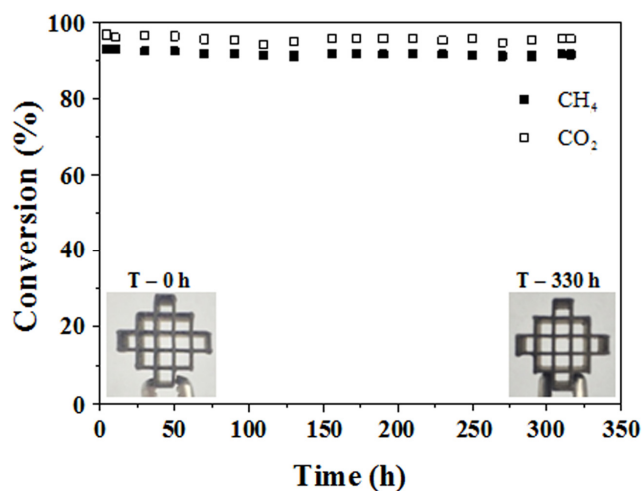


Figure 9. Conversion of CH₄ and CO₂ at 900 °C on stream over 0.9 wt% CRZ/M-1; Feed composition: 40% CH₄, 40% CO₂, N₂ balance, Total flow: 110 mL min⁻¹ (1 atm), GHSV: 4,200 h⁻¹, Prior to activity test, all catalysts were pre-treated at 900 °C in feed stream.

loading and content control were important for actual reaction operation performance and prevention of carbon deposition.

4. Conclusion

This study attempted to verify the viability of monolithic catalyst for demonstration process of CO₂ (dry) reforming reaction using CO₂ and CH₄ as raw materials. Cobalt-based (Co-Ru-Zr/SiO₂, CRZ/S) bead-type catalyst consisting of Cobalt (Co), Ruthenium (Ru), and Zirconium (Zr) known as excellent performance and durability in CO₂ reforming reaction was compared with monolithic catalyst in similar environmental set up. In the case of CRZ/S-1 bead-type catalyst previously reported, big beads were used in making the catalyst to increase its size and it was found that catalytic performance varied per pore characteristics of bead substrates and the catalyst was crushed following reaction, posing issues for application to demonstration process. In particular, it was believed that the catalyst was crushed because the silica bead structure was destroyed by coke generated during reaction. As these catalyst crushing and carbon deposition disrupt reaction gas flow, causing pressure differential issue and changing the equilibrium of dry reforming reaction that depends on pressure, we conducted a study on substrates that had excellent mechanical strength and high resistance to degradation and carbon deposition. Monolithic substrates, widely used in environmental catalysts such as automotive catalyst with more freedom from pressure differential issue, was loaded with CRZ to manufacture CRZ/M-1 catalyst and dry reforming catalyst activity was confirmed. It was confirmed that Cordierite-based monolithic catalyst featured excellent performance and the catalyst could be manufactured simply by coating it with active metal precursor directly. In addition, it was confirmed that when the catalyst coating was set to about 0.9 wt%, excellent performance was retained and carbon deposition during reaction was drastically reduced at the same time. Also in the long-term catalyst service life evaluation at 900 °C, 0.9 wt% CRZ/M catalyst maintained 90% CO₂ conversion rate for 300 h and carbon deposition during reaction was also minimal.

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