

# 論文内容の要旨

## 1. Introduction

Metal oxides generally have high thermal and chemical stability due to their rigid and dense structure, but are therefore almost inert in their bulk. For this reason, metal oxides in practical use are functionalized by various means such as nanoparticulation, porosity, and compositing. In addition, many functional materials are composites consisting of two or more components, such as supported metal catalysts and solid solutions, where their composite states greatly affect the performance of the materials. In general, the further contacts of the components in the materials result in the higher performance of the materials. Then, it is desirable to have fine and homogeneous composite states of the functional composites. Therefore, it is very important to establish a simple synthetic technique for such materials and to create functional metal oxides with desirable structures for specific purposes. In this study, I aimed at developing a simple synthetic method for porous metal oxides and composites with highly controlled structure such as morphology, structure, composition, and valence state, by the solvothermal method.

## 2. $\text{Ce}^{3+}$ -enriched Spherical Porous Ceria with an Enhanced Oxygen Storage Capacity

Cerium oxide ( $\text{CeO}_{2-x}$ , ceria) has a unique redox cycle with storage and release of oxygen concomitant with a reversible change in valence states of  $\text{Ce}^{4+}$  and  $\text{Ce}^{3+}$ .  $\text{CeO}_{2-x}$  has been used as catalysts and catalyst supports in a variety of catalytic reactions. The amount of oxygen absorbed and released by a unit amount of  $\text{CeO}_{2-x}$  is defined as the oxygen storage capacity, which is one of the important factors used to evaluate the performance of  $\text{CeO}_{2-x}$ . The oxygen defects ( $\text{Ce}^{3+}$  sites) in  $\text{CeO}_{2-x}$  are one of the most important factors in the performance of  $\text{CeO}_{2-x}$ -based catalysts and are believed to enhance the oxygen storage capacity as well as the low-temperature activity of the catalysts.<sup>1</sup> In this study, the development of the synthetic method of porous  $\text{CeO}_{2-x}$  spheres with high specific surface area and  $\text{Ce}^{3+}$  content was aimed.

Monodispersed spherical  $\text{CeO}_{2-x}$  was obtained by a simple one-pot and single-step solvothermal reaction using

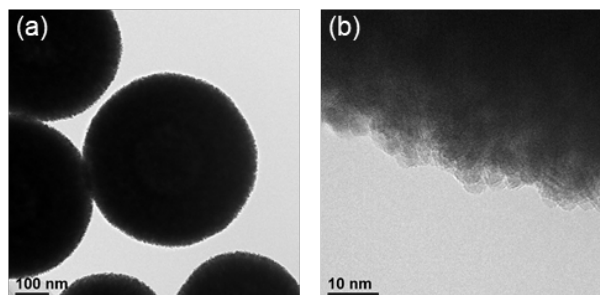


Figure 1. TEM images of porous  $\text{CeO}_{2-x}$  spheres. Low (a) and high (b) magnification.

acetonitrile (MeCN) as a solvent and triethylene glycol with reducing ability as an additive. The resulting  $\text{CeO}_{2-x}$  formed spherical secondary particles by aggregation of nanometer-sized primary particles, and

Table 1. Crystallite size and  $\text{Ce}^{3+}$  ratio of  $\text{CeO}_{2-x}$  synthesized in reactions using different ratios of  $\text{H}_2\text{O}/\text{MeCN}$ .

Entry	$\text{H}_2\text{O} / \text{MeCN} (\text{v/v})$	Crystallite size /nm	$\text{Ce}^{3+}$ ratio /at%
1	0 / 100	3.3	57.4
2	30 / 70	6.8	36.7
3	70 / 30	10.2	36.3
4	100 / 0	21.4	22.6

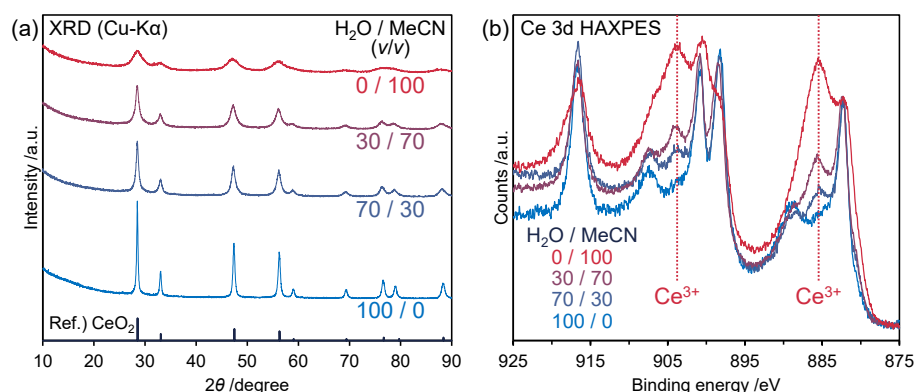


Figure 2. XRD patterns (a) and HAXPES spectra (b) of  $\text{CeO}_{2-x}$  obtained by the reactions using different ratios of  $\text{H}_2\text{O}/\text{MeCN}$ .

nano-concave-convex structures derived from the primary particles were formed on the surface (Figure 1). In order to investigate the performance of porous  $\text{CeO}_{2-x}$  spheres as catalyst supports,  $\text{Pt}/\text{CeO}_{2-x}$  catalyst was prepared and applied as catalysts for CO oxidation reactions. As a result,  $\text{Pt}/\text{CeO}_{2-x}$  showed superior low-temperature activity than that of the reference catalyst using reference  $\text{CeO}_2$  as a support. In addition, the  $\text{CeO}_{2-x}$  spheres themselves also showed better low-temperature activity for CO oxidation than the reference catalyst  $\text{CeO}_2$ . To elucidate the origin of the unexpected catalytic activity of  $\text{CeO}_{2-x}$  spheres, the valences of the Ce ions in the  $\text{CeO}_{2-x}$  were assessed using hard X-ray photoelectron spectroscopy (HAXPES) analysis. The HAXPES analysis of the  $\text{CeO}_{2-x}$  spheres revealed that the  $\text{CeO}_{2-x}$  spheres have stable  $\text{Ce}^{3+}$  species in an extremely high concentration (57.4 at%), more than twice that of conventional  $\text{CeO}_2$ . The small crystallite size of the  $\text{CeO}_{2-x}$  spheres could be one reason for the existence of an appreciable amount of  $\text{Ce}^{3+}$  in their nanocrystals,<sup>2</sup> and the existence of a lot of  $\text{Ce}^{3+}$  would be the reason for their superior catalytic performance. The presence of  $\text{H}_2\text{O}$  in the solvent would be expected to increase the crystallite size and correspondingly decrease the  $\text{Ce}^{3+}$  content. In other words, the  $\text{Ce}^{3+}$  content can be controlled by controlling the crystallite size. To test the hypothesis, mixtures of MeCN and  $\text{H}_2\text{O}$  were applied as the reaction media in solvothermal reaction (Table 1). As a result, crystallite size of  $\text{CeO}_{2-x}$  can be increased from 3.3 nm to 21.4 nm by increasing  $\text{H}_2\text{O}$  ratio, and found that the ratio of  $\text{Ce}^{3+}$  decreased with increasing crystallite diameter (Table 1 and Figure 2). Thus, the  $\text{Ce}^{3+}/\text{Ce}^{4+}$  ratio in the  $\text{CeO}_{2-x}$  spheres could be readily adjusted by varying the  $\text{H}_2\text{O}/\text{MeCN}$  ratio. Furthermore, the oxygen storage capacity of the  $\text{CeO}_{2-x}$  spheres was found to

be  $268 \mu\text{mol-O g}^{-1}$ , more than twice that of the reference  $\text{CeO}_2$ . This would be due to the high concentration of  $\text{Ce}^{3+}$  species in the  $\text{CeO}_{2-x}$  spheres.

### 3. Insights into the Solvothermal Reaction for Synthesizing Tin(IV) Oxide Porous Spheres

Tin oxide ( $\text{SnO}_2$ ) is a typical n-type semiconductor oxide but exhibits relatively high electrical conductivity compared with other metal oxides<sup>1</sup> and has practical applications as a semiconductor for gas sensors. Recently, it is expected to be used as a support for electrocatalysts in polymer electrolyte fuel cells. In such cases, the oxide must exhibit a high specific surface area and good electrical conductivity. Specifically,  $\text{SnO}_2$  supports having increased surface areas with porous structures provide greater collision frequencies with the substrate as well as higher mass diffusion rates that accelerate reactions at the electrodes. Doping with heteroatoms (including P, Nb, and Sb) also improves the electrical conductivity of the oxide, and a number of different  $\text{SnO}_2$ -based materials have been studied. Various  $\text{SnO}_2$ -based composites have been produced under different conditions with different techniques,<sup>3</sup> while no simple reaction affording  $\text{SnO}_2$ -based materials modified with different elements by one-pot and single-step procedure was reported to my best knowledge. In this study, I aimed to develop a versatile single-step synthetic method of  $\text{SnO}_2$ -based composites by solvothermal reaction.

First, the reaction conditions were optimized to obtain porous  $\text{SnO}_2$ . The effects of metal sources, solvents, additives, and heating conditions on the composition, crystal structure, and morphology of the product were investigated in detail. When  $^n\text{Bu}_2\text{Sn}(\text{OAc})_2$  was used as the Sn source material,  $\text{SnO}_2$ ,  $\text{SnO}$ , and  $\text{Sn}_6\text{O}_4(\text{OH})_4$  were afforded as products depending on the reaction parameters that were employed, such as the solvent and temperature. Finally, a simple one-pot technique using  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  as the Sn source, triethylene glycol as an additive, and methanol as a solvent readily produced porous  $\text{SnO}_2$  spheres (Figure 3).  $\text{SnO}_2$  spheres possessed a highly-ordered spherical structure based on the aggregation of nanometer-sized primary particles, and the spheres were porous with a high specific surface area of more than  $200 \text{ m}^2 \text{ g}^{-1}$  as-synthesized and  $100 \text{ m}^2 \text{ g}^{-1}$  after calcination at  $400^\circ\text{C}$ . The electrical conductivity was  $7.67 \times 10^{-1} \text{ S cm}^{-1}$ , which equaled or exceeded that of commercially available  $\text{SnO}_2$  ( $1.98 \times 10^{-2} \text{ S cm}^{-1}$ ). The optimized reaction conditions for the synthesis of porous  $\text{SnO}_2$  spheres were subsequently used to fabricate various  $\text{SnO}_2$ -based composites. Using a similar procedure, different  $\text{SnO}_2$  composites with one or two different elements (P, V, Nb, Pd, Ir, and Pt) were obtained from the precursor

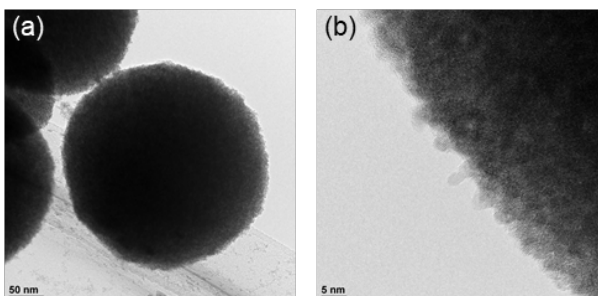


Figure 3. TEM images of porous  $\text{SnO}_2$  spheres. Low (a) and high (b) magnification.

solutions under optimum conditions (Figure 4). The obtained SnO<sub>2</sub>-based composites mainly formed spherical secondary particles, and TEM/EDX analysis revealed that the additional elements were uniformly distributed throughout the porous particles at the nanometer scale. The specific surface areas of these calcined (400 °C) composites were at least 90 m<sup>2</sup> g<sup>-1</sup>. Thus, a facile, versatile, and useful technique for the synthesis of porous SnO<sub>2</sub>-based composites was developed.

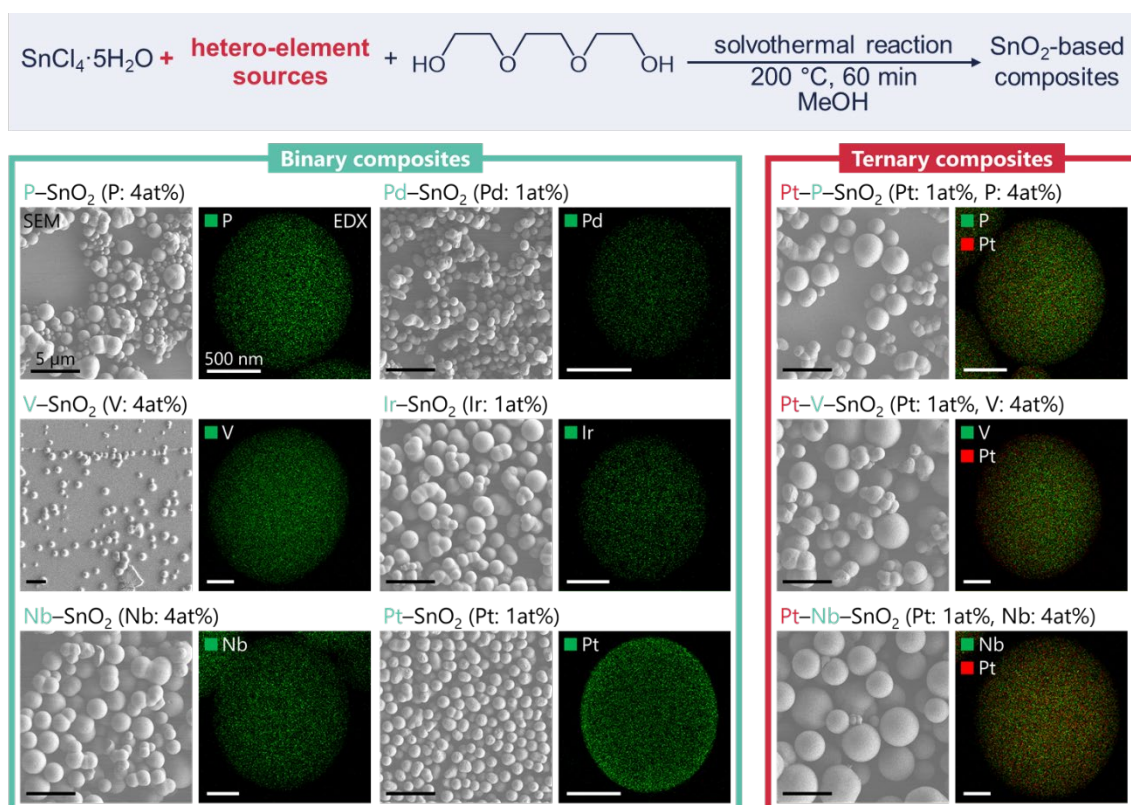


Figure 4. Synthetic scheme and SEM and EDX mapping images of nine-type SnO<sub>2</sub>-based composites.

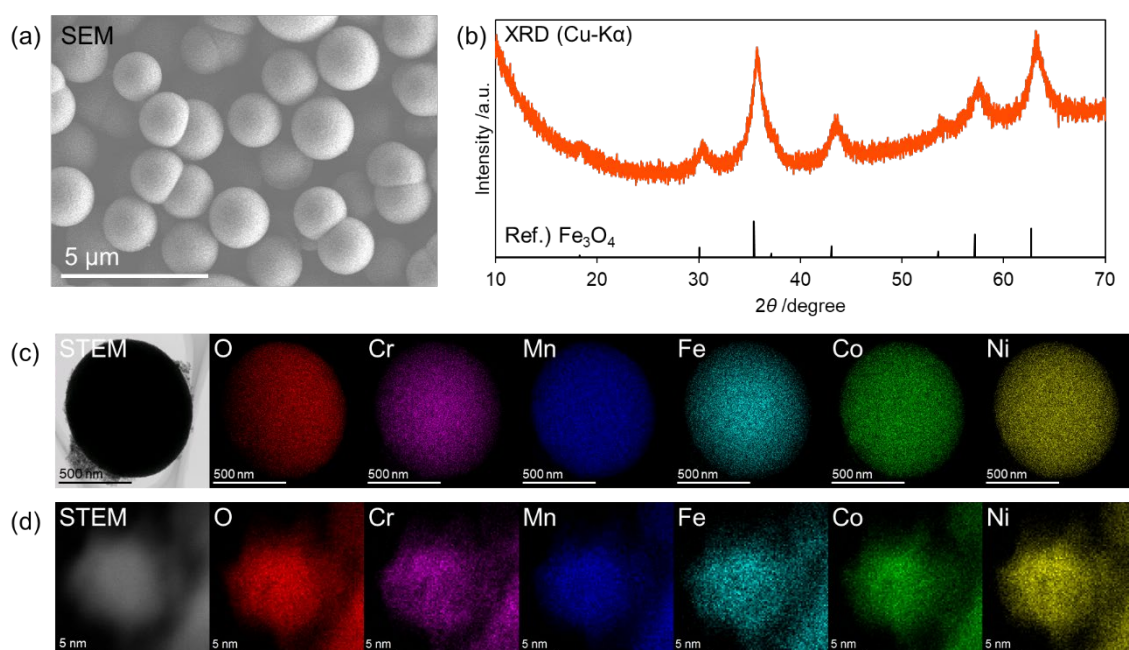


Figure 5. SEM image of as-synthesized HE-MARIMO (before calcination, a). XRD pattern (b) and STEM and EDX mapping images (c,d) of HE-MARIMO (after calcination). (c) and (d) show spherical secondary particle and primary particle, respectively.

#### 4. Low-Temperature Synthesis of Porous High-Entropy (Co<sub>0.2</sub>Cr<sub>0.2</sub>Fe<sub>0.2</sub>Mn<sub>0.2</sub>Ni<sub>0.2</sub>)<sub>3</sub>O<sub>4</sub> Spheres and Their Application to Reverse Water-Gas Shift Reaction as Catalysts

High-entropy oxides (HEOs), which are defined as single-phase solid solutions containing equimolar amounts of more than five cations, are attracting much attention. Research on the application of HEOs to battery and electrode materials has been actively carried out recently,<sup>4</sup> while their use for thermal catalysts and other applications has been limited. The reason would be the difficulty in producing HEOs with porous structures with large specific surface area (small crystallite size). Typically, high-temperature methods (around 1000 °C) have been used to form HEOs as a single-phase solid solution, such as standard solid-state synthesis and spray pyrolysis,<sup>5</sup> resulting in large particles with low specific surface area. The synthesis of HEOs with small crystallite size by low-temperature approach is an important issue to improve their catalytic activity and expand their availability for wide applications. However, research on low-temperature synthesis of HEOs has not yet been fully investigated. Previously, various metal oxide composites with porous and spherical structures (SiO<sub>2</sub>-TiO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub>, CoFeMnO<sub>x</sub>, etc.) were synthesized by one-pot and single-step solvothermal reactions using non-aqueous solvents. I considered that synthesis of HEOs would be possible by utilizing previous experience in the solvothermal synthesis of porous metal oxides, called “MARIMO” (**m**icro/**m**esoporously **a**rchitected **r**oundly **i**ntegrated **m**etal **o**xides).

Here, a porous high-entropy  $(\text{Co}_{0.2}\text{Cr}_{0.2}\text{Fe}_{0.2}\text{Mn}_{0.2}\text{Ni}_{0.2}\text{O})_3\text{O}_4$  sphere (named HE-MARIMO) with spinel structure was synthesized by low-temperature (below 500 °C) approach involving solvothermal reaction followed by calcination. HE-MARIMO formed spherical higher-order structures (Figure 5a,c) and showed single-phase spinel structure (Figure 5b). STEM and EDX mapping images of HE-MARIMO (Figure 5d) revealed that five cations were homogeneously distributed in primary particles. Thus, based on XRD pattern and STEM/EDX analyses, the HE-MARIMO formed a high-entropy oxide with a single-phase spinel structure by low-temperature method. Besides, five kinds of quaternary MARIMOs (Cr-free, Mn-free, Fe-free, Co-free, and Ni-free MARIMOs) with one missing element were also easily synthesized by simply changing the metal sources used in the precursor solution of the solvothermal reaction. Obtained MARIMOs have a small crystallite size of <8 nm and a well-constructed porous higher-order structure derived from small primary particles. HE-MARIMO, quaternary MARIMOs, and a reference composite (prepared by standard solid-state reaction with corresponding metal oxides at 500 °C, which did not afford solid solution in such mild conditions) were applied to the catalysts for reverse water-gas shift (RWGS) reaction (Figure 6a–d). As a result, HE-MARIMO showed higher catalytic activity, product selectivity, and long-term stability than a reference composite prepared by solid-state synthesis. The catalytic tests of quaternary MARIMOs also revealed the difference in catalytic performance between Cr-free and other quaternary MARIMOs. XRD analyses of the spent catalysts revealed that the transformation of spinel structure to rock-salt structure in Cr-free MARIMO indicated the important contribution of Cr to stabilize the spinel crystal structure (Figure 6e).

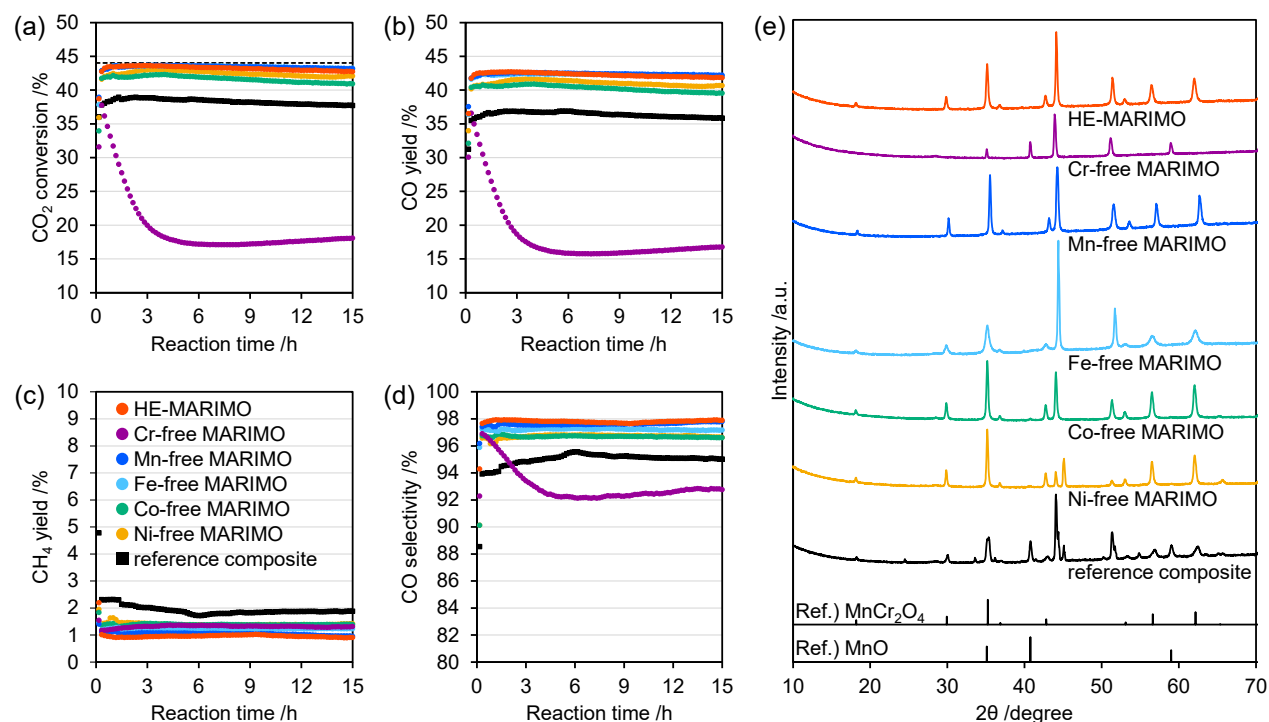


Figure 6. Catalytic performance of MARIMOs and the reference composite for the RWGS reaction. CO<sub>2</sub> conversion (a), CO yield (b), CH<sub>4</sub> yield (c), and CO selectivity (d) at 700 °C for 15 h (H<sub>2</sub>/CO<sub>2</sub> ratio of 1:1). XRD patterns of the spent MARIMOs and spent reference composite (e).

## 6. References

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