

Ru/CeO₂ 촉매를 이용한 메탄 건식 개질

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Methane Dry Reforming over Ru/CeO₂ catalysts

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Abstract >> Ru catalysts supported on CeO₂ were synthesized by an impregnation method and characterized by numerous analytical techniques including X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), transmission electron microscopy (TEM), and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS). Upon utilization of these catalysts for methane dry reforming with a CH₄/CO₂ ratio of 1:1 at different temperatures ranging from 550 to 750°C, the Ru/CeO₂ catalysts have shown to be active. In particular, Ru(0.55wt%) supported on CeO₂ (1) prepared by a hydrothermal method exhibited excellent activity with the conversion of > 75% at 750°C. In addition, the catalyst also proved to be highly stable for at least 47 h without catalyst deactivation under the dry reforming conditions.

Key words : Ruthenium(루테튬), CeO₂(세리아), Methane dry reforming(메탄 건식 개질), Biogas reforming(바이오 가스 개질), catalysis(촉매반응)

1. Introduction

To mitigate the current energy and environmental concerns, there have been increasing efforts to employ carbon dioxide as a building block for the potential preparation of C1 fuels. Biogas has methane and carbon dioxide as the main constituents, and methane dry reforming or biogas reforming (CH₄ + CO₂ → 2CO + 2H₂) can thus provide a viable route for a renewable and

low-cost source of hydrogen as well as valuable fuels via chemical transformation of carbon dioxide¹⁻³. Despite the potential applicability, the development of highly stable catalysts is still one of the main challenges for the commercialization of methane dry reforming.

Ni-based catalysts have generally been employed to catalyze methane reforming reaction using H₂O or CO₂ as oxidants^{4,5}. However, Ni-based catalysts are susceptible to deactivation via considerable carbon coking and/or sintering during the reactions^{6,7}. One of the strategies to suppress the deactivation process is the utilization of noble metal and/or use of supports that have high

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resistance against carbon deposition. In the first instance, noble metals have shown to be highly resistant to carbon coking^{8,9}. Secondly, the type of support is also critical for minimizing deactivation processes¹⁰. Alumina, Al₂O₃, has been employed as a support for reforming reactions, and strong mechanical and acidic properties of Al₂O₃ can help facilitate desired reactions¹¹. Despite their co-catalytic abilities, the catalysts supported onto alumina can readily be deactivated by coke formation¹². In contrast, CeO₂ has been found to suppress carbon coking with enhanced catalytic activity possibly because its oxygen storage capacity can promote conversion of carbon deposited at the catalyst surface into gas products (e.g., CO₂) through the dual-function mechanism¹³.

In this paper, we report Ru catalysts supported on CeO₂ for methane dry reforming reaction. The as-synthesized catalysts were characterized using a number of analytical techniques. Our preliminary studies with Ru/CeO₂ catalysts proved to catalyze the desired reactions with high stability.

2. Results and Discussion

Two types of ceria supports, CeO₂ (1) and CeO₂ (2) were employed in this study. CeO₂ (1) was synthesized by a conventional method while CeO₂ (2) was prepared using MCM-48 as a template, producing mesoporous ceria. TEM images of the as-prepared CeO₂ are shown in Fig. 1(a), 1(b). Compared to CeO₂ (1), CeO₂ (2) obtained with the MCM-48 template exhibits well packed nanoarrays with ca. 4-5 nm. Upon preparation of CeO₂ with the template, polymeric hydrous oxide likely reacted first with the MCM-48 and then precipitates, which could produce mesoporous CeO₂ (2) with an increased surface area. Consistent with the hypothesis, CeO₂ (2) showed a higher surface area of 196 m²·g⁻¹ than CeO₂ (1) (Table 1).

Since CeO₂ has high thermal stability and the ability to store and release oxygen, the as-synthesized CeO₂ supports could play an important role in enhancing catalyst durability (vide infra).

Ruthenium metals were then loaded onto the CeO₂ supports using an impregnation method. SEM analysis showed that the Ru contents were in the ranges of 0.55 – 3.9 wt%. TEM analysis further indicated that metal deposition did not perturb the CeO₂ structure, and in the case of CeO₂ (2), porous network with channels was not affected in the course of metal loading. XRD analysis showed the diffraction peaks at 2θ of 28.7°, 33.1°, 47.6°, and 56.4°, which corresponds to the (111), (200), (220), and (331) planes of CeO₂, respectively. The XRD patterns of Ru/CeO₂ (1) and Ru/CeO₂ (2) are essentially identical (Fig. 2).

The presence of active oxygen species in a support is

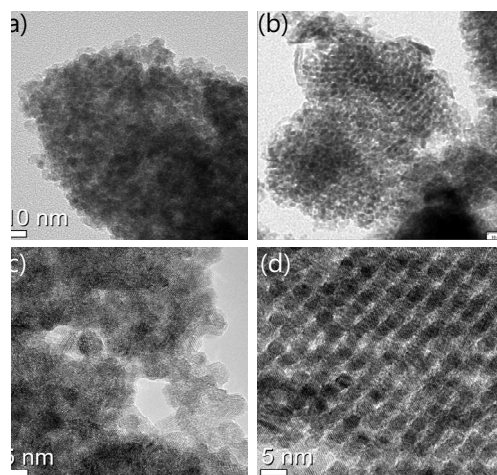


Fig. 1 TEM images: (a) CeO₂ (1), (b) CeO₂ (2), (c) Ru/CeO₂ (1) and (d) Ru/CeO₂ (2)

Table 1 BET surface area, pore volume, and pore diameter of the CeO₂ supports

Support	BET (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
CeO ₂ (1)	131	0.29	3.7
CeO ₂ (2)	196	0.24	4.9

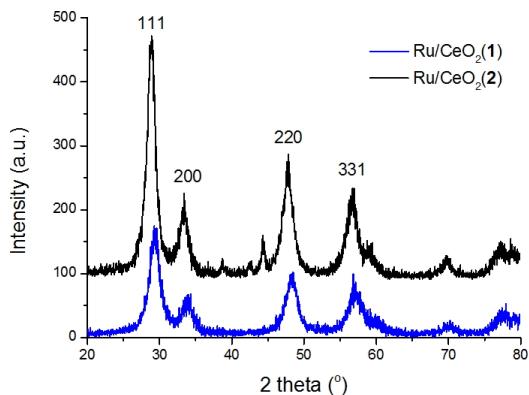


Fig. 2 XRD profile with the prepared Ru/CeO₂ catalysts

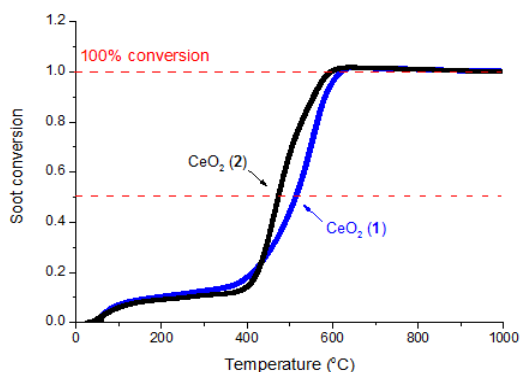


Fig. 3 Soot oxidation in the present of the CeO₂ (1) and CeO₂ (2)

known to play a pivotal role in preventing carbon deposition¹⁴. We further conducted soot oxidation to assess the relative oxygen conductivity (or oxygen storage capacity, OSC) in the CeO₂ supports. In the experiment, a support with a higher OSC would give a lower light-off temperatures ($T_{1/2}$) of supports, defined as temperatures at 50% conversion of soot¹⁵; i.e., the active oxygen ions in a support with higher OSC react with soot to produce CO₂ at an decreased temperature. CeO₂ (2) displayed a slightly lower $T_{1/2}$ of 473 °C than CeO₂ (1) (Fig. 3), indicating increased OSC of CeO₂ (2).

To determine catalytic performance of the prepared catalysts, methane dry reforming was carried out using the GHSV of 30,000 h⁻¹ by varying temperature (Fig.

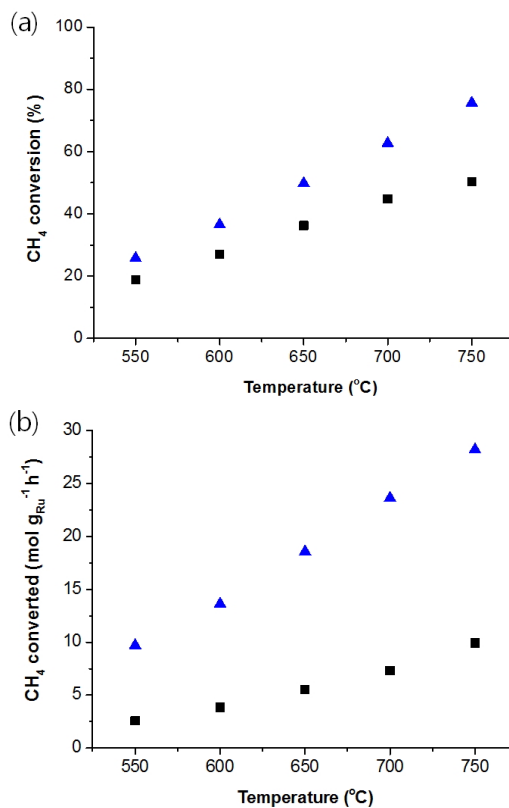


Fig. 4 CH₄ conversions (a) and amounts of reacted CH₄ normalized by Ru loadings (b) following methane dry reforming over the catalysts using the CH₄:CO₂:N₂ ratio of 1:1:2 and the GHSV of 30,000 h⁻¹: (▲) Ru/CeO₂ (1) and (■) Ru/CeO₂ (2)

4(a)). Note that the Ru contents in the catalysts are different even with an attempt to introduce the same quantities of Ru: For Ru/CeO₂ (1), 0.55 wt% Ru; for Ru/CeO₂ (2), 1.0 wt% Ru. Ru/CeO₂ (1) exhibited better activity for methane dry reforming although Ru/CeO₂ (2) has the higher Ru content. For instance, the methane conversion of Ru/CeO₂ (1) was found to be ca. 76% while that of Ru/CeO₂ (2) was calculated to be 50% at 750°C. The quantities of reacted methane were further normalized by the Ru contents of the catalysts, and the difference in reforming activity between Ru/CeO₂ (1) and Ru/CeO₂ (2) became bigger (Fig. 4(b)).

Based on the temperature-dependent rate data with

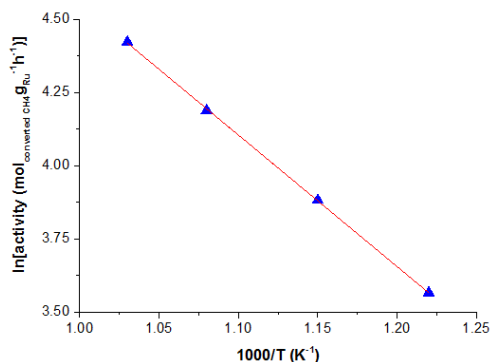


Fig. 5 An Arrhenius plot using the temperature dependent kinetic data with Ru/CeO₂ (1)

Ru/CeO₂ (1), an Arrhenius plot gave an activation energy of 37 kJ/mol. This energy is lower than those obtained by Ru based catalysts¹⁶⁾ (Fig. 5).

To determine the durability of the as-synthesized Ru/CeO₂ catalysts, the CO₂ reforming reactions of methane were performed for > 45 h with a CH₄/CO₂ ratio of 1 at 750°C (Fig. 6). Ru (0.55 wt%)/CeO₂ (1) displayed high stability for 47 h without apparent deactivation. In contrast, the activity of Ru (1.0 wt%)/CeO₂ (2) decreased with time. The origin of the observed instability for Ru (1.0 wt%)/CeO₂ (2) is now under investigation.

3. Experimental

3.1 Preparation of CeO₂ and Ru/CeO₂

For CeO₂ (1) without a template, sodium hydroxide solution (NaOH, 1M) dissolved in 275 g of deionized water was stirred at room temperature for 30 min in a Teflon autoclave reactor. Cerium(III) nitrate hexahydrate compound (Ce(NO₃)₃·6H₂O, 1.7g) was then added to the aqueous solution. The resulting mixture was stirred at room temperature for 1 h, followed by maintaining its temperature to 75°C for 24 h. The produced solids were initially centrifuged, followed by repeated washing with

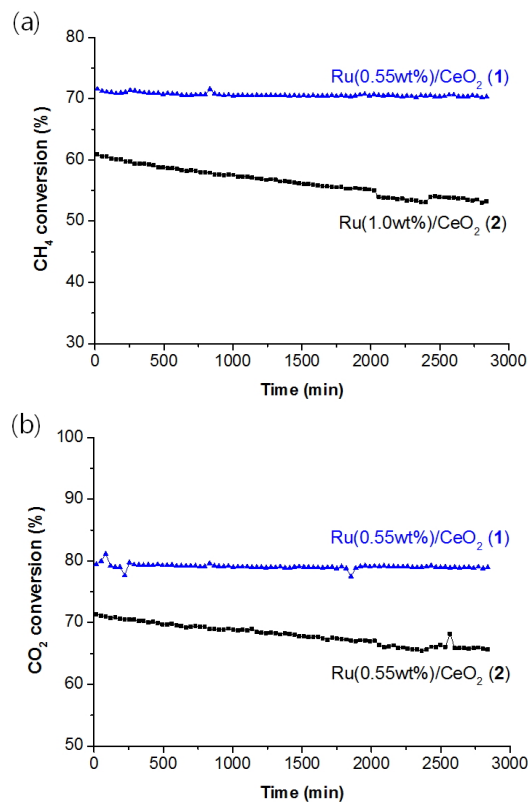


Fig. 6 Long-term stability tests: (a) CH₄ conversions and (b) CO₂ conversions as a function of time

deionized water. The obtained CeO₂ solids were dried overnight in an oven pre-heated at 60°C.

To prepare CeO₂ (2), we initially synthesized MCM-48 according to a previously reported procedure¹⁷⁾. Next, Ce(NO₃)₃·6H₂O (2.1 g) was dispersed into D.I. water (6.0 mL). The as-prepared MCM-48 material (1.0 g) was added into the aqueous solution, followed by stirring at room temperature for 30 min and standing overnight. Then, water was removed from the resulting mixture at 100°C for 8 h, followed by calcination at 550°C for 4 h with a heating rate of 2.5 K/min. To remove the silica template, the as-prepared CeO₂/MCM-48 (1g) was treated with 2 M NaOH solution at 80°C. After stirring overnight, the solids were centrifuged out and the recovered CeO₂ materials were washed several times with 500 mL D.I.

water, producing CeO₂ (2).

To introduce Ru metals onto the as-synthesized CeO₂ materials, an impregnation method was employed. In a typical experiment, the mixture of RuCl₃·6H₂O and either CeO₂ (1) or CeO₂ (2) were dispersed in D.I. water, followed by stirring for 3 h. Then, ammonium hydroxide was added into the mixture dropwise until the pH of the solution reached to 10. The obtained, transparent solution was filtered after additional stirring for 2 h, followed by calcination at 550°C for 4 h.

3.2 Characterization of CeO₂ and Ru/CeO₂

Powder XRD data were collected by a Rigaku X-ray diffractometer, using CuKα radiation at 40 kV and 20 mA. BET surface areas of the as-synthesized Ru catalysts were determined by a micromeritics Quantachrome instrument. Analysis with high resolution TEM (HR-TEM) was performed using a FEI TECNAI field emission electron microscope at the electron beam energy of 300 kV. Ru contents were analyzed by SEM-EDS at the Korea Institute of Science and Technology.

3.3 Methane dry reforming over Ru/CeO₂

Dry reforming of methane was carried out using a fixed-bed flow reactor under atmospheric pressure (Fig. 7). In a typical experiment, a desired amount of catalyst (0.2 g) was loaded in a quartz tubular reactor. Gases with the CH₄:CO₂:N₂ ratio of 1:1:2 were supplied into the reactor using mass flow controllers. Prior to the desired reaction, a catalyst was first reduced using H₂/N₂ at 500°C for 1 h. Then, reactions were conducted at the temperature range between 550°C and 750°C. The effluent gases were analyzed by gas chromatography using a thermal conductivity detector.

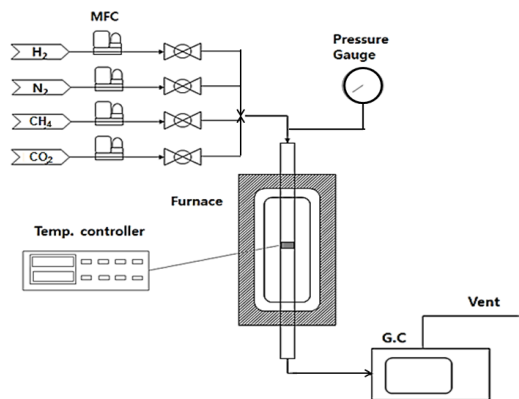


Fig. 7 A schematic diagram for methane dry reforming

4. Conclusions

In summary, Ru catalysts supported on CeO₂ were prepared by an impregnation method. The as-synthesized Ru/CeO₂ (1) catalyst was active for methane dry reforming with high stability without catalyst deterioration. Although Ru catalyst supported on CeO₂ (2) prepared using MCM-48 proved to have slightly higher OSC and surface area than Ru/CeO₂ (1), Ru/CeO₂ (2) showed a decreased stability, which could come from structural instability for mesoporous CeO₂ at high temperature; i.e., the enhanced OSC of CeO₂ (2) may induce pore collapse upon dry reforming at high temperature. To understand the observed instability of CeO₂ (2), however, it is necessary to conduct additional experiments. Nonetheless, the results obtained here provide an useful insight into developing CeO₂ containing catalysts to achieve high durability.

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