

# Design and Application of Homogeneously Mixed Oxide Composites in Nano-level

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# 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.<sup>[1]</sup> 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 **micro/meso-porously architected roundly integrated metal oxides (MARIMOs)**.<sup>[2]</sup> Various MARIMO assemblies such as SiO<sub>2</sub>, TiO<sub>2</sub>, ZnO, ZrO<sub>2</sub>, and CeO<sub>2</sub> 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<sub>2</sub>-TiO<sub>2</sub> Composite Nanoparticle Assemblies with Hollow Spherical Morphology

Despite of many inherent excellent properties, TiO<sub>2</sub> 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<sub>2</sub>, since SiO<sub>2</sub> 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<sub>2</sub>-TiO<sub>2</sub> material usually is difficult due to a big different hydrolysis rate of alkoxy silane and alkoxytitanium precursors during the

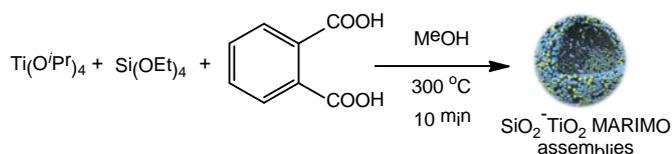


Figure 1. Schematic of synthesis of SiO<sub>2</sub>-TiO<sub>2</sub> NP composite

hydrolysis. In this study, I applied our approach to obtain homogeneous SiO<sub>2</sub>-TiO<sub>2</sub> composite NP assemblies with and without alkyl groups having hollow morphology by controlling the hydrolysis rate of the precursors in solvothermal reactions.

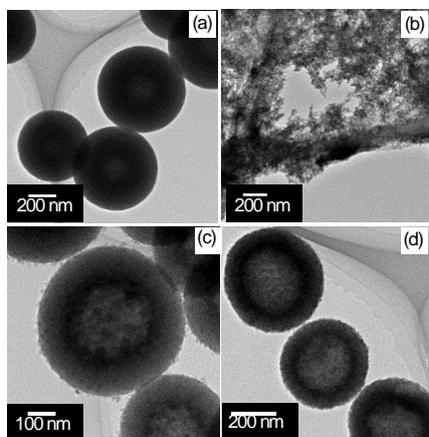


Figure 2. TEM images of (a) SiO<sub>2</sub>-TiO<sub>2</sub> NPs, (b) SiO<sub>2</sub> agglomerates, (c) SiO<sub>2</sub>-TiO<sub>2</sub> NPs formed in the presence of AcOH, and (d) Modified SiO<sub>2</sub>-TiO<sub>2</sub> NPs

In the synthesis of SiO<sub>2</sub>-TiO<sub>2</sub> NP assemblies (Figure 1), a precursor solution containing an equimolar amount of Si(OEt)<sub>4</sub> and Ti(O<sup>i</sup>Pr)<sub>4</sub> yielded NP assemblies with a beautiful hollow spherical morphology as expected (Figure 2a). Similar reactions of precursor solutions containing low amounts of Si(OEt)<sub>4</sub> also resulted in composite NP assemblies with hollow spherical morphologies, while higher amounts of Si(OEt)<sub>4</sub> 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)<sub>4</sub> amount. Those results indicate that the Si:Ti ratio in the composite NP assemblies can be easily controlled by adjusting the Si(OEt)<sub>4</sub>:Ti(O<sup>i</sup>Pr)<sub>4</sub> ratio in the corresponding precursor solutions. To accelerate the hydrolysis rate of Si(OEt)<sub>4</sub>, 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).

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)<sub>3</sub>), instead of Si(OEt)<sub>4</sub>, and Ti(O<sup>i</sup>Pr)<sub>4</sub> in methanol easily afforded hollow spherical assemblies (Figures 2d and Figure 3). To accelerate the reaction rate of *n*-octyl-Si(OMe)<sub>3</sub>, the addition of the second acid (AcOH or formic acid) is necessary to obtain 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

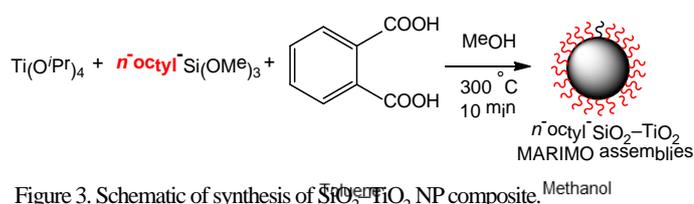


Figure 3. Schematic of synthesis of SiO<sub>2</sub>-TiO<sub>2</sub> NP composite.

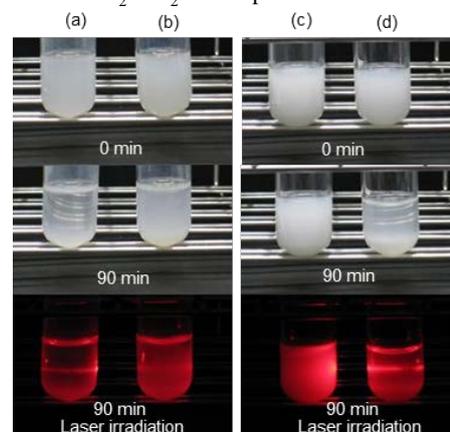


Figure 4. Dispersibility test of (a), (c) TiO<sub>2</sub> MARIMO NP assemblies and (b), (d) *n*-octyl-SiO<sub>2</sub>-TiO<sub>2</sub> NPs assemblies in toluene and methanol.

assessed by their dispersibility in toluene and MeOH as representative nonpolar and polar solvents, respectively (Figure 4). Native TiO<sub>2</sub> composite NP assemblies showed good dispersibility to polar solvent, methanol, while *n*-octyl-SiO<sub>2</sub>-TiO<sub>2</sub> ones exhibited good dispersibility to non-polar solvent, toluene. Thus, hydrophilic lipophilic balance of the SiO<sub>2</sub>-TiO<sub>2</sub> composite NP assemblies with hollow spherical morphology were easily controlled.

### 3. A new approach to higher heat tolerance of CeO<sub>2</sub> nanoparticles by mixing with SiO<sub>2</sub> in nano-level through one-pot solvothermal method

Nano-scaled ceria (CeO<sub>2</sub>) is a well-known material utilized in wide range of applications especially in catalytic fields due to its high catalytic activity. CeO<sub>2</sub>, however, exhibits a poor thermal stability at high temperature or under severe conditions. Herein, I applied our approach to afford SiO<sub>2</sub>-CeO<sub>2</sub> NP composites, since SiO<sub>2</sub> is highly attractive material to improve specific surface area and heat tolerance of CeO<sub>2</sub>. In a previous part, I mentioned synthesis of the SiO<sub>2</sub>-TiO<sub>2</sub> composite NP assemblies. To accelerate the hydrolysis rate of Si(OEt)<sub>4</sub> and to obtain homogeneously mixed composite SiO<sub>2</sub>-TiO<sub>2</sub> 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<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.05 mol/L) in methanol resulted in the formation of cerium formate (Ce(OCHO)<sub>3</sub>) instead of CeO<sub>2</sub>. Then, I tried to synthesize SiO<sub>2</sub>-CeO<sub>2</sub> composite NP assemblies in the basic conditions using amine to accelerate the hydrolysis of Si(OEt)<sub>4</sub> instead of acid catalyst (Figure 5).

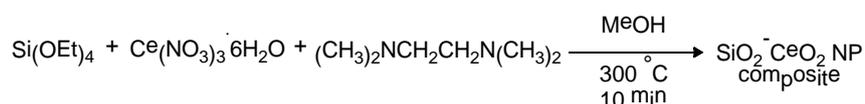


Figure 5. Synthesis of SiO<sub>2</sub>-CeO<sub>2</sub> NP composite

In the synthesis of SiO<sub>2</sub>-CeO<sub>2</sub> NP composite, a precursor solution containing an equimolar amount of Si(OEt)<sub>4</sub> (0.1 mol) and Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (0.1 mol), and *N,N,N',N'*-tetramethylethylenediamine (0.2 mol) in methanol (3.5 mL) was slowly heated up to 300 °C and the temperature was kept for 10 min. Subsequent centrifuge and washing by methanol gave powdery product, 0.5-SiO<sub>2</sub>-CeO<sub>2</sub>, where the number 0.5 denotes

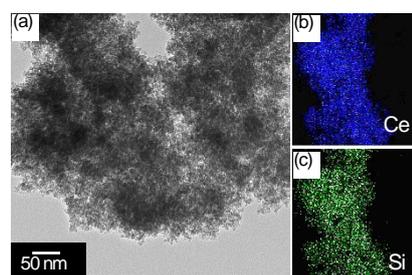


Figure 6. TEM image (a) and EDX mappings (b, c) of the 0.5-SiO<sub>2</sub>-CeO<sub>2</sub> composite.

atomic fraction of Si to total amount of Si and Ce atoms in the precursor solution. The obtained material 0.5-SiO<sub>2</sub>-CeO<sub>2</sub> 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<sup>2</sup>/g for CeO<sub>2</sub> itself to

314 m<sup>2</sup>/g for 0.5-SiO<sub>2</sub>-CeO<sub>2</sub> composite. Similar reactions using precursor solutions with different Si:Ce ratios also afforded homogeneously mixed SiO<sub>2</sub>-CeO<sub>2</sub> NP composites.

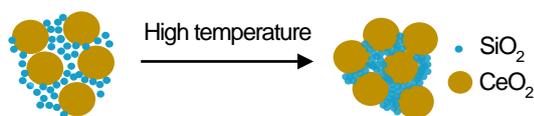


Figure 7. Plausible mechanism for thermal stabilization of SiO<sub>2</sub>-CeO<sub>2</sub> composite assemblies.

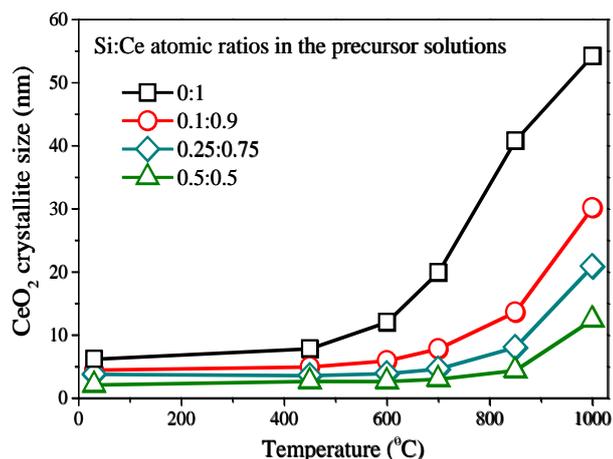


Figure 8. CeO<sub>2</sub> crystallite size change of in SiO<sub>2</sub>-CeO<sub>2</sub> composites after calcination at different temperatures for 3 h.

High heat tolerance can be expected for the SiO<sub>2</sub>-CeO<sub>2</sub> NP composites since CeO<sub>2</sub> domains are encapsulated by the amorphous SiO<sub>2</sub> matrix even high temperature conditions, where the diffusion of CeO<sub>2</sub> crystallites favorably would be restricted (Figure 7).

To evaluate heat tolerance of CeO<sub>2</sub> in the composites, crystallite sizes of CeO<sub>2</sub> before and after calcination were estimated by Scherrer's equation (Figure 8). Almost no crystallite size change was observed below 600 °C. Smaller crystallite size change was observed in the cases of SiO<sub>2</sub>-CeO<sub>2</sub> NP composites in comparison with that of CeO<sub>2</sub> itself, which indicates that the crystal growth of CeO<sub>2</sub> was suppressed by SiO<sub>2</sub>. Especially, CeO<sub>2</sub> crystallite size was almost retained or only slightly enlarged in the

case of 0.5-SiO<sub>2</sub>-CeO<sub>2</sub> NP composite even under harsh high temperature conditions of 850 °C for 3 h. Moreover, 0.5-SiO<sub>2</sub>-CeO<sub>2</sub> NP composite also exhibited a long-term heat tolerance with almost no sintering of CeO<sub>2</sub> after calcination at 700 °C 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.<sup>[3]</sup> 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<sub>2</sub>-CeO<sub>2</sub> 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

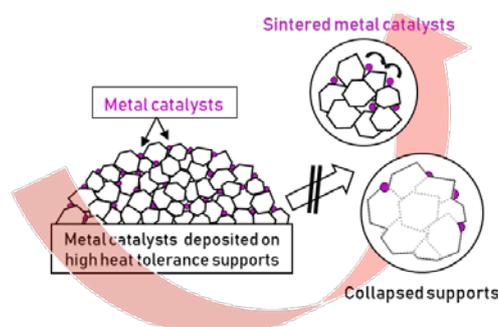


Figure 9. A proposed mechanism for high sintering prevention of metal supported catalysts on solvothermally prepared composites.

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

Consequently, the catalyst activity can be kept stable (Figure 9). In order to evaluate the sintering resistance of the catalysts, highly exothermic CO<sub>2</sub> 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.

As shown in Figure 10, the maximum CH<sub>4</sub> yield was achieved at 350 °C to reach 55% over Ru/commercial CeO<sub>2</sub>, while higher yields of ca. 80% were obtained in the cases of Ru/CeO<sub>2</sub>, Ru/SiO<sub>2</sub>-CeO<sub>2</sub>, and Ru/TiO<sub>2</sub>-CeO<sub>2</sub>. When the reaction was repeated twice in the case of Ru/commercial CeO<sub>2</sub>, the CH<sub>4</sub> 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<sub>2</sub> 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<sub>2</sub>-CeO<sub>2</sub> and Ru/TiO<sub>2</sub>-CeO<sub>2</sub> 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<sub>2</sub> support was observed (Figure 11a). In contrast, the growth of only small Ru nanoparticles was observed in the cases of Ru/SiO<sub>2</sub>-CeO<sub>2</sub> and Ru/TiO<sub>2</sub>-CeO<sub>2</sub>, and the particle size still remained

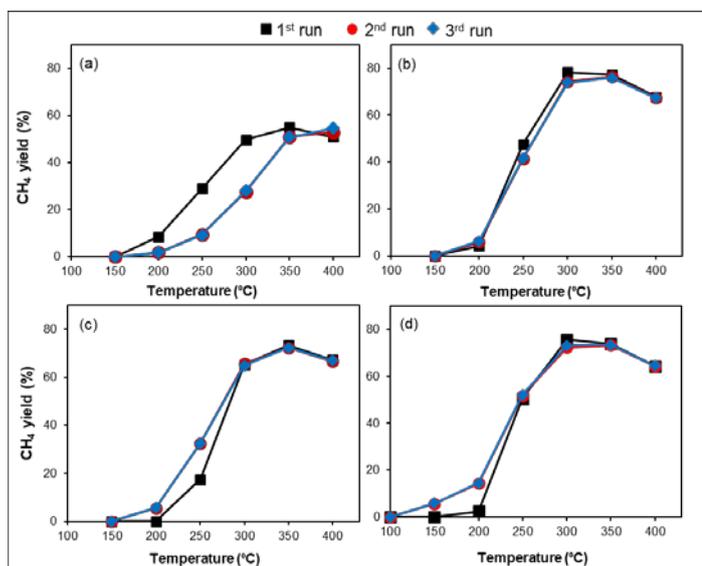


Figure 10. CH<sub>4</sub> production of the three-run test over the catalysts: (a) Ru/commercial CeO<sub>2</sub>, (b) Ru/CeO<sub>2</sub>, (c) Ru/SiO<sub>2</sub>-CeO<sub>2</sub>, and (d) Ru/TiO<sub>2</sub>-CeO<sub>2</sub>.

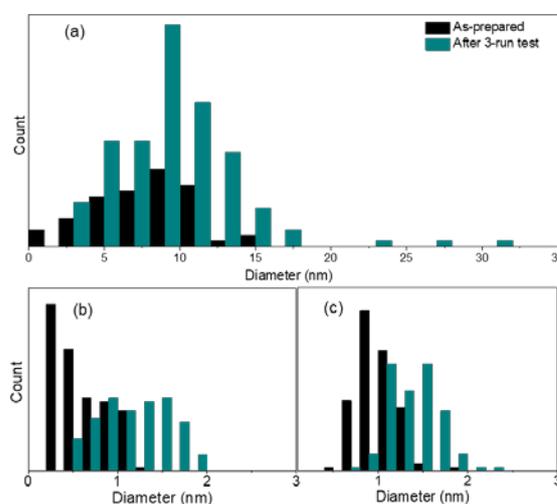


Figure 11. Ru particle size distributions in the as-prepared state and after the three-run test of the catalysts: (a) Ru/commercial CeO<sub>2</sub>, (b) Ru/SiO<sub>2</sub>-CeO<sub>2</sub>, and (c) Ru/TiO<sub>2</sub>-CeO<sub>2</sub>.

1–2 nm (Figures 11b and 11c). Moreover, no enlargement of the CeO<sub>2</sub> crystallites was observed, revealing the effective sintering suppression of Ru nanoparticles as well as CeO<sub>2</sub> crystallites on/in both SiO<sub>2</sub>–CeO<sub>2</sub> and TiO<sub>2</sub>–CeO<sub>2</sub> 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<sub>4</sub> yield between the 1<sup>st</sup> and the 10<sup>th</sup> cycles and a constant CH<sub>4</sub> yield over 24 h at 400 °C were achieved for Ru/CeO<sub>2</sub> and Ru/TiO<sub>2</sub>–CeO<sub>2</sub>. Therefore, the three prepared CeO<sub>2</sub>, SiO<sub>2</sub>–CeO<sub>2</sub>, and TiO<sub>2</sub>–CeO<sub>2</sub> nanocomposites were effective supports in enhancing the catalyst activity and durability of the Ru catalysts for CO<sub>2</sub> methanation.

## 5. Conclusions

The combination of SiO<sub>2</sub> 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<sub>2</sub>–TiO<sub>2</sub> and SiO<sub>2</sub>–CeO<sub>2</sub> 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<sub>2</sub> 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. Kobi, *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 Kobi, One-Step Direct Synthesis of SiO<sub>2</sub>–TiO<sub>2</sub> 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 Kobi, One-pot synthesis of SiO<sub>2</sub>–CeO<sub>2</sub> nanoparticle composites with enhanced heat tolerance, *Microporous and Mesoporous Materials* **2019**, *273*, 35–40 (Q1).
- Another manuscript of “CeO<sub>2</sub> Nanocomposites for Sintering–Resistant Catalyst Supports” submitted to an

appropriate journal.

## List of Conferences

### *International Conferences*

- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiros, The 17<sup>th</sup> Asian Pacific Confederation of Chemical Engineering, August 2017, Hong Kong (Poster).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiros, The 6<sup>th</sup> International Symposium on Frontier Technology, November 2017, Kochi University of Technology, Japan (Oral).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiros, The 10<sup>th</sup> International Conference on Supercritical Fluids, December 2017, Nagoya, Japan (Oral).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiros, The 6<sup>th</sup> International Solvothermal Hydrothermal Association Conference, August 2018, Sendai, Japan (Oral).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiros, The 6<sup>th</sup> 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 Kobiros, The Chemical Society of Kochi, August 2016, Kochi University (Poster).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiros, Nanotechnology Symposium, November 2016, Kochi University of Technology (Poster).
- Hien Thi Thu Nguyen, Teppei Habu, Yuna Umemoto, Yukino Masaoka, Masataka Ohtani, and Kazuya Kobiros, The 97<sup>th</sup> CSJ Annual Meeting, March 2017, Yokohama, Japan (Oral).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiros, 第11回触媒道場, September 2017, Kochi, Japan (Poster–**Poster Award**).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiros, Nanotechnology Symposium, November 2017, Kochi University of Technology (Poster).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiros, The 98<sup>th</sup> CSJ Annual Meeting, March 2018, Chiba, Japan (Oral).
- Hien Thi Thu Nguyen, Masataka Ohtani, and Kazuya Kobiros, The Chemical Society of Kochi, October 2018, Kochi University of Technology (Poster).
- Hien Thi Thu Nguyen, Ryochiro Sakamoto, Kai Kan, Masataka Ohtani, and Kazuya Kobiros, Nanosymposium, November 2018, Kochi University of Technology (Poster).