論 文 内 容 の 要 旨

1. Introduction

Much attention has been paid to nano-scaled materials because they exhibit novel and unique properties as compared to macro-sized ones.[1] Notably, their properties depend majorly on the synthetic methods, by which their shape, morphology, size, structure, and composition are determined. Thus the preparation approaches are extremely important to achieve the advanced nanomaterials.

Meanwhile, we recently developed a new solvothermal approach to fabricate metal oxide nanoparticle (NP) assemblies with solid or hollow spherical morphologies, named as **m**icro/**m**eso-porously **a**rchitected **r**oundly **i**ntegrated **m**etal **o**xides (MARIMOs).[2] Various MARIMO assemblies such as SiO_2, TiO_2, ZnO, ZrO_2, and CeO_2 as well as their composites were prepared by a similar solvothermal method. In this study, I applied our approach to afford different metal oxide nanocomposites with homogeneous mixing level, which have been recognized as difficult to prepare so far.

Besides, the advantages of high heat tolerance, large surface area, and surface of the solvothermally prepared NP assemblies are taken into consideration. Herein, I propose an application of the prepared nanocomposites as sintering-resistant catalyst supports towards exothermic reactions in expectation of good dispersion of catalyst metals and sintering prevention of the catalysts during catalytic processes.

2. One-Step Direct Synthesis of SiO_2–TiO_2 Composite Nanoparticle Assemblies with Hollow Spherical Morphology

Despite of many inherent excellent properties, TiO_2 NPs have several drawbacks such as agglomeration and poor interaction with organic media. However, these problems can be overcome through modification of these NPs by combining them with SiO_2, since SiO_2 increases the mechanical and thermal stability, adsorption ability, and specific surface area of the NPs. In addition, surface modification by alkylsilane coupling reagents can easily control the dispersibility of NP assemblies in various media. However, synthesis of SiO_2–TiO_2 material usually is difficult due to a big different hydrolysis rate of alkoxysilane and alkoxytitanium precursors during the

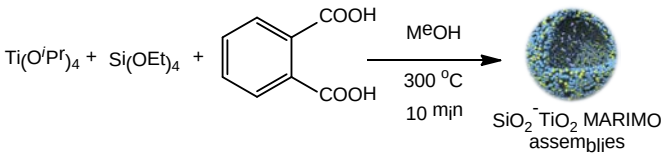

Figure 1. Schematic of synthesis of SiO_2–TiO_2 NP composite

hydrolysis. In this study, I applied our approach to obtain homogeneous SiO_2–TiO_2 composite NP assemblies with and without alkyl groups having hollow morphology by controlling the hydrolysis rate of the precursors in solvothermal reactions.

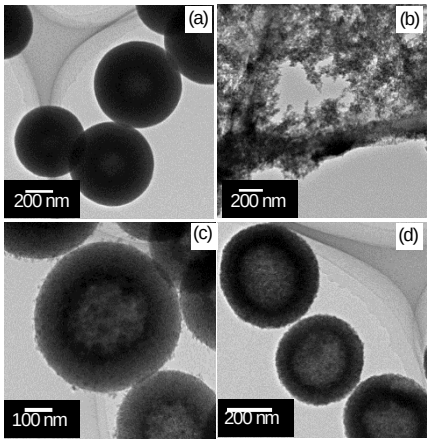

Figure 2. TEM images of (a) SiO_2–TiO_2 NPs, (b) SiO_2 agglomerates, (c) SiO_2–TiO_2 NPs formed in the presence of AcOH, and (d) Modified SiO_2–TiO_2 NPs

In the synthesis of SiO_2–TiO_2 NP assemblies (Figure 1), a precursor solution containing an equimolar amount of $Si(OEt)_4$ and $Ti(O^iPr)_4$ yielded NP assemblies with a beautiful hollow spherical morphology as expected (Figure 2a). Similar reactions of precursor solutions containing low amounts of $Si(OEt)_4$ also resulted in composite NP assemblies with hollow spherical morphologies, while higher amounts of $Si(OEt)_4$ resulted in a very low product yield. BET specific surface area and diameters of the composite NP assemblies became larger with increase of $Si(OEt)_4$ amount. Those results indicate that the Si:Ti ratio in the composite NP assemblies can be easily controlled by adjusting the $Si(OEt)_4$:$Ti(O^iPr)_4$ ratio in the corresponding precursor solutions. To accelerate the hydrolysis rate of $Si(OEt)_4$, acetic acid (AcOH) was selected as the second acid catalyst to be mixed in the precursor solutions. As a result, the addition of 0.25 mol/L amount of AcOH increased the yields of the corresponding composite NP assemblies with smaller diameters (mini-MARIMO) as well as larger primary particles and induced a higher Si content (Figure 2c).

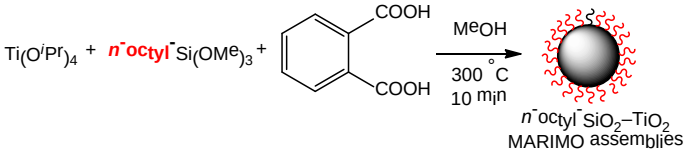

Figure 3. Schematic of synthesis of SiO_2–TiO_2 NP composite.

Controlling the hydrophilic–lipophilic balance (HLB) is one of the most important surface factors. A similar solvothermal reaction of trimethoxy-*n*-octylsilane (*n*-octyl-$Si(OMe)_3$), instead of $Si(OEt)_4$, and $Ti(O^iPr)_4$ in methanol easily afforded hollow spherical assemblies (Figures 2d and Figure 3). To accelerate the reaction rate of *n*-octyl-$Si(OMe)_3$, the addition of the second acid (AcOH or formic acid) is necessary to obtained composite assemblies with higher yield and higher Si content. The effect of the alkyl groups attached on the surface of the spherical NP assemblies was

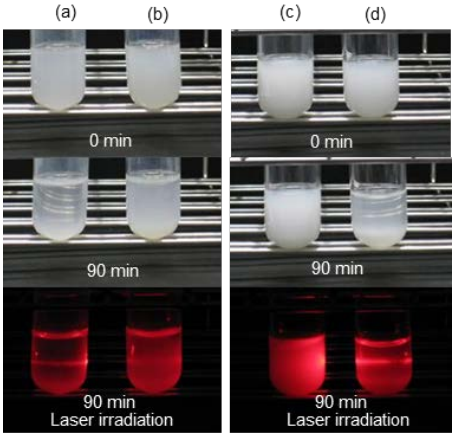

Figure 4. Dispersibility test of (a), (c) TiO_2 MARIMO NP assemblies and (b), (d) *n*-octyl-SiO_2–TiO_2 NPs assemblies in toluene and methanol.

assessed by their dispersibility in toluene and MeOH as representative nonpolar and polar solvents, respectively (Figure 4). Native TiO_2 composite NP assemblies showed good dispensability to polar solvent, methanol, while *n*-octyl–SiO_2–TiO_2 ones exhibited good dispensability to non-polar solvent, toluene. Thus, hydrophilic lipophilic balance of the SiO_2–TiO_2 composite NP assemblies with hollow spherical morphology were easily controlled.

3. A new approach to higher heat tolerance of CeO_2 nanoparticles by mixing with SiO_2 in nano-level through one-pot solvothermal method

Nano-scaled ceria (CeO_2) is a well-known material utilized in wide range of applications especially in catalytic fields due to its high catalytic activity. CeO_2, however, exhibits a poor thermal stability at high temperature or under severe conditions. Herein, I applied our approach to afford SiO_2–CeO_2 NP composites, since SiO_2 is highly attractive material to improve specific surface area and heat tolerance of CeO_2. In a previous part, I mentioned synthesis of the SiO_2–TiO_2 composite NP assemblies. To accelerate the hydrolysis rate of $Si(OEt)_4$ and to obtain homogeneously mixed composite SiO_2–TiO_2 NP assemblies, I proposed to add formic acid to the precursor solution as the acid catalyst. However, the use of formic acid (0.5 mol/L) with $Ce(NO_3)_3 \cdot 6H_2O$ (0.05 mol/L) in methanol resulted in the formation of cerium formate ($Ce(OCHO)_3$) instead of CeO_2. Then, I tried to synthesize SiO_2–CeO_2 composite NP assemblies in the basic conditions using amine to accelerate the hydrolysis of $Si(OEt)_4$ instead of acid catalyst (Figure 5).

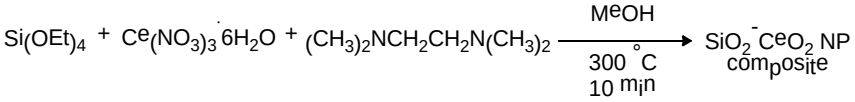

Figure 5. Synthesis of SiO_2–CeO_2 NP composite

In the synthesis of SiO_2–CeO_2 NP composite, a precursor solution containing an equimolar amount of $Si(OEt)_4$ (0.1 mol) and $Ce(NO_3)_3 \cdot 6H_2O$ (0.1 mol), and *N,N,N',N'*-tetramethylethylenediamine (0.2 mol) in methanol (3.5 mL) was slowly heated up to 300 ºC and the temperature was kept for 10 min. Subsequent centrifuge and washing by methanol gave powdery product, 0.5-SiO_2–CeO_2, where the number 0.5 denotes atomic fraction of Si to total amount of Si and Ce atoms in the precursor solution. The obtained material 0.5-SiO_2–CeO_2 is an NP assembly composed by ultrafine primary particles, in which Si and Ce atoms are homogeneously mixed (Figure 6). The specific surface area jumped drastically from 82 m^2/g for CeO_2 itself to

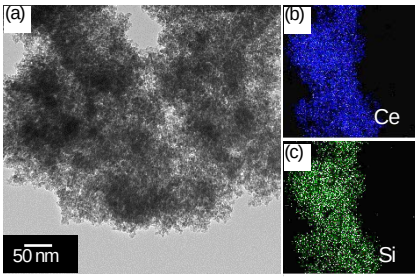

Figure 6. TEM image (a) and EDX mappings (b, c) of the 0.5-SiO_2–CeO_2 composite.

314 m^2/g for 0.5-SiO_2–CeO_2 composite. Similar reactions using precursor solutions with different Si:Ce ratios also afforded homogeneously mixed SiO_2–CeO_2 NP composites.

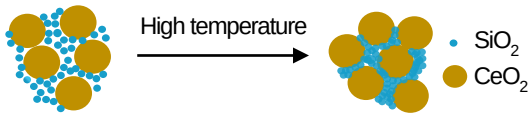

Figure 7. Plausible mechanism for thermal stabilization of SiO_2–CeO_2 composite assemblies.

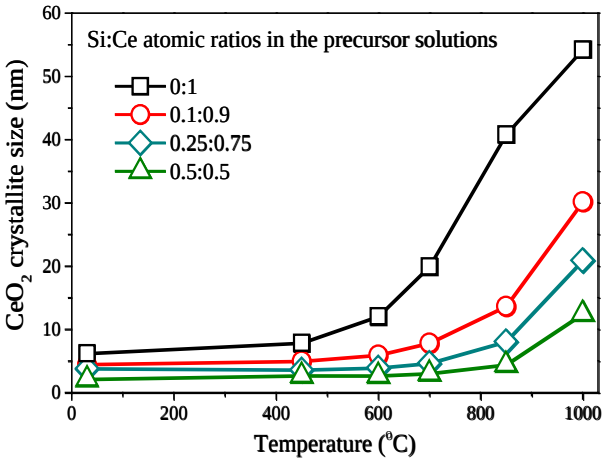

Figure 8. CeO_2 crystallite size change of in SiO_2–CeO_2 composites after calcination at different temperatures for 3 h.

High heat tolerance can be expected for the SiO_2–CeO_2 NP composites since CeO_2 domains are encapsulated by the amorphous SiO_2 matrix even high temperature conditions, where the diffusion of CeO_2 crystallites favorably would be restricted (Figure 7).

To evaluate heat tolerance of CeO_2 in the composites, crystallite sizes of CeO_2 before and after calcination were estimated by Scherrer's equation (Figure 8). Almost no crystallite size change was observed below 600 ºC. Smaller crystallite size change was observed in the cases of SiO_2–CeO_2 NP composites in comparison with that of CeO_2 itself, which indicates that the crystal growth of CeO_2 was suppressed by SiO_2. Especially, CeO_2 crystallite size was almost retained or only slightly enlarged in the case of 0.5-SiO_2–CeO_2 NP composite even under harsh high temperature conditions of 850 ºC for 3 h. Moreover, 0.5-SiO_2–CeO_2 NP composite also exhibited a long-term heat tolerance with almost no sintering of CeO_2 after calcination at 700 ºC for 72 h.

4. Application of the solvothermally prepared nanocomposites as sintering-resistant catalyst supports.

The suppression of thermal sintering of metal nanoparticles and thermal deformation of catalyst supports in supported catalysts are a critical issue in practical use, especially for high-temperature catalytic processes.[3] Due to the fact that the large specific surface area and excellent heat tolerance of catalyst supports are quite suitable for good dispersion and stabilization of catalyst metals, the prepared SiO_2–CeO_2 nanocomposites are potential supports to suppress the sintering of catalyst metals.

For catalyst preparation, the nanocomposites with a 1:1 molar ratio of Si:Ce or Ti:Ce were used. Supported Ru catalysts with an

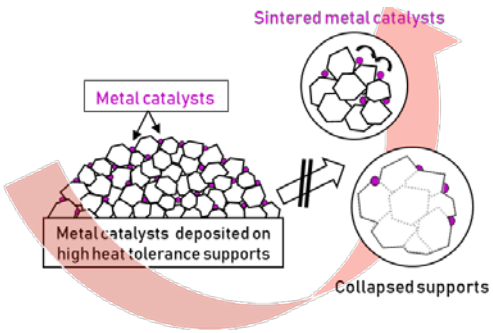

Figure 9. A proposed mechanism for high sintering prevention of metal supported catalysts on solvothermally prepared composites.

intended Ru amount of 3 wt% were prepared by precipitation-deposition method. Ru particle size deposited on the prepared CeO_2, SiO_2-CeO_2 nanocomposite, and TiO_2–CeO_2 nanocomposite was so small (1–2 nm) as compared to that on the commercial CeO_2 (7.7 nm). In addition, specific surface areas of Ru supported catalysts on CeO_2 (Ru/CeO_2) (93 m^2/g), on SiO_2–CeO_2 (Ru/SiO_2–CeO_2) (180 m^2/g), and on TiO_2–CeO_2 (Ru/TiO_2–CeO_2) (177 m^2/g) are much larger than that of Ru/commercial CeO_2 (4.0 m^2/g).

Consequently, the catalyst activity can be kept stable (Figure 9). In order to evaluate the sintering resistance of the catalysts, highly exothermic CO_2 methanation was selected as a probe reaction. The catalytic activity and durability of the prepared catalysts were studied by a three-run experiment in a temperature range of 150–600 °C.

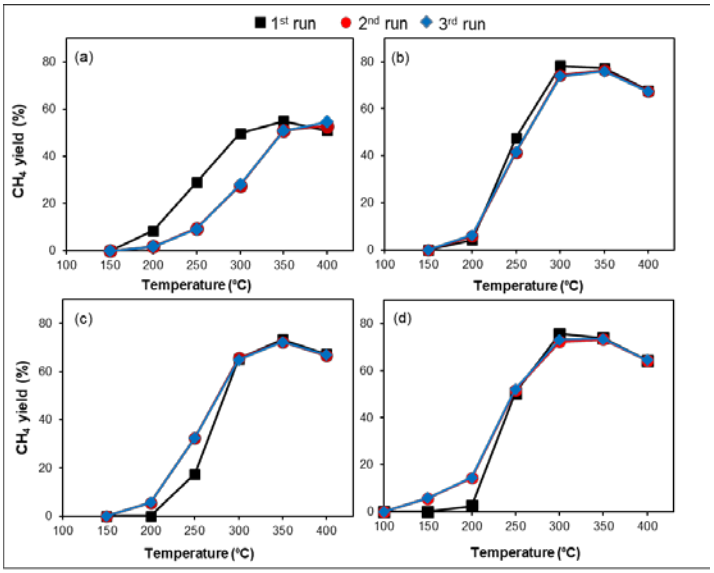

Figure 10. CH_4 production of the three-run test over the catalysts: (a) Ru/commercial CeO_2, (b) Ru/CeO_2, (c) Ru/SiO_2–CeO_2, and (d) Ru/TiO_2–CeO_2.

As shown in Figure 10, the maximum CH_4 yield was achieved at 350 °C to reach 55% over Ru/commercial CeO_2, while higher yields of ca. 80% were obtained in the cases of Ru/CeO_2, Ru/SiO_2–CeO_2, and Ru/TiO_2–CeO_2. When the reaction was repeated twice in the case of Ru/commercial CeO_2, the CH_4 yield profile drastically shifted to a higher temperature; namely, the catalytic activity clearly decreased (Figure 10a). On the contrary, almost no deactivation was observed in the prepared Ru/CeO_2 even after the third run of the reaction (Figure 10b). Interestingly, the low-temperature activity at 150–200 °C was obviously improved in the cases of Ru/SiO_2–CeO_2 and Ru/TiO_2–CeO_2 when the reactions were repeated (Figures 10c and 10d).

After the three-run test under severe conditions, the existence of large-sized Ru nanoparticles with a small amount of much larger Ru nanoparticles (20–30 nm) deposited on the commercial CeO_2 support was observed (Figure 11a). In contrast, the growth of only small Ru nanoparticles was observed in the cases of Ru/SiO_2–CeO_2 and Ru/TiO_2–CeO_2, and the particle size still remained

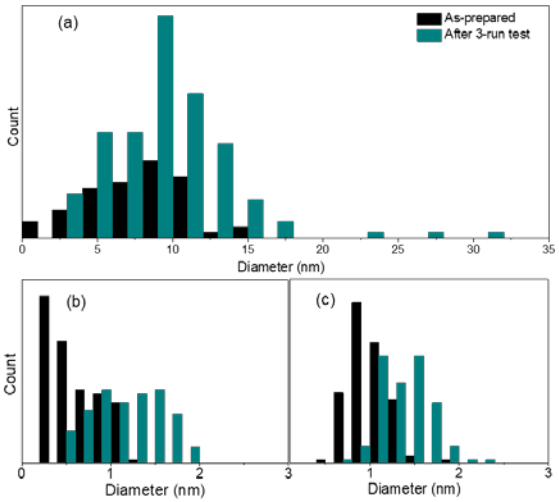

Figure 11. Ru particle size distributions in the as-prepared state and after the three-run test of the catalysts: (a) Ru/commercial CeO_2, (b) Ru/SiO_2–CeO_2, and (c) Ru/TiO_2–CeO_2.

1–2 nm (Figures 11b and 11c). Moreover, no enlargement of the CeO_2 crystallites was observed, revealing the effective sintering suppression of Ru nanoparticles as well as CeO_2 crystallites on/in both SiO_2–CeO_2 and TiO_2–CeO_2 supports.

In order to support the aforementioned discussions further, the stability and durability of the catalysts were confirmed through two different experiments: a 10-cycle test and a long-term experiment. As expected, stable catalytic performances with almost no change in the CH_4 yield between the 1st and the 10th cycles and a constant CH_4 yield over 24 h at 400 °C were achieved for Ru/CeO_2 and Ru/TiO_2–CeO_2. Therefore, the three prepared CeO_2, SiO_2–CeO_2, and TiO_2–CeO_2 nanocomposites were effective supports in enhancing the catalyst activity and durability of the Ru catalysts for CO_2 methanation.

5. Conclusions

The combination of SiO_2 with the other oxides in nanoparticle assemblies has been recognized as difficult because of their different hydrolysis rates of the precursors. However, this study provided the optimal solvothermal conditions to afford the mixed SiO_2–TiO_2 and SiO_2–CeO_2 with the high homogeneity, adjustable compositions, HLB control, high heat tolerance, and large surface area. In addition, the prepared nanocomposites presented high catalytic activity and sinter-stable ability for exothermic methanation of CO_2 at elevated-temperature conditions. Their further applications in other high temperature systems are highly expected.

References

[1] G. Cao, Y. Wang, in *Nanostructures and Nanomaterials: Synthesis, Properties, and Applications*, Vol 2, World Scientific, Singapore, **2011**, 1–17.

[2] P. Wang, K. Kobiro, *Pure Appl. Chem.* **2014**, *86*, 785–800.

[3] T. Hansen, A. Delariva, S. Challa, A. Datye, *Acc. Chem. Res.* **2013**, *46*, 1720−1730.

List of Publications

- Hien Thi Thu Nguyen, Teppei Habu, Masataka Ohtani, Kazuya Kobiro, One-Step Direct Synthesis of SiO_2–TiO_2 Composite Nanoparticle Assemblies with Hollow Spherical Morphology, *European Journal of Inorganic Chemistry* **2017**, 2017, 3017–3023 (Q2). The article was selected as a Very Important Paper by Editors. In addition, a profile, a front cover page, and a video for the paper also were provided.
- Hien Thi Thu Nguyen, Masataka Ohtani, Kazuya Kobiro, One-pot synthesis of SiO_2–CeO_2 nanoparticle composites with enhanced heat tolerance, *Microporous and Mesoporous Materials* **2019**, 273, 35–40 (Q1).
- Another manuscript of "CeO_2 Nanocomposites for Sintering–Resistant Catalyst Supports" submitted to an

appropriate journal.

List of Conferences

International Conferences

- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiro, The 17th Asian Pacific Confederation of Chemical Engineering, August 2017, Hong Kong (Poster).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiro, The 6th International Symposium on Frontier Technology, November 2017, Kochi University of Technology, Japan (Oral).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiro, The 10th International Conference on Supercritical Fluids, December 2017, Nagoya, Japan (Oral).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiro, The 6th International Solvothermal Hydrothermal Association Conference, August 2018, Sendai, Japan (Oral).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiro, The 6th International Solvothermal Hydrothermal Association Conference, August 2018, Sendai, Japan (Poster– **Graduate Student Awards**).

Domestic Conferences

- Hien Thi Thu Nguyen, Teppei Habu, Yuna Umemoto, Yukino Masaoka, Masataka Ohtani, and Kazuya Kobiro, The Chemical Society of Kochi, August 2016, Kochi University (Poster).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiro, Nanotechnology Symposium, November 2016, Kochi University of Technology (Poster).
- Hien Thi Thu Nguyen, Teppei Habu, Yuna Umemoto, Yukino Masaoka, Masataka Ohtani, and Kazuya Kobiro, The 97th CSJ Annual Meeting, March 2017, Yokohama, Japan (Oral).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiro, 第11回触媒道場**,** September 2017, Kochi, Japan (Poster–**Poster Award**).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiro, Nanotechnology Symposium, November 2017, Kochi University of Technology (Poster).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiro, The 98th CSJ Annual Meeting, March 2018, Chiba, Japan (Oral).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiro, The Chemical Society of Kochi, October 2018, Kochi University of Technology (Poster).
- Hien Thi Thu Nguyen, Ryochiro Sakamoto, Kai Kan, Masataka Ohtani, and Kazuya Kobiro, Nanosymposium, November 2018, Kochi University of Technology (Poster).