

論文内容の要旨

In this modern era, nanomaterials that have dimensions ranging from 1 to 100 nm are becoming one of the promising materials in the research and industrial fields due to their unique physical and chemical properties. Among nanomaterials, metal oxides have been attractive materials in many fields. In addition, composites composed of several metal oxides in nanoscale offer an opportunity to solve the obstacles and enhance the properties for wider applications, including heterogeneous catalysts, catalyst supports, and sensor materials [1]. However, they sometimes suffer from poor stability when they are placed in harsh conditions, such as high-temperature, especially in catalyst and catalyst support applications [2]. To address this issue, embedded noble metal nanoparticles (NPs) in pores of (base metal) oxides is one of the most effective approaches to improve catalysts stabilities, since sintering phenomenon of noble metal NPs at high temperature can be suppressed by physical separation of the metal NPs, which can enhance their performance for the use in wider applications.

To suppress the sintering of nanometal catalysts, porous metal oxides as supports with large surface area and high porosity have been used [3]. In this context, I propose a new strategy of “embedded metal NPs catalysts in porous catalyst supports.” To clarify this strategy, spherical mesoporous metal oxide nanoparticle assemblies were synthesized by a simple one-pot and single-step solvothermal method with a short reaction time [4]. The size of primary and secondary particles of the nanomaterials are controlled by simple modifications of the reaction conditions, such as solvents, additives, reaction temperatures, and reaction time. Taking these advantages, I expected that the embedded noble metal NPs in porous ZrO_2 support and porous ZrO_2 composites supports, which are synthesized in the one-pot and single-step solvothermal approach, would exhibit higher sintering resistance and higher durability in catalytic reactions at high temperatures.

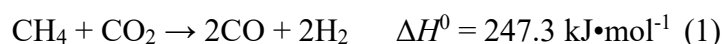
On the other hand, catalysts’ performance as well as stability also strongly depend on the inherent properties of the supports on which the metal is dispersed [5]. Those two parameters can be controlled by modifying the synthetic conditions of the supports. To interpret this concept, I synthesize CeO_2 porous spheres and their composites by developing the simple one-pot and single-step method. The properties of the nanomaterials, such as their high Ce^{3+} content and oxygen storage capacity, are easily controlled by this synthesis method.

Adopting this versatility, I expect that attaching metal NPs to CeO_2 porous spheres and its composites, which are synthesized in a one-pot and single-step solvothermal approach, would provide better catalytic performances in some catalytic reactions. As a probe reaction to investigate the role of the inherent properties of the CeO_2 support, I selected methane oxidation and CO_2 methanation reactions.

1. One-Step Solvothermal Synthesis of Ni Catalysts Supported on ZrO₂-Based Porous Spheres and Their Catalytic Activity for Dry Reforming of Methane

Dry reforming of methane (DRM, eq. 1) is one of the most important processes for CO₂ recycling. However, carbon deposition on catalysts and the sintering of catalysts are the most serious drawbacks. Recently, several new approaches have been developed to solve the drawbacks in a simple, efficient, and sustainable way [6]. Embedded morphology of metal nanoparticles (NPs) in catalyst supports is one of the most effective approaches to preventing agglomeration and sintering of the metal NPs in catalytic reactions, since the metal NPs are physically separated by the supports [7]. ZrO₂ composites with different metal oxides have been studied as catalyst supports in expectation of longer lifetime of catalyst at elevated reaction temperatures. ZrO₂ porous spheres were selected as catalyst supports because of their high heat tolerance. We also selected additional metals oxides to be composited to ZrO₂ yielding SiO₂-ZrO₂ composite to extend the surface area, MgO-ZrO₂ composite in expectation of positive acid-base interactions between CO₂ and MgO [8,9], and Y₂O₅-ZrO₂ in anticipation of long-lifetime of catalyst by suppressing the sintering of the catalyst support. Then, I supposed that i) the embedded morphology would suppress the carbon deposition on DRM catalysts at low temperatures, and ii) the composite catalyst supports consisted of ZrO₂ with different metal oxides would exhibit higher sintering resistance.

Here, I propose a new synthetic strategy to produce embedded metal NP catalysts in composite metal oxide supported by the original one-pot and single-step solvothermal approach. In order to investigate the effect of the embedded morphology of Ni NPs on ZrO₂ based porous spheres, the DRM was selected as a probe reaction (eq 1).



A precursor solution of zirconium butoxide, acetylacetonate, nickel nitrate, and water in ethanol was heated in a sealed SUS-316 reactor at 250 °C for 60 min. In the same manner, the addition of tetraethoxysilane, magnesium acetylacetonate, and yttrium isopropoxide to the precursor solution led to Ni catalysts supported in ZrO₂ composites, Ni@SiO₂-ZrO₂-C, Ni@MgO-ZrO₂, and Ni@Y₂O₃-ZrO₂-C, respectively. From SEM observations, Ni@ZrO₂-M composites exhibited unique porous spherical morphologies with particle diameters are ca. 700 nm and specific surface areas ranged from 71 to 238 m²/g. However, the high specific surface areas were drastically reduced to 2–6 m²/g, when the catalysts were reduced by H₂ at 450 °C for 2 h.

Thus, we thought that the porous spheres consisting of slightly larger ZrO₂ primary particles would tolerate sintering even at the high temperatures, and smaller (spherical) secondary particles would be effective for gas diffusion into and out of porous sphere catalysts. Therefore, the reaction conditions, such as solvent, reaction temperature, and reaction time, were optimized to produce small (spherical) secondary particles with slightly larger primary particle. Finally, we found that the addition of a small volume of water to the precursor solutions dramatically reduced the secondary particle sizes from to 600–700 nm to 60–120 nm. The Ni catalysts embedded in the small porous supports are denoted as mini-Ni@ZrO₂-C, mini-Ni/SiO₂-ZrO₂-C, mini-Ni/MgO-ZrO₂-C, and mini-Ni/Y₂O₃-ZrO₂-C.

To demonstrate the stability of those catalysts, a low-temperature DRM reaction at 550 °C was selected as a probe reaction. As expected, the embedded Ni NPs catalysts in mixed metal oxides (mini-Ni/SiO₂-ZrO₂-C, mini-Ni/MgO-ZrO₂-C, and mini-Ni/Y₂O₃-ZrO₂-C) showed better catalytic

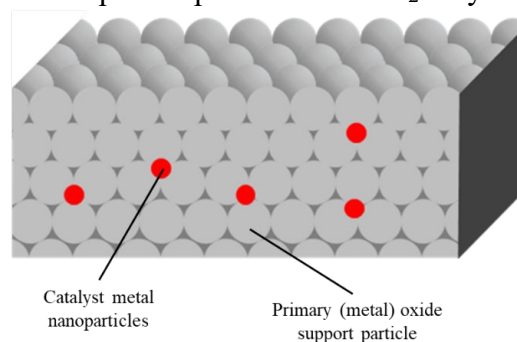
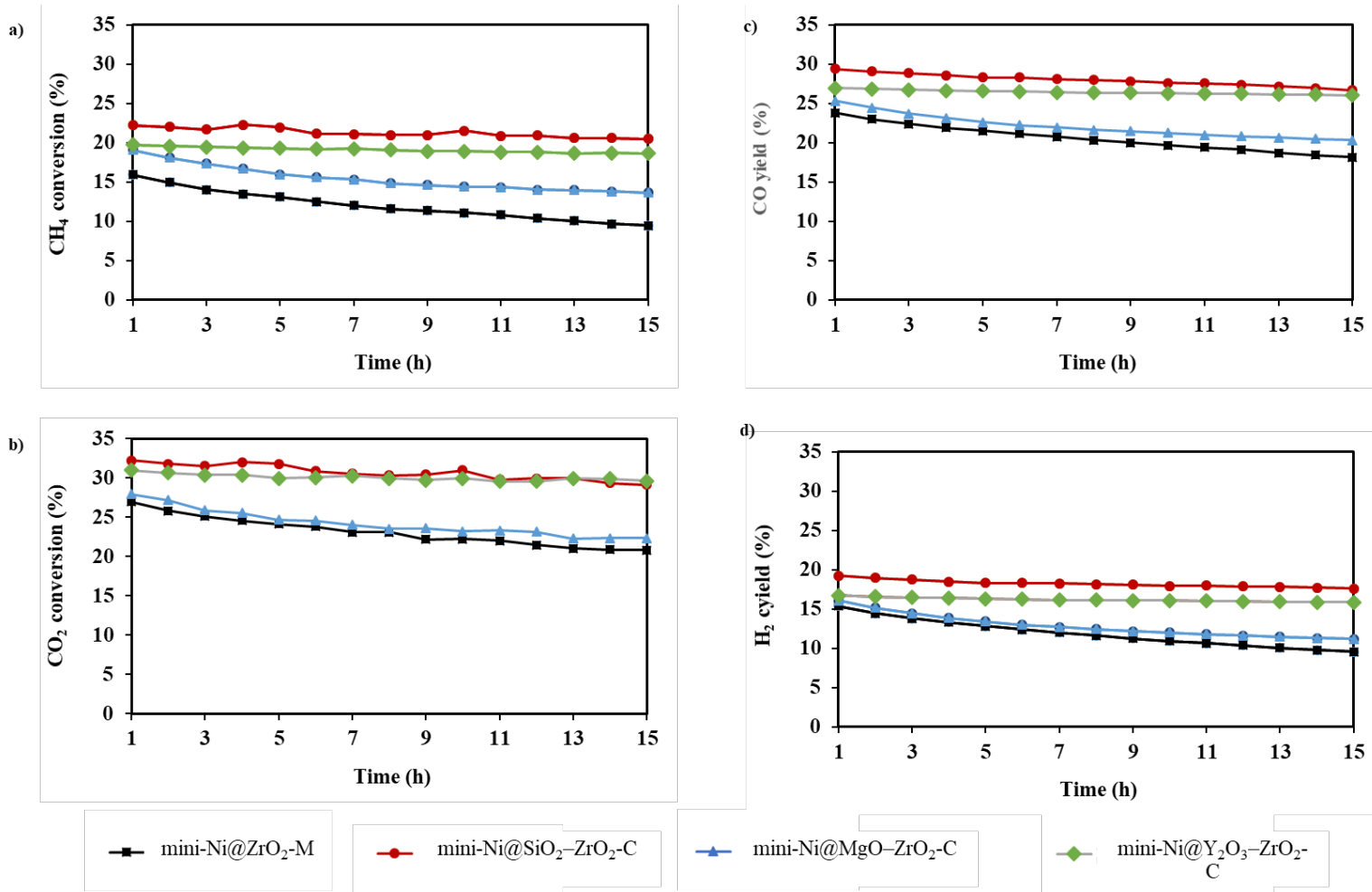


Fig. 1 Schematic of embedded nanometal in gaps of primary (metal) oxide support nanoparticles.

performance in the low-temperature DRM reactions than a reference Ni/ZrO₂-M catalyst. Especially, Ni/SiO₂-ZrO₂-C, with a high specific surface area of 196 m²/g showed excellent catalytic activity and stability with a small amount of carbon deposition.

Fig. 2. CH₄ and CO₂ conversions; CO and H₂ yields of DRM reactions catalyzed by mini-Ni@ZrO₂-M, mini-Ni/SiO₂-ZrO₂-C, mini-Ni@MgO-ZrO₂-C, and mini-Ni@Y₂O₃-ZrO₂-C.



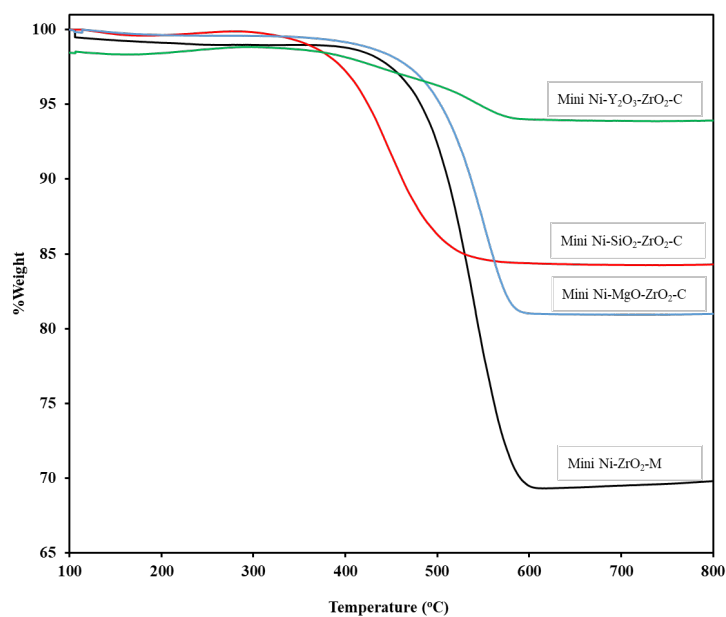


Fig. 3. TGA profiles of spent catalysts for mini-Ni@ZrO₂-M, mini-Ni@SiO₂-ZrO₂-C, mini-Ni@MgO-ZrO₂-C, and mini-Ni@Y₂O₃-ZrO₂-C.

The formation of carbon deposition on the spent catalysts was confirmed by SEM observations. The amounts of carbon deposition on the spent catalysts were estimated by TG analysis (Fig. 3). In the cases of mini-Ni@ZrO₂-M and mini-Ni@MgO-ZrO₂-C, weight loss started at approximately 400 °C and was almost complete at 600 °C, with weight losses corresponding to 30 and 19%, respectively. However, in the cases of mini-Ni@SiO₂-ZrO₂-C and mini-Ni@Y₂O₃-ZrO₂-C, weight losses started at a lower temperature, approximately 350 °C, and had almost completed by 550 or 600 °C, with weight losses corresponding to 15 and 5%, respectively. Thus, the catalysts suppressing carbon deposition in the DRM were successfully obtained.

2. Nitrothermal synthesis of CeO₂-based composite nanoparticles as Ru catalyst support for CO₂ methanation and Pd catalyst support for CO₂ methanation and CH₄ oxidation

CeO₂ has been extensively used as a catalyst and catalyst support for noble metal catalysts in various applications due to its good dispersibility noble metal nanoparticles. Additionally, CeO₂ also has good oxygen storage capacity (OSC) through redox cycle and promote reactions that need oxygen transfer. However, CeO₂ itself is often sintered at elevated temperatures, which leads to the loss of its surface area [10]. Previously, a study utilized acetonitrile as a solvent in solvothermal reactions that yielded CeO₂ with extremely rich Ce³⁺ content [11]. In this chapter, I extended the acetonitrile-based solvothermal synthetic approach termed ‘nitrothermal’ synthesis to the preparation of CeO₂ and CeO₂-based composites, Al₂O₃-ZrO₂-C, SiO₂-CeO₂-C, Y₂O₃-CeO₂-C, and ZrO₂-CeO₂-C; and explored their OSCs as well as their use as supports for Ru and Pd nanometal catalysts for CO₂ methanation and CH₄ oxidation, respectively.

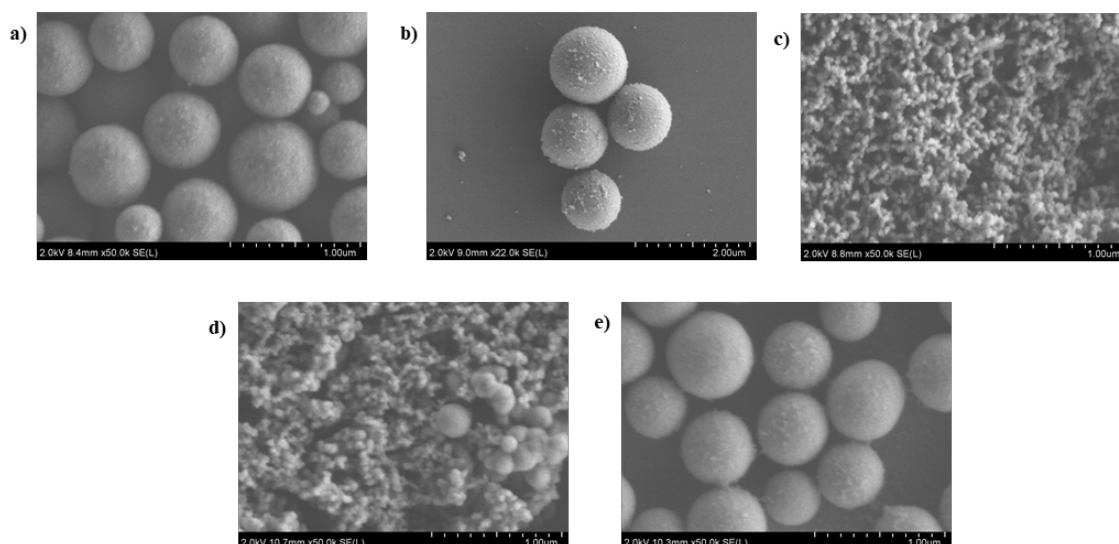


Fig. 4. SEM images of the CeO₂-based composites.: a) CeO₂-M, b) ZrO₂-CeO₂-C, c) SiO₂-CeO₂-C, d) Al₂O₃-CeO₂-C, and e) Y₂O₃-CeO₂-C.

A precursor solution containing cerium nitrate, zirconyl nitrate dihydrate, tetraethoxysilane, aluminum nitrate nonahydrate, or yttrium nitrate n-hydrate, triethylene glycol in acetonitrile was heated up to 300 °C and kept the temperature for 10 min. SEM observation showed that CeO₂-M, Y₂O₃-CeO₂-C, and ZrO₂-CeO₂-C have almost spherical morphologies with secondary particle sizes ranging from 440–1120 nm. The cubic CeO₂ reflection pattern in the XRD spectra was observed in the obtained products. The impregnation method was selected to introduce Ru and Pd nanometals to CeO₂-based supports. To elucidate the performance and stability of the catalysts, CO₂ methanation and methane oxidation were selected as probe reactions for Ru/CeO₂ and Pd/CeO₂-based composites, respectively. However, Ru/SiO₂-CeO₂-C composite resulted in slightly better performance than Ru/CeO₂-M, the others Ru/CeO₂-based composites not significantly so.

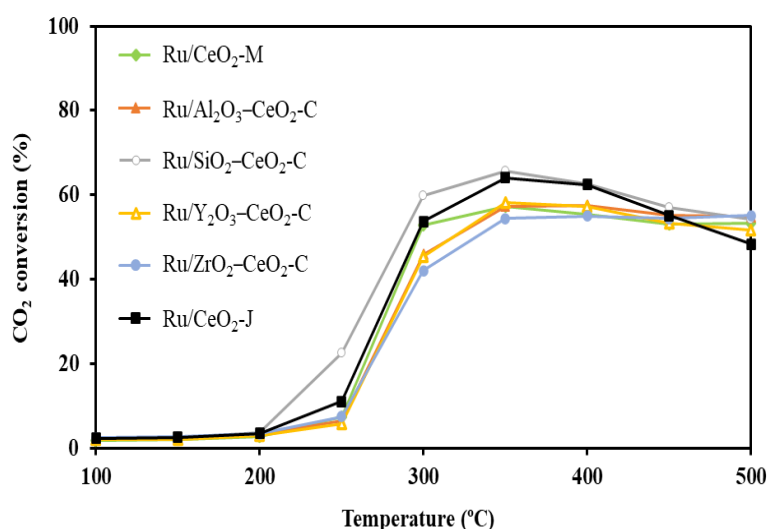


Fig. 5. CO₂ conversion vs. temperature for CO₂ methanation over Ru/CeO₂-based catalysts.

Meanwhile, methane oxidation (Eq. 2) is a reaction that requires oxygen transfer. The higher oxygen storage capacity achieved through $\text{Ce}^{3+}/\text{Ce}^{4+}$ redox change in CeO_2 catalysts and/or catalyst supports is one of the most important factors for their application to oxidation reactions [12]. As expected, two of the Pd catalysts supported on CeO_2 -based composites, $\text{Pd}/\text{Al}_2\text{O}_3\text{-ZrO}_2\text{-C}$ and $\text{Pd}/\text{SiO}_2\text{-CeO}_2\text{-C}$, demonstrated superior low-temperature activity for methane oxidation.

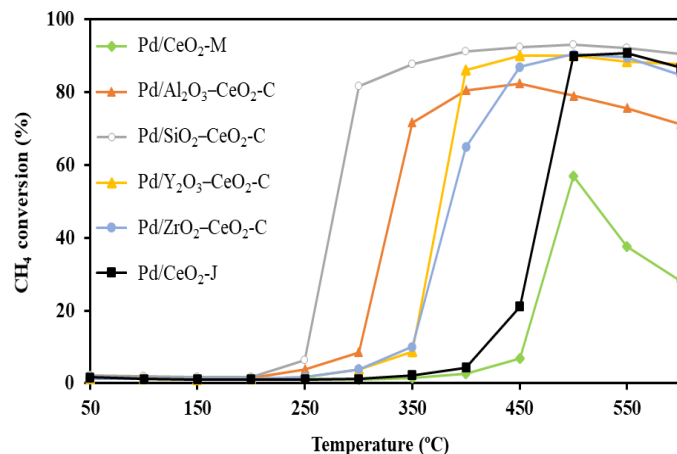


Fig. 6. CH_4 conversion vs. temperature for CH_4 oxidation over Pd/ CeO_2 -based catalysts.

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