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Low-temperature CO₂ methanation over Ru nanoparticles supported on Monoclinic Zirconia

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Abstract

CO₂ methanation is a critical reaction for achieving carbon neutrality. Low-temperature operation (below 250 °C) is important to promote selective CH₄ production. In this study, we focused on Ru/m-ZrO₂ catalysts, examining how the catalyst preparation method influenced CO₂ methanation. Interestingly, Ru/m-ZrO₂ catalysts prepared via a selective deposition method exhibited remarkably high activity, achieving a CO₂ conversion of 82% and CH₄ selectivity of >99% at 250 °C. This exceptional low-temperature performance can be attributed to the robust interaction between Ru and ZrO₂, which enhanced the activation of CO₂. The catalytic performance remained unchanged for 70 h.

Keywords:

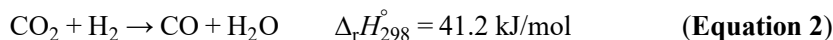
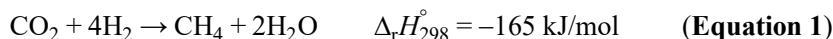
CO₂ methanation; Zirconia; Ruthenium; Preparation method; Stability

1. Introduction

Carbon neutrality can be achieved through “carbon recycling,” which involves capturing and utilizing CO₂ as a raw material for various products, including chemicals and fuels. CO₂ methanation produces CH₄, the primary component of natural gas, by the combination of CO₂ and H₂. Although CH₄ combustion generates CO₂, net-zero carbon emission can be attained via carbon recycling by capturing and repurposing CO₂ as a feedstock for methanation. The production of H₂, another feedstock for methanation, through water electrolysis using electricity from renewable sources is one approach to

storing the surplus electricity generated by renewable energy sources. Another benefit of this approach is that existing gas infrastructure and facilities can be used even if synthetic CH₄ eventually replaces natural gas.

In 1902, Paul Sabatier and Jean-Baptiste Senderens achieved a pioneering breakthrough by employing a nickel catalyst to methanate CO₂, commonly known as the Sabatier reaction. This exothermic reaction (**Equation 1**) proceeds with a reasonable rate at temperatures above 200 °C and is driven to the product side under low-temperature and high-pressure conditions owing to Le Chatelier's principle. However, below 250 °C, CO₂ is insufficiently activated, thereby decreasing the CH₄ yield. CO is generated as a by-product at high temperatures owing to the endothermic reverse shift reaction (**Equation 2**). Thus, developing a catalyst that can activate CO₂ at low temperatures is essential for enhancing the CH₄ production efficiency.



Ni-based catalysts specific to CO₂ methanation, with Al₂O₃, TiO₂, SiO₂, ZrO₂, and CeO₂ as the support, have been extensively studied.^{1,2} Ni/ZrO₂ efficiently promotes CO₂ methanation.³⁻⁵ Habazaki and Hashimoto developed Ni/Y-doped ZrO₂ catalysts possessing many oxygen vacancies around Y³⁺.⁶ Despite the very high methane production rate obtained with the catalyst, the operating temperature is as high as 400 °C, with a maximal CO₂ conversion of 80% owing to the equilibrium limitation. Since 2012, we have been studying Ni/CeO₂ catalysts, motivated by their higher activity in CO₂ methanation than that of Ni/α-Al₂O₃, Ni/TiO₂, and Ni/MgO.⁷ The oxygen vacancies formed on the CeO₂ support are the key to activating CO₂.^{8,9} Fan and Yao's group prepared Ni/CeO₂ catalysts via the sol-gel method.¹⁰ The developed catalyst achieved an impressive CO₂ conversion rate of 80.5% and a CH₄ selectivity of 95.8%, even under demanding conditions, such as a high space velocity of 40,000 mL g⁻¹ h⁻¹ and a reaction temperature of 250 °C. Fujiwara *et al.* prepared an 80 wt% NiO/CeO₂ catalyst precursor through flame spray pyrolysis.¹¹ Hydrogen reduction of this catalyst precursor resulted in a structural transformation, wherein CeO₂ particles with a size of several nanometers encapsulated Ni particles with a size of *ca.* 10–20 nm. Furthermore, this catalyst afforded high CO₂ conversion (47% at 250 °C). Zhang, Ning, and colleagues recently reported Ni/CeO₂-nanorods that enabled high CO₂ conversion (84.2%) at 225 °C.¹² Although Ni-based catalysts are highly effective for CO₂ methanation, the activity of Ni-based catalysts is still limited at temperatures below 250 °C. We expected that metallic Ni nanoparticles are easily oxidized by CO₂ and H₂O generated below 250°C, leading to the formation of partially oxidized Ni species that are inactive for CO₂ methanation. This partial oxidation

degrades the catalytic performance of the Ni-based catalysts, making them unsuitable as low-temperature CO₂ methanation catalysts.

Ru is one of the most active species that can be used for methanation.¹³⁻¹⁵ Nørskov *et al.*¹⁶ revealed that Ru induces moderate CO dissociation with relatively low adsorption energy, contributing to its higher activity compared to that of other metals in groups 8-10. The support choice is crucial for Ru-based catalysts: CeO₂,¹⁷⁻²³ Al₂O₃,²⁴ TiO₂,²⁵⁻²⁷ ZrO₂,^{28,29} and metal-organic frameworks³⁰ have been used as supports. For example, Dreyer, Zhang, and coworkers¹⁹ reported that Ru/CeO₂ exhibited better CO₂ methanation ability than Ru/Al₂O₃, Ru/MnO_x, and Ru/ZnO. The favorable interaction between CeO₂ and Ru was thought to lead to establishing an optimal electronic state for Ru. This interaction weakens the C=O bond of the adsorbed CO species, while providing a site for dissociative H₂ adsorption. Ru/CeO₂²³ and Ru/TiO₂²⁷ are recognized as catalysts with notably high activity, especially in the low-temperature regime below 250 °C (CO₂ conversion = ca. 40% at 200 °C, H₂/CO₂ in the reactant gas = 4/1).

We previously reported that Ru nanoparticles supported on amorphous ZrO₂ (Ru/am-ZrO₂) induced CO₂ methanation with a conversion of 73% at 250 °C.²⁹ The selective deposition method proposed by Muramatsu *et al.*³¹ was utilized to form Ru particles. Ru nanoparticles were precipitated on am-ZrO₂ by aging Ru nitrate solution in a basic solution (NaOH or NH₃) containing suspended am-ZrO₂. When NaOH solution was used to adjust the pH, some Na residue was also deposited on the catalyst surface. The residual Na species on Ru/am-ZrO₂ enhanced the CO₂ methanation performance, in line with the recent report of Ru/t-ZrO₂ (t-: tetragonal) by Zheng *et al.*²⁸ The Na species plausibly facilitated the hydrogenation of formate,²⁹ which is an intermediate in CO₂ methanation.³² The selection of am-ZrO₂ in our previous research was solely motivated by the possibility that its peculiar CO₂ activation ability in CO₂-to-methanol hydrogenation³³⁻³⁶ could be extended to CO₂ methanation. In this study, we evaluated the performance of catalysts using crystallized ZrO₂ as a support. Through combined experimental and computational approaches,³⁷ it is shown that CO₂ molecules are more strongly adsorbed on crystalline ZrO₂ than on am-ZrO₂; in other words, crystalline ZrO₂ may efficiently activate CO₂ molecules. Herein, several types of Ru/m-ZrO₂ (m-: monoclinic) were prepared via incipient wetness impregnation and selective deposition methods, and the influence of the preparation methods on CO₂ methanation over Ru/m-ZrO₂ was investigated.

2. Experimental

2.1 Chemicals

Three types of m-ZrO₂ (PCS90, PCS110, and PCS140) were provided by Nippon Denko. Ruthenium(III) nitrosyl nitrate solution (1.5% Ru), ammonia solution (28–30 wt.%), and quartz sand were supplied by Fujifilm Wako. All the materials were used as received.

2.2 Catalyst preparation

Several types of Ru/m-ZrO₂ were prepared by either incipient wetness impregnation (IWI) or selective deposition (SD) methods. For the IWI method, m-ZrO₂ was impregnated with an aqueous solution of Ru(III) nitrosyl nitrate. The material was dried at 110 °C for 12 h and then calcined at 500 °C for 3 h. The sample is hereinafter termed “IWI sample.” For the SD method, a 0.1 M ammonia aqueous solution was added dropwise to Ru(III) nitrosyl nitrate aqueous solution until the pH reached ~9. Thereafter, m-ZrO₂ was added to the solution and stirred for 10 min. The mixture was then centrifuged and rinsed thrice with deionized water. The resulting material was transferred to an alumina crucible and dried at 70 °C overnight to yield the desired powder. The sample is hereinafter termed “SD sample.” The SD sample was further calcined at 500 °C for 3 h. This sample is hereinafter termed “SD-cal sample.”

2.3 Characterization

X-ray diffraction (XRD). The crystal structure of the catalyst was analyzed by XRD using a Rigaku Ultima IV instrument with a Cu-K α radiation source. During the measurements, the voltage and current were set to 40 kV and 30 mA, respectively, while the scan speed was maintained at 20 ° min⁻¹. The crystallite size was calculated from the peak of the m-ZrO₂ (-111) plane ($D_{\text{m-ZrO}_2(-111)}$) by applying Scherrer's equation (**Equation 3**).

$$D_{\text{m-ZrO}_2(-111)} = \frac{K\lambda}{\beta \cos \theta} \quad (\text{Equation 3})$$

In the equation, K is the shape factor (0.9), λ is the X-ray wavelength (0.154 nm), β is the line broadening at half the maximum intensity in radians, and θ is the Bragg angle.

X-ray fluorescence (XRF). For quantitative analysis of the catalyst, XRF measurements were carried out using an Epsilon 1 instrument (Malvern Panalytical) with Ag radiation. Omnic software (Malvern Panalytical) was employed for the analysis.

N₂ adsorption. To confirm the specific surface area of the catalyst, N₂ adsorption was carried out using a BELSORP-MINI II apparatus (MicrotracBEL). Before the adsorption measurement, the catalyst powder (0.1 g) was heated under vacuum at 150 °C for 2 h using a BELPREP-VAC II instrument (MicrotracBEL). N₂ adsorption was performed at a temperature of -196 °C (liquid nitrogen temperature), and the specific surface area of the catalyst was calculated via the Brunauer-Emmett-Teller (BET) method.

CO chemisorption. The number of surface Ru atoms was quantified by CO chemisorption (BELCAT II; MicrotracBEL). First, 0.05–0.10 g of catalyst powder was placed in a quartz tube and pretreated with 5% H₂/Ar gas at a flow rate of 30 mL min⁻¹, at 350 °C, for 1 h. The temperature was then lowered to 50 °C under the Ar atmosphere. Successive 1% CO/Ar pulses (0.44 μmol_{CO} pulse⁻¹) were dosed into the catalyst bed. The outlet gas was analyzed by a TCD detector. The ratio of CO to Ru was 0.93 (n [mol_{CO} mol_{Ru}⁻¹]).²⁹ The number of surface metallic Ru atoms (n_{Ru} [μmol g_{cat}⁻¹]) and average size of Ru nanoparticles (d_{Ru} [nm]) were calculated from the CO uptake and the following equations (**Equations 4 and 5**).

$$n_{Ru} = \frac{Y \times N_{av}}{W_{Ru} \times n} \quad (\text{Equation 4})$$

$$d_{Ru} = \frac{6A_{Ru}}{n_{Ru} \times \rho} \quad (\text{Equation 5})$$

where Y is the CO uptake [mol g_{cat}⁻¹], W_{Ru} is the Ru loading [g_{Ru} g_{cat}⁻¹], N_{av} is the Avogadro's number (6.02×10^{23} [atom mol⁻¹]), A_{Ru} is the number of Ru surface atoms per unit area (16.3 [atom nm⁻²]), and ρ is the density of metallic Ru (12.6 [g_{Ru} cm⁻³]).²⁹

X-ray photoelectron spectroscopy (XPS). The oxidation state of Ru, Zr, and O in the as-prepared samples was determined by XPS measurements using a JEOL JPS-9200 instrument with a Mg-K α radiation source. XPS analyses of the reduced samples were conducted using a JEOL JPS-9010MC instrument. The samples were reduced under a H₂ stream at 300 °C for 30 min and then transferred to the chamber without exposure to air. The binding energy was referenced to the O 1s peak (530.0 eV).

Scanning transmission electron microscopy (STEM). STEM was used to observe the catalyst powder directly (JEOL, JEM-ARM200F). The samples were dispersed in ethanol, then dropped onto Cu microgrids (Ohkenshoji, NP-C15), and dried. The elemental maps of Ru and Zr were recorded using an energy-dispersive X-ray detector (EDX).

In situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS). In situ DRIFTS was used for direct observation of the surface intermediate species on Ru/PCS90(SD) and Ru/PCS90(IWI) during CO₂ methanation using a Harrick Praying Mantis cell with pure ZnSe windows. The cell was placed inside a JASCO FTIR6100 infrared spectrometer equipped with a JASCO MCT6000M mercury-cadmium-telluride detector. The sample was loaded into the cell and then reduced using a mixture of 25% H₂/Ar at 300 °C for 10 min. Subsequently, the sample was cooled to 200 °C under an atmosphere of pure Ar. During this period, a background spectrum was recorded. The inlet gas was

switched to a mixture of 25% CO₂/Ar to produce the surface intermediate species. To observe the hydrogenation of the surface intermediate species, the inlet gas was further switched to 25% H₂/Ar. To capture a single spectrum, a total of 30 scans were accumulated at a resolution of 4 cm⁻¹.

2.4 Reaction test

The reaction was conducted using a fixed-bed tubular reactor. The reaction tube was a stainless-steel tube with an inner diameter of 6 mm. By transforming the powder into tablets and crushing them, the catalyst was granulated to a size of 1.18–1.70 mm. The catalyst layer was formed by packing 0.3 g of granulated catalyst and 1.0 g of quartz sand into the reaction tube. The temperature was measured using a thermocouple inserted into the catalyst layer. Before the reaction, a mixture of Ar: H₂ = 9:1 gas (100 mL min⁻¹) was introduced into the catalyst bed at 300 °C over 1 h. The reaction gas comprising a mixture of CO₂: H₂: N₂ = 1: 4: 5 was introduced into the catalyst bed at a flow rate of 50 mL min⁻¹. The outlet gas was dried using an ice-cold trap. The CO₂, CO, and CH₄ concentrations in the dried outlet gas were analyzed using a Horiba VA-3111 multi-gas analyzer.

3. Results and Discussion

3.1 Crystal structure and morphology

The crystal structure of the prepared Ru/m-ZrO₂ catalysts was evaluated by XRD (**Figure 1**, **Table 1**). None of the patterns shows any peaks of Ru species, indicating that the Ru species are smaller than the XRD detection limit (smaller than 5 nm) and/or amorphous. The peaks at 24°, 28°, 31°, 34°, 35°, 38°, 41°, 45°, 49°, 50°, 54°, and 55° in the XRD patterns are attributed to m-ZrO₂. Using the peak at 28°, the crystallite size of the m-ZrO₂ (–111) plane, $D_{m-ZrO_2(-111)}$, was calculated (**Table 1**). The size depends on the type of support material, not on the preparation method: *ca.* 11, 8.8, and 8.4 nm for Ru/PCS90, Ru/PCS110, and Ru/PCS140, respectively.

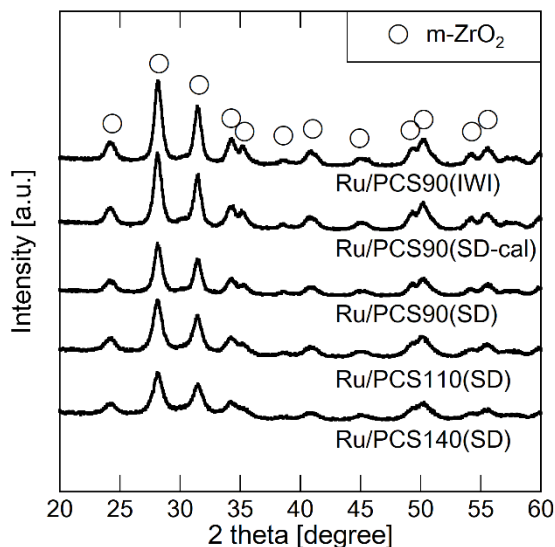


Figure 1 XRD patterns of the prepared Ru/m-ZrO₂ catalysts.

The specific surface area and total pore volume of the Ru/m-ZrO₂ catalysts were determined from the N₂ adsorption isotherms. The specific surface area depends on the type of m-ZrO₂: *ca.* 90, 140, and 170 m² g⁻¹ for the PCS90- PCS110-, and PCS140-based catalysts, respectively (**Table 1**). The total pore volumes are in the range of 0.2–0.5 cm³ g⁻¹.

Table 1 ZrO₂ crystal phase, specific surface area, and total pore volumes of the prepared Ru/m-ZrO₂ catalysts

Sample	Support	ZrO ₂ crystal phase ^a	$D_{m\text{-ZrO}_2(-111)}$ ^b [nm]	Specific surface area ^c [m ² g ⁻¹]	Total pore volume ^{c, d} [cm ³ g ⁻¹]
Ru/PCS90 (IWI)	PCS90	Monoclinic	11	80	0.53
Ru/PCS90 (SD-cal)	PCS90	Monoclinic	11	86	0.49
Ru/PCS90 (SD)	PCS90	Monoclinic	11	89	0.26
Ru/PCS110 (SD)	PCS110	Monoclinic	8.8	140	0.44
Ru/PCS140 (SD)	PCS140	Monoclinic	8.4	170	0.45

^aDetermined by XRD. ^bCrystallite size of m-ZrO₂ (–111) determined using XRD and Scherrer's equation. ^cDetermined by N₂ adsorption. ^d $p/p_0 = 0.98$.

Figure 2 presents the STEM images of Ru/PCS90(IWI), Ru/PCS90(SD), and Ru/PCS140(SD) which were reduced by H₂ at 300 °C. The particle sizes range from 10–20 nm. From the elemental mapping data, these particles are identified as ZrO₂. Distinct, small white grains of approximately 1 nm in size (0.97±0.27 nm, **Figure S1 and Table 2**) are deposited on ZrO₂ in the case of Ru/PCS90(SD). Elemental mapping indicates that these grains are Ru particles. Furthermore, several Ru particles approximately 1 nm in size are also detected on Ru/PCS90(IWI) (0.85±0.34 nm, **Figure S1 and Table 2**). Nonetheless, compared to Ru/PCS90(SD), discerning the Ru particles on Ru/PCS90(IWI) is more challenging. In-depth analysis by EDS (**Figure S2**) suggests the existence of numerous, minute Ru species that are difficult to identify through STEM imaging. The STEM image of Ru/PCS140(SD) is very similar to that of Ru/PCS90(SD), where the average particle size of Ru is 0.82±0.22 nm (**Figure S1 and Table 2**). Notably, during the long-term test for 70 h at 275 °C, the particle size of Ru in Ru/PCS140(SD) changes negligibly (**Figure S1**), indicating that the Ru nanoparticles are stably supported on ZrO₂. Nevertheless, given the limitations in the precision of EDS mapping, the existence of Ru species <1 nm cannot be excluded.²⁹ Moreover, there is an aperiodic pattern on ZrO₂; the presence of Ru particles of size <1 nm in this pattern makes it difficult to distinguish them.

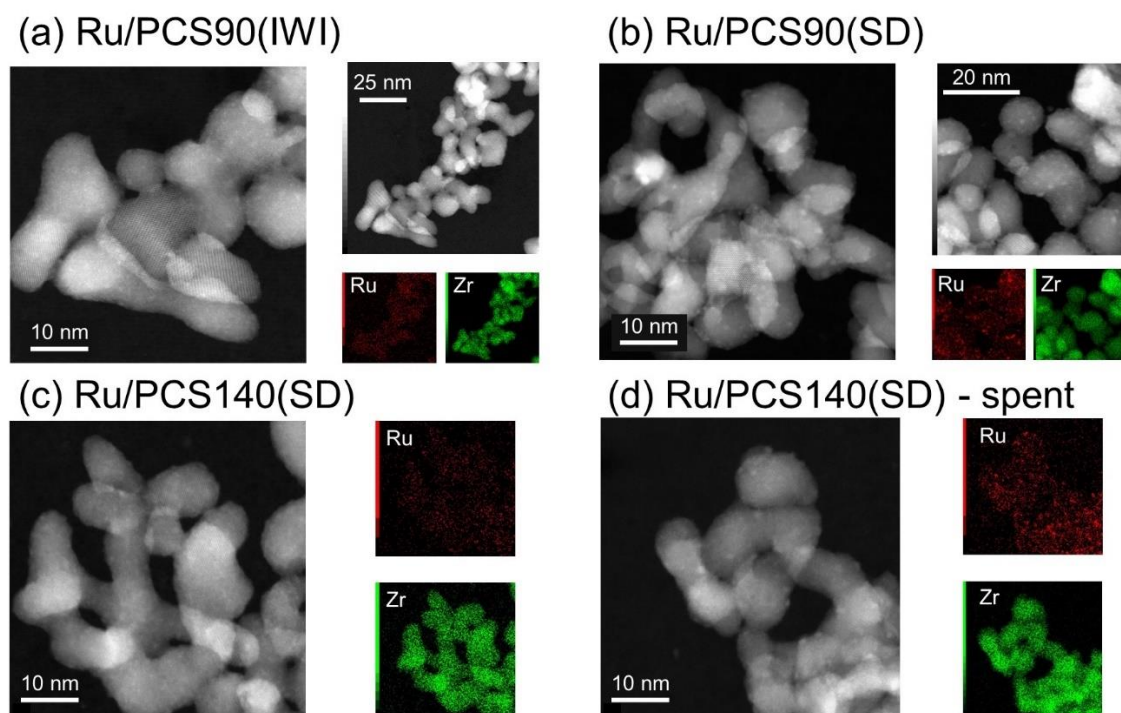


Figure 2 STEM images of (a) Ru/PCS90(IWI), (b) Ru/PCS90(SD), and (c) Ru/PCS140(SD) reduced by H₂ at 300 °C. (d) STEM image of Ru/PCS140(SD) 70 h after CO₂ methanation test at 275 °C.

Table 2 Ru particle size, Ru/Zr mol ratio and concentration of surface Ru atoms

Sample	Ru particle size [nm]		Ru/Zr molar ratio [mol _{Ru} mol _{Zr} ⁻¹]		Surface Ru atoms ^{a, c} [μmol g _{cat} ⁻¹]
	CO chemisorption	STEM	Bulk ^a	Surface ^b	
Ru/PCS90 (IWI)	0.81	0.85±0.34	0.030	0.052	390
Ru/PCS90 (SD-cal)	0.26	N.A.	0.032	0.053	1300
Ru/PCS90 (SD)	3.0	0.98±0.27	0.031	0.100	120
Ru/PCS140 (SD)	2.1	0.82±0.22	0.032	0.086	160

^aDetermined by XRF. ^bDetermined by XPS analysis of the reduced catalysts. ^cDetermined by CO chemisorption.

3.2 Oxidation state

XPS was used to determine the oxidation state of Ru and Zr in the Ru/m-ZrO₂ catalysts. **Figures 3** and **S3** show the XPS data for the as-prepared and reduced catalysts. All the reduced samples were analyzed after hydrogen reduction without exposure to the atmosphere. The peaks at 182.0 and 184.4 eV correspond to the 3d_{5/2} and 3d_{3/2} peaks of Zr⁴⁺, respectively (**Figure S3**).²⁹ No other peaks are observed for Zr 3d, indicating that the Zr species are present solely as ZrO₂, despite H₂ reduction.

Figure 3a shows the Ru 3p_{3/2} spectra of the as-prepared catalysts. A peak appears at 463.4 eV in the spectrum of Ru/PCS90(IWI). In contrast, the spectra of Ru/PCS90(SD) and Ru/PCS140(SD) show peaks at 462.1–462.5 eV, differing from the spectrum of Ru/PCS90(IWI). The spectrum of Ru/PCS90(SD-cal) has a weak and broad peak corresponding to Ru cations (462–464 eV). According to the literature,^{38,39} the Ru 3p_{3/2} peaks at 462–464 eV are assignable to RuO_x; however, determining the value of *x* is difficult. **Figure 3b** shows a photograph of the as-prepared Ru/ZrO₂ catalysts. Because pure ZrO₂ is white, the powder color must be derived from Ru cations. Ru/PCS90(IWI) and Ru/PCS90(SD-cal) are black, which is derived from Ru⁴⁺.^{40,41} In contrast, Ru/PCS90(SD), Ru/PCS110(SD), and Ru/PCS140(SD) are pale yellow. The yellow color is considered to be related to Ru³⁺ cations.⁴² Because the precursor solution with Ru³⁺ cations was solely treated with an alkaline NH₃ solution, no change in the Ru³⁺ oxidation state is expected; thus, Ru³⁺ species were retained in the Ru/m-ZrO₂ catalysts prepared by the SD method.

Figure 3a also shows the Ru 3p_{3/2} spectra of the reduced catalysts. The peak at a binding energy of 461.6–461.8 eV is indicative of metallic Ru,^{39,43,44} which is in line with our previous analysis of Ru/ZrO₂ catalysts.²⁹

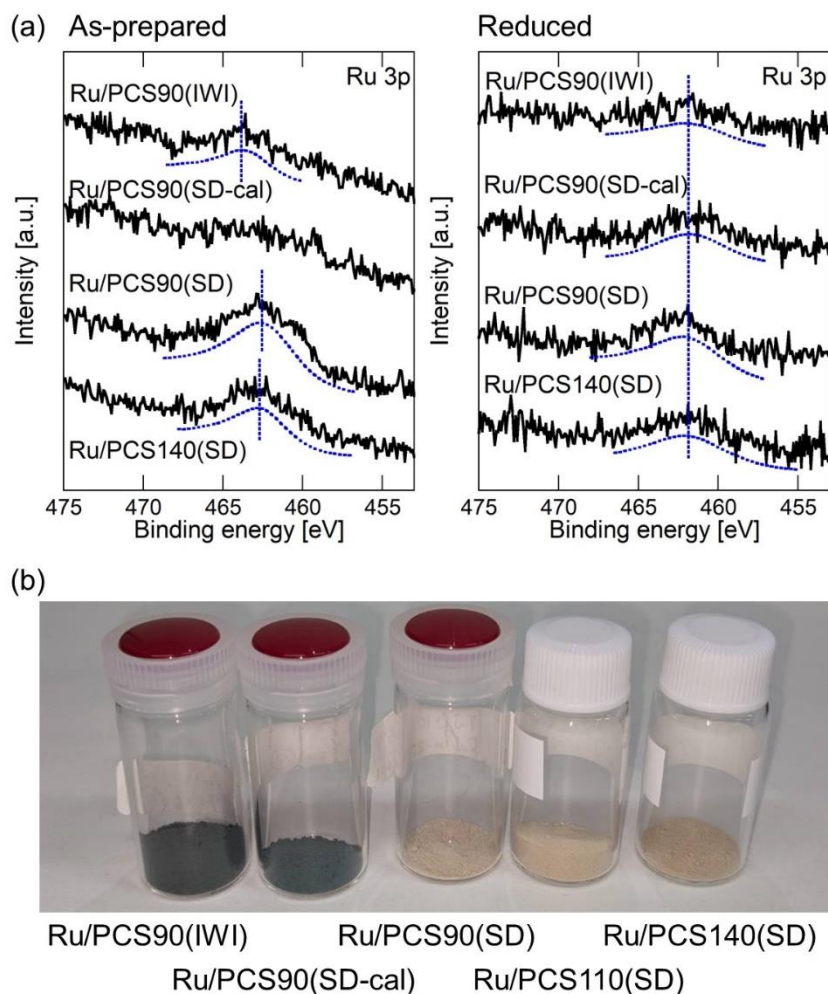


Figure 3 (a) Ru 3p_{3/2} spectra of as-prepared and reduced Ru/m-ZrO₂ catalysts. (b) Photographs of as-prepared Ru/m-ZrO₂ catalysts.

3.3 Bulk and surface composition

XRF was used to determine the Ru/Zr mole ratio of the Ru/m-ZrO₂ catalysts. The results are presented in **Table 2** under the heading “Bulk.” Irrespective of the substrate type and preparation method, the calculated ratio is approximately 0.03. The Ru to Zr ratio in the catalyst surface was calculated from the XPS data (**Table 2**). The surface ratio is higher than that of the bulk, indicating that Ru species are unevenly distributed on the catalyst surface. The surface molar ratios of Ru/PCS90(IWI) and Ru/PCS90(SD-cal) are approximately 0.05, while those of Ru/PCS90(SD) and Ru/PCS140(SD) are *ca.* 0.10. Therefore, the catalysts prepared by the SD method have a higher Ru dispersion; in other words, a more significant number of surface Ru atoms.

The number of Ru atoms on the catalyst surface was determined through CO chemisorption (**Table 2**). The number for Ru/PCS90(IWI) is 390 μmol g_{cat}⁻¹. The average Ru particle size calculated

from the CO uptake is 0.81 nm, aligning with the particle size estimated through STEM (0.85 ± 0.34 nm), as shown in **Table 2**. This outcome validates the feasibility of estimating the quantity of exposed metal Ru through CO chemisorption. Notably, Ru/PCS90 (IWI) and Ru/PCS90 (SD-cal) contain more Ru atoms, exceeding $390 \mu\text{mol g}_{\text{cat}}^{-1}$. In contrast, Ru/PCS90(SD) and Ru/PCS140(SD) possess fewer Ru atoms ($<160 \mu\text{mol g}_{\text{cat}}^{-1}$). The data indicate a decrease in the concentration of metallic Ru atoms on the catalyst surface owing to the SD method; these atoms are essential for CO chemisorption. Upon cursory examination, this might suggest a lower dispersion of Ru, which appears to contradict the findings from the XPS analysis. Furthermore, for these two catalysts, the average Ru particle size estimated from CO adsorption is 2–3 nm (**Table 2**), which is larger than the particle size estimated from STEM (approximately 1 nm, **Table 2**). In other words, the results of CO chemisorption and STEM observation do not match. These contradictions can be elucidated by considering that CO cannot be adsorbed on a portion of the Ru particle surface in the SD catalyst.

This inhibition of chemisorption can be attributed to the strong interaction between metal oxide support and the supported metal. This phenomenon is frequently observed in catalysts employing easily reducible oxide supports like TiO_2 and CeO_2 . When Ru/ TiO_2 catalysts underwent high-temperature reduction, the interaction appeared, leading to a decrease in the amount of CO adsorption, i.e., a reduction in Ru dispersion.⁴⁵ Nevertheless, catalysts with low Ru dispersion exhibited high CO_2 methanation performance. In such instances, high-temperature reduction results in the formation of a TiO_x layer covering Ru, giving rise to specific active sites.^{45,46} We hypothesize that similar metal-support interactions may occur with ZrO_2 . To illustrate, N_2O decomposition was suppressed in the presence of the Cu/ ZrO_2 catalysts with Cu- ZrO_2 solid interactions. Based on the N_2O decomposition, the number of exposed Cu atoms for this catalyst was estimated to be low.⁴⁷⁻⁴⁹ A similar effect was previously noticed even in the case of H_2 chemisorption for Cu/ SiO_2 . The hindrance of H_2 chemisorption is caused by embedding Cu nanoparticles in SiO_2 .⁵⁰ The phenomenon of inhibited chemisorption was also observed with Ru/ ZrO_2 catalysts in our prior study.²⁹ The present results indicate that Ru- ZrO_2 strong interactions are operative in the Ru/m- ZrO_2 catalysts, particularly in those prepared using the SD method.

3.4 Reaction mechanism

The mechanism of the reaction over the developed Ru/m- ZrO_2 catalyst was analyzed using in situ DRIFTS measurements (**Figure 4**). In this case, Ru/PCS90(SD) was used as a representative of the Ru/m- ZrO_2 catalysts.

One minute after introducing CO_2 gas into the chamber at 200°C (**Figure 4a**), seven characteristic peaks are observed at 2029, 1847, 1630, 1563, 1420, 1334, and 1224 cm^{-1} . The five peaks at 1630, 1563, 1420, 1334, and 1224 cm^{-1} are related to CO_2 -derived adsorbed species on ZrO_2 . The peaks at 1630 and 1224 cm^{-1} are associated with bidentate bicarbonate species ($\text{b-CO}_3\text{H}$), and the peak at 1420

cm^{-1} is assigned to ionic bicarbonate species ($\text{i-CO}_3\text{H}$).^{51,52} The peaks at 1563 and 1334 cm^{-1} are assigned to bidentate carbonate species (b-CO_3) on ZrO_2 .^{51,52} The peak at 1847 cm^{-1} is assigned to bridging CO bonded to Ru metal ($\text{Ru-CO}_{\text{bridged}}$), and the peak at 2029 cm^{-1} is assigned to linear CO bound to Ru ($\text{Ru-CO}_{\text{linear}}$).⁵³⁻⁵⁶ **Figure 4a** shows that CO_2 is adsorbed on ZrO_2 as bicarbonate species and carbonate species. The peaks at 1420 cm^{-1} ($\text{i-CO}_3\text{H}$) and 1630 cm^{-1} ($\text{b-CO}_3\text{H}$) are particularly intense. The peak of $\text{Ru-CO}_{\text{linear}}$ reaches the maximum in ~ 1 min, after which the peak intensity decreases. As the intensity of the $\text{Ru-CO}_{\text{linear}}$ peak decays ($t = 3$ min), the $\text{Ru-CO}_{\text{bridged}}$ peak becomes more intense. This result indicates that $\text{Ru-CO}_{\text{linear}}$ is the predominant CO species formed on Ru in the initial stage, but $\text{Ru-CO}_{\text{bridged}}$ gradually becomes more abundant.

When the introduced gas is switched from 25% CO_2/Ar to 25% H_2/Ar at 200 °C (**Figure 4b**), various peaks emerge within 1 min, indicating the adsorption of CO species on Ru (2042, 1992, 1972, and 1910 cm^{-1}) and formate species on ZrO_2 (2965, 2870, 1576, 1383, 1357 cm^{-1}).⁵³⁻⁵⁹ The peaks of the formate species (b-HCOO) appear ~ 1 min after introducing the 25% H_2/Ar mixture, and simultaneously, the peaks associated with bicarbonate/carbonate species ($\text{b-CO}_3\text{H}$, $\text{i-CO}_3\text{H}$, and b-CO_3) on ZrO_2 disappear. Hence, the bicarbonate and carbonate species on ZrO_2 are transformed into formate species. The intensity of the peaks of the formate species reduces over time, with a corresponding increase in the intensity of the CO species-derived peaks. Examining the changes in the adsorbed CO species peaks over time shows a significant increase in the intensity of the peak at 2042 cm^{-1} at $t = 1$ min, and several peaks related to adsorbed CO species appear at $t = 3$ min. Interestingly, the $\text{Ru-CO}_{\text{bridged}}$ peak (1847 cm^{-1}) vanishes 1 min after the reaction commences. Gas phase CH_4 (3015 cm^{-1}) is produced at $t = 1$ -10 min.

These results indicate that bicarbonate and carbonate species on ZrO_2 are converted to formate species during the hydrogenation process, and these formate species are rapidly decomposed and converted into CO species. The resulting CO species, particularly $\text{Ru-CO}_{\text{bridged}}$, are promptly consumed by H_2 , indicating hydrogenation. This mechanism is in line with that of $\text{Ru}/\text{PCS90}(\text{IWI})$ (**Figure S4**) and reported Ru/ZrO_2 catalysts.^{58,59}

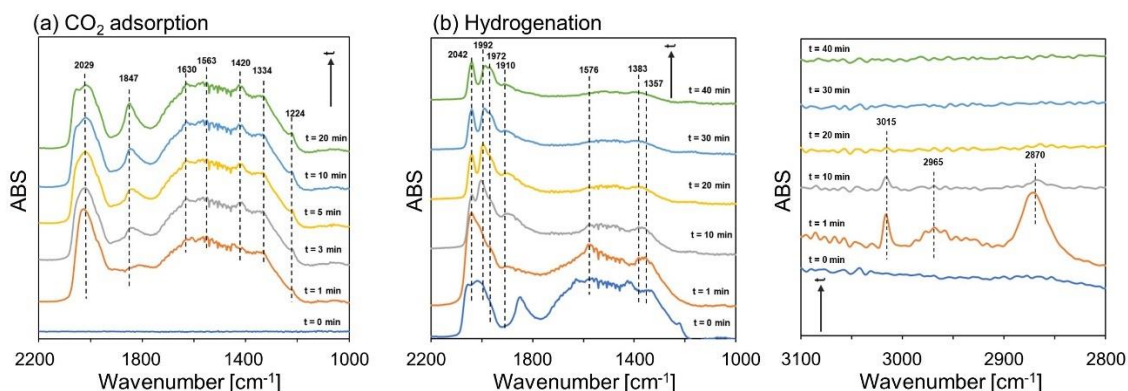


Figure 4 In situ DRIFTS spectra of Ru/PCS90(SD) during (a) CO₂ adsorption and (b) hydrogenation at 200 °C.

3.5 Catalytic performance

CO₂ methanation tests were conducted using three different Ru/PCS90 catalysts prepared using different methods. The CH₄ selectivity is >99% between 200 and 300 °C (**Figure S5**). In other words, no CO molecules are detected in the product gas. CO₂ methanation on the Ru/m-ZrO₂ catalysts follows a mechanism in which CO₂ is first converted to CO *via* the RWGS reaction, after which the produced CO is methanated (see **Section 3.4**). Therefore, CO methanation in the presence of the prepared catalyst is expected to be much faster than the RWGS reaction in the investigated temperature range. **Figure 5** shows the change in the equilibrium conversion of CO₂ with temperature. The CO₂ conversion for all catalysts increases with an increase in the reaction temperature. Among the catalysts prepared by the three methods evaluated in this study, Ru/PCS90(SD) affords the highest conversion (78%), followed by the catalysts prepared by the IWI method (68%) and SD-cal method (56%) at a temperature of 250 °C. These findings are consistent with the results of our previous study on Ru/am-ZrO₂ (am-: amorphous) catalysts, wherein the SD method was also determined to be the most effective among the preparation techniques evaluated.²⁹

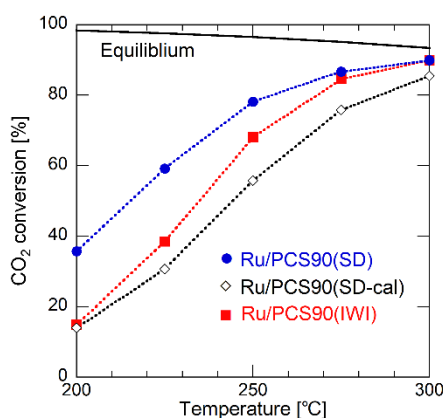


Figure 5 CO₂ conversion using Ru/PCS90 prepared by IWI, SD-cal, and SD.

The influence of the type of ZrO₂ support on CO₂ methanation was investigated. **Figure 6** shows the CO₂ conversion, and **Figure S6** shows the CH₄ selectivity using Ru/PCS90(SD), Ru/PCS110(SD), and Ru/PCS140(SD). For comparison, the results obtained with Ru/am-ZrO₂ (Ru/Zr mole ratio = 0.036 measured by XRF) are included; this catalyst demonstrated the high activity in our previous work.²⁹ Remarkably, all four of these catalysts achieve >99% CH₄ selectivity. Although the differences among the three catalysts prepared in this study are not particularly pronounced, Ru/PCS140(SD) demonstrates the highest CO₂ conversion, reaching 82% at 250 °C. Notably, these catalysts exhibit superior CO₂ conversion to Ru/am-ZrO₂.

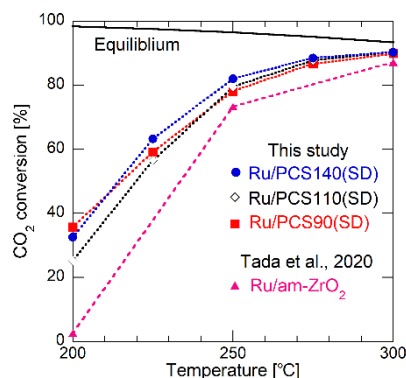


Figure 6 CO₂ conversion of Ru/PCS90(SD), Ru/PCS110(SD), Ru/PCS140(SD), and Ru/am-ZrO₂.²⁹ Reproduced with permission from Ref. 29. Copyright 2020 The Royal Society of Chemistry.

3.6 Long-term stability

Finally, the long-term stability of Ru/PCS140(SD) was evaluated, as shown in **Figures 7** and **S7**. At 275 °C, a CO₂ conversion of 88% and a CH₄ selectivity of >99% are consistently maintained for a duration of 70 h. These values are close to those at equilibrium (CO₂ conversion = 95%, CH₄ selectivity >99%, see **Figures 6** and **S6**). However, when evaluating the long-term stability of the catalyst, the CO₂ conversion should be evaluated under conditions far below the equilibrium conditions. Thus, a reaction was also carried out at 225 °C. Even at this lower reaction temperature, the catalyst sustains a CO₂ conversion of 47% and CH₄ selectivity of >99% for 70 h. The data demonstrate that the Ru/PCS140(SD) catalyst maintains a high CO₂ conversion despite the relatively low temperature of 225 °C.

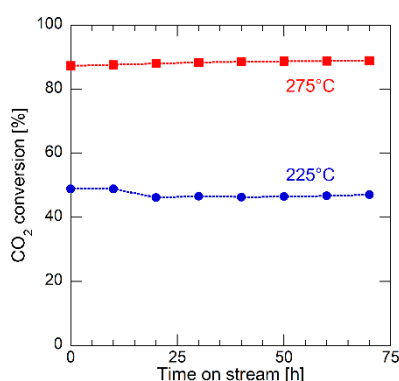


Figure 7 Plot of CO₂ conversion over time using Ru/PCS140(SD) at 225 and 275 °C.

3.7 Origin of the superiority of Ru/m-ZrO₂ prepared by SD method

First, the origin of the superior performance of the catalysts prepared using the SD method was evaluated. The CO₂ methanation reaction comprises two sequential steps: first, the reverse shift

reaction converts CO₂ to CO, after which CO methanation converts CO to CH₄. Catalysts prepared using the SD method have fewer available Ru sites, judging from the CO chemisorption data (**Table 2**). This aligns with the strong interaction between Ru and ZrO₂. Comparison of the test results with the characterization data indicates that this interaction indeed improves the reverse shift reaction.

What causes the SD catalyst to generate Ru species that exhibit pronounced interaction with m-ZrO₂? We understood by comparing the catalytic performance of SD and SD-cal catalysts that skipping a calcination process in catalyst preparation results in the formation of the Ru species. In addition, the skipping contributes to (i) facilitating the formation of Ru³⁺ species on m-ZrO₂ and (ii) preventing the generation of Ru⁴⁺ species, as elaborated in **Section 3.2**. It is evident that a correlation exists between the "supporting highly active Ru nanoparticles on the catalyst" and the "formation of Ru³⁺ in the catalyst precursor."

Despite attempts to understand this interaction, it remains unclear. It was first proposed that the Ru species were physically covered with ZrO₂. However, this postulate was contradicted by the high Ru/Zr ratios from the XPS analysis of the SD-prepared catalysts. Subsequently, we proposed that a slightly δ^+ charged Ru species might be formed at the Ru-ZrO₂ interface, which could be an active site for the reverse shift reaction. However, the XPS analysis of the reduced catalysts showed no differences in the peak positions for the Ru species, regardless of the preparation method. It is challenging to determine the electronic state of the Ru species only through XPS. We intend to gain more clarity on this interaction in the future.

The influence of the ZrO₂ crystal structure on CO₂ methanation was evaluated. Compared to Ru/am-ZrO₂, which was found to be highly active in our previous study,²⁹ Ru/PCS90(SD), Ru/PCS110(SD), and Ru/PCS140(SD) exhibit superior performance (**Figure 5**). This discrepancy can be explained by the differences in the CO₂ adsorption ability. Previously, we examined the relationship between the crystal structure of ZrO₂ and the CO₂ adsorption ability through experimental and computational chemistry.³⁷ Our findings revealed that CO₂ molecules are strongly adsorbed, or easily activated, on m-ZrO₂ compared to amorphous ZrO₂. Indeed, similar results have been observed in methanol synthesis studies, where Cu/m-ZrO₂ outperformed Cu/am-ZrO₂, specifically in terms of CO₂ conversion.³³

4. Conclusion

Ru/m-ZrO₂ catalysts were prepared by incipient wetness impregnation and selective deposition methods. The effect of the preparation methods on CO₂ methanation was investigated. The selective deposition method allowed for the dispersion of ~1 nm Ru nanoparticles on m-ZrO₂. Notably, the interaction between the Ru nanoparticles and m-ZrO₂ was particularly strong, leading to high CO₂ conversion even at lower temperatures, specifically below 250 °C. Among the catalysts investigated in this study, Ru/PCS140(SD) exhibited the highest activity, with a CO₂ conversion of 82% and CH₄

selectivity of >99% at 250 °C. The catalytic performance was maintained for over 70 h.

Supporting information

Particle size distribution of Ru, STEM images, Zr 3d XPS spectra, in situ DRIFTS spectra, CH₄ selectivity.

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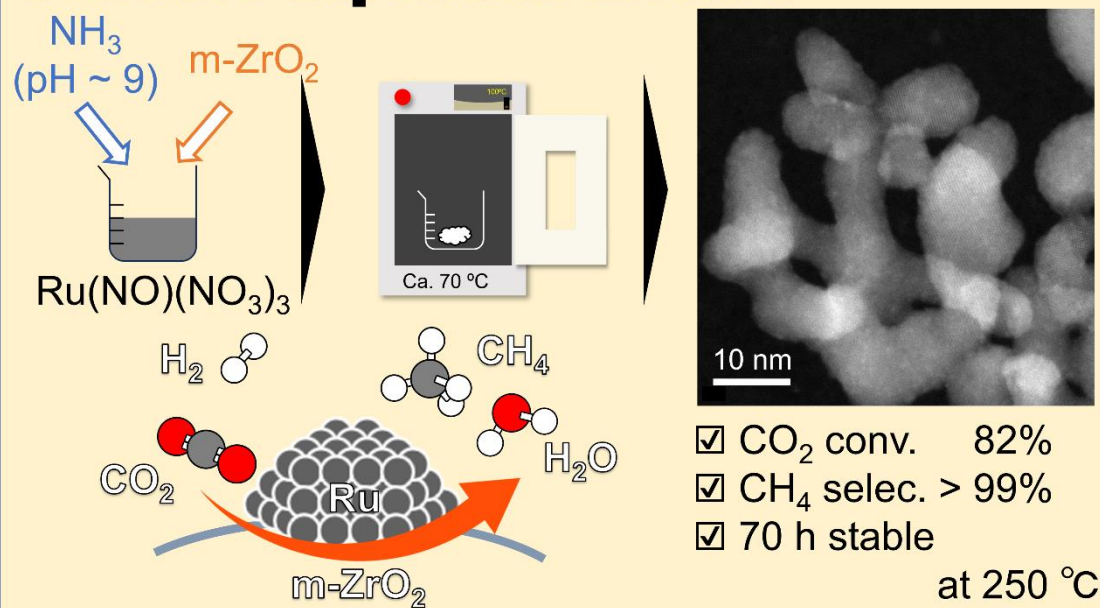
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Selective deposition method



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