Synthesis of brownmillerite $Ca_2Fe_{2-x}Co_xO_5$ ultrafine particles with nano metric dimension on titanium dioxide surface by reverse micelle method

Ryosuke Nanbu*,[a] **Takeyuki Watanabe,**[a] **Etsushi Tsuji,**[a] **Satoshi Suganuma,**[b] **Naonobu Katada**[a]
[a]*Department of Chemistry and Biotechnology, Tottori University, Tottori, 680-8552, Japan*
[b]*Center for Research on Green Sustainable Chemistry, Tottori, 680-8552, Japan*
**Corresponding author: Fax number +81-857-31-5684 E-mail address lyxwhf4s@gmail.com*

Abstract: Brownmillerite type Ca_2FeCoO_5 ultrafine particles were synthesized by a reverse micelle (RM) method. The particle size of Ca_2FeCoO_5 loaded on TiO_2 by the RM method was 5-10 nm. The size of particles prepared in the absence of TiO_2 support was 30 nm, indicating that aggregation of Ca_2FeCoO_5 precursor was suppressed by interaction with TiO_2 surface.

Keywords: brownmillerite, reverse micelle method, ultrafine particles

1. Introduction

Photocatalytic water splitting is one of promising methods for hydrogen production without carbon dioxide emission. However, the energy conversion efficiency of the reaction has been limited by the overpotential of oxygen evolution reaction (OER). Thereby, development of efficient cocatalyst for OER has strongly been demanded. Noble metal oxides such as RuO_2 and IrO_2 have been known to exhibit high activity for OER[1]. Recently we found that Ca_2FeCoO_5 with brownmillerite (BM)-type crystal structure, i.e., perovskite-related structure with oxygen deficient, possessed remarkably high OER activity, even if it was compared to the noble metal oxides[2]. In this previous study[2], preparation of the BM-type Ca_2FeCoO_5 was carried out by means of a sol-gel method, and the particle size was 30-40 nm. For apply the BM Ca_2FeCoO_5 to a cocatalyst of typical photocatalyst TiO_2, usually possessing the particle size in several hundreds of nanometers, ultrafine particles smaller than 5-10 nm are desired to achieve the sufficient contact area. Perovskite-type $LaMnO_3$ had been reported to form nanoparticles on carbon nanoparticles by means of a reverse micelle (RM) method[3]. Based on these backgrounds, we here apply the RM method to synthesize ultrafine particles of BM-type $Ca_2Fe_{2-x}Co_xO_5$ ($0 \leqq x \leqq 1$) with nanometric dimension on the TiO_2 surface.

2. Experimental

An aqueous solution of stoichiometric mixture of $Ca(NO_3)_2$, $Fe(NO_3)_3$ and $Co(NO_3)_2$ was titrated into a mixture of cyclohexane and hexaethyleneglycol nonylphenyl ether (NP-6) chilled by a water bath at 10 ºC to obtain a RM solution. On the other hand, another RM solution was prepared from cyclohexane, NP-6 and 10% tetramethylammonium hydroxide (TMAH) aqueous solution. These RM solutions were mixed and stirred for 1 h at 10 ºC. After ultrasonication, TiO_2 powders dispersed in cyclohexane was added and stirred for 15 min at room temperature. Then, excess ethanol was added to break the RM. The formed precipitates were collected, dried at 110 ºC for overnight and calcined at 600 ºC for 5 h in air.

The crystallinity was determined by the intensity of X-ray diffraction (XRD, RIGAKU Ultima IV). The morphology, particle size and chemical composition were analyzed using transmission microscopy (TEM, JEOL, 1400plus) and scanning microscopy - energy dispersive X-ray spectroscopy (SEM-EDX, HITACHI, S-4800).

3. Results and discussion

Figure 1 shows XRD patterns of the $Ca_2Fe_{2-x}Co_xO_5/TiO_2$ synthesized by the RM method with varying Co/Fe ratio; the value of x, which was 0 to 1, is based on the composition of precursor solution. Regardless of the existence of TiO_2 particles, $Ca_2Fe_{2-x}Co_xO_5/TiO_2$ synthesized by the RM method showed the same XRD pattern as that of BM type Ca_2FeCoO_5 synthesized by the conventional sol-gel method. Peaks assigned to impurities such as CoO_x were not observed. The peak at ca. 32 ° shifted to higher angle with increasing Co (x). Table 1 lists the chemical composition analyzed by EDX. The $Ca_2Fe_{2-x}Co_xO_5/TiO_2$ prepared by the RM method had approximately equivalent Co and Fe contents (relative to Ca content) to the precursor solution which is shown by $x/2$ and $(2-x)/2$, respectively.

Figure 2 shows the TEM image of Ca_2FeCoO_5/TiO_2 prepared by the RM method. On TiO_2 support with size of several hundreds of nanometers, small black dots with 5-10 nm diameter were found. They are presumed to be the ultrafine nanoparticles of BM type Ca_2FeCoO_5. As stated before, the conventional sol-gel method resulted in 30-40 nm of the particle size. It was observed that the RM method without TiO_2 support gave Ca_2FeCoO_5 particles with about 30 nm of the diameter (data not shown). These findings indicate that the ultrafine nanoparticle was obtained by combination of the RM method and use of TiO_2 support. The aggregation of Ca_2FeCoO_5 precursors occurred during the calcination process, but in the presence of TiO_2, the aggregation was suppressed by the interaction between the precursors and TiO_2 surface. It is speculated that the interaction was induced by hydrophilikecity of the TiO_2 surface.

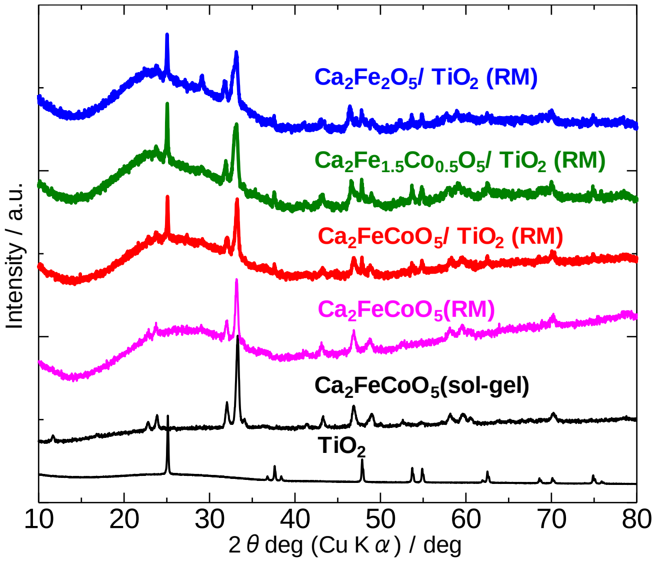

Figure 1. XRD patterns.

Table 1. Chemical composition of $Ca_2Fe_{2-x}Co_xO_5/TiO_2$ analyzed by EDX

Sample	Detected element	Element concentration of *avarage / atom%	M/Ca ratio
x = 1	Ca	11.3	1.00
	Fe	5.1	0.45
	Co	5.2	0.46
x = 0.5	Ca	8.0	1.00
	Fe	6.0	0.75
	Co	2.3	0.29
x = 0	Ca	12.1	1.00
	Fe	12.6	1.01
	Co	-	-

*Avarage of 6 points

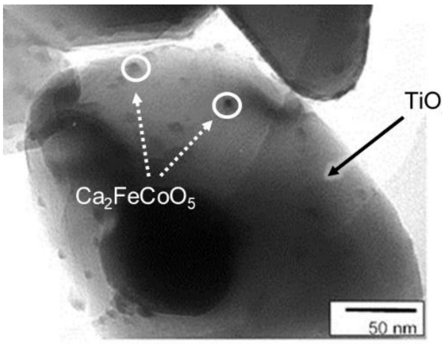

Figure 2. TEM image of Ca_2FeCoO_5/TiO_2 prepared by RM method.

4. Conclusions

Ultrafine particles of BM type $Ca_2Fe_{2-x}Co_xO_5$ with 5 - 10 nm dimension was synthesized on TiO_2 surface by the RM method. The Fe and Co contents were controlled by those of precursor solution. Because the particle sizes given by the sol-gel method and the RM method without TiO_2 were >30 nm, it is speculated that the aggregation of Ca_2FeCoO_5 precursors during the calcination process was suppressed by the hydrophilic interaction between the precursors and TiO_2 surface.

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