Combustion activities of the Ru catalysts supported on hexagonal YbFeO₃

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Hexagonal YbFeO₃ (*h*-YbFeO₃) were prepared by solvothermal and Pechini methods. Although the morphology of *h*-YbFeO₃ synthesized by solvothermal method was hexagonal plate, *h*-YbFeO₃ synthesized by the Pechini method was composed of large aggregates of irregularly-shaped fine particles. Activities of Ru catalysts supported on *h*-YbFeO₃ for combustion reaction of propane or propene were investigated. For the support of the Ru catalyst, *h*-YbFeO₃ synthesized by the solvothermal method was superior to that prepared by the Pechini method. Effects of the reaction temperatures of the solvothermal synthesis upon the activities of the Ru catalysts supported on the products were examined and it was found that the catalyst supported on crystallized *h*-YbFeO₃ showed higher activity than the catalyst supported on an amorphous product having a large surface area.

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1. Introduction

Mixed oxides of rare earth (RE) and iron having garnet (RE₃Fe₅O₁₂), perovskite (REFeO₃) and magnetoplumbite (RE_{1-x}M_xFe₁₂O₁₉; M = Ba, Sr, Pb) structures have been applied in various fields such as magnetism, fuel cells (cathode material for SOFC), gas sensors, catalysts, and so on.¹⁻⁵⁾ Orthorhombic REFeO₃ (*o*-REFeO₃) with the perovskite structure has recently received much attention in the catalyst field. For example, Nishihata et al.⁶⁾ reported that LaFe_{0.57}Co_{0.38}Pd_{0.05}O₃ with the perovskite structure is successfully applied as a catalyst for the vehicle exhaust treatment. Andrews et al. reported that LaFe_{0.95}Pd_{0.05}O₃ is an effective catalyst for Suzuki–Miyaura coupling reaction in organic chemistry.⁷⁾

o-REFeO₃ with the perovskite structure (*Pbnm*) is thermodynamically stable for all the RE elements, and hexagonal REFeO₃ (*h*-REFeO₃) belonging to the space group of *P6₃cm* is known as a metastable phase.^{8,9)} *o*-REFeO₃ is preferentially synthesized by conventional methods such as solid state reaction or coprecipitation method: calcination at high temperatures required by these methods facilitates the formation of *o*-REFeO₃. On the other hand, the synthesis of *h*-REFeO₃ is rather difficult; however, several synthetic methods for *h*-REFeO₃ have been reported; i.e., the thermal treatment of an amorphous phase obtained by hydrolysis of a yttrium–iron double alkoxide,¹⁰⁾ and quenching a melt (RE = Lu).¹¹⁾

We found that *h*-REFeO₃ (Tm–Lu) was synthesized by the solvothermal reaction of RE acetates with iron acetylacetonate in 1,4-butanediol.⁸⁾ We also reported that *o*- and *h*-REFeO₃ could be selectively synthesized by the choice of starting materials and the addition of suitable amines as additives.¹²⁾

Only few works have studied the catalytic property of *h*-REFeO₃. Li et al. have studied the CO oxidation activity of *h*-YFe_{1-x}Pd_xO_{3-δ} obtained by calcination of the precursor synthesized by a sol–gel process.¹³⁾ In a previous paper, we

compared the catalytic activities of *o*- and *h*-YbFeO₃ phases and found that the *h*-YbFeO₃ sample, which had a high surface area (29 m² g⁻¹) even after calcination at 800°C, had a higher catalytic activity for methane combustion than the *o*-YbFeO₃ sample calcined at 800°C.¹⁴⁾

In this work, properties of *h*- and *o*-YbFeO₃ samples for the supports of the noble metal catalysts were examined: combustion reactions of propane or propene on these catalysts were investigated. Since we found that the *h*-YbFeO₃ could be synthesized by the Pechini method, the effect of preparation method on catalytic activity was also examined.

2. Experimental

h-YbFeO₃ was prepared by the solvothermal (ST) method. Ytterbium acetate hydrate [Yb(OAc)₃·4H₂O, Wako], and iron acetylacetonate [Fe(acac)₃, Dojin] were used without further purification. Yb(OAc)₃ (15 mmol) and Fe(acac)₃ (15 mmol) were suspended with the aid of ultrasonication in 120 ml of 1,4-butanediol (1,4-BG) in a test tube serving as autoclave liner. The test tube was placed in a 300 mL autoclave. An additional 30 mL of 1,4-BG was placed in the gap between the autoclave wall and the test tube. The autoclave was purged with nitrogen, heated to 230, 250, 285 or 315°C at a rate of 2.3°C min⁻¹ and kept at that temperature for 2 h. After the assembly was cooled to room temperature, the resulting product was centrifuged. To the sedimented part of the product, methanol was added and vigorously mixed to peptize the colloidal particles. The mixture was centrifuged saving the supernatant. This procedure was repeated for several times, finally discarding the sediment. All the supernatant parts were gathered together, and a small amount of the concentrated ammonia solution was added to coagulate the particles. The product was repeatedly washed with methanol and dried in air. The ceramic yield of the product was above 80%. These samples are designated as *h*-YbFeO₃(ST-xx), in which xx is the temperature for the solvothermal reaction.

For comparison, *h*-YbFeO₃ was also synthesized by the Pechini (PC) method. 0.4 mol of citric acid was dissolved in 180 ml of water at 80°C. Then, iron nitrate nonahydrate

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[Fe(NO₃)₃·9H₂O, 10 mmol] and ytterbium carbonate hydrate [Yb₂(CO₃)₃·*n*H₂O, 5 mmol] were added and the mixture was magnetically stirred for 2 h at 80°C to obtain a solution containing metal citrate complexes. Ethylene glycol (0.4 mol) was added to this solution and the solution was stirred at 130°C for 3 h to obtain a gelatinous solution. After the gel was heated in a mantle heater at 350°C for over 5 h, the thus-obtained brown powder was calcined at 700 or 800°C for 2 h. These samples were designated as *h*-YbFeO₃(PC-yy), in which yy is the calcination temperature.

Supported catalysts were prepared by an impregnation method: 1.0 g of a support was added to a solution of Ru(acac)₃, Rh(acac)₃ or Pd(OAc)₂ in 10 ml of THF or methanol at room temperature, and after the evaporation of the solvent, the resulting powder was calcined at 500°C for 30 min to afford the noble-metal/support catalysts. The molar ratio of noble-metal/Fe was fixed to 0.05. A Ru/Al₂O₃ catalyst was prepared by the same impregnation method. Commercial Al₂O₃ (Sumitomo Chemical Co., Ltd., AKP-G015; JRC-ALO-8 equivalent) was used without further purification. The Ru loading was 2 wt % on a metal basis.

Catalyst tests for propane or propene combustion were performed in a fixed-bed reactor. The catalyst was tabletted, pulverized into 10–22 mesh, and set in the reactor. The reaction gas composed of 3000 ppm hydrocarbons, 17 or 14% O₂, and He balance was introduced to the catalyst bed at *W/F* = 0.3 g s ml⁻¹. The effluent gases from the reactor were analyzed with a gas chromatograph (GC-8A, Porapak Q).

The physical properties of the products were analyzed by X-ray powder diffraction (XRD: Shimadzu XD-D1), by the BET single point method (Micromeritics Flowsorb II 2300 sorption-meter), and by a transmission electron microscope (TEM: Hitachi H-800). Ru K-edge X-ray absorption fine structure (XAFS) measurements were performed at the BL01B1 beamline of SPRing-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI). The storage ring was operated at 8 GeV with a ring current of 98–100 mA. A double-mirror system was used to avoid higher harmonics in the X-ray beam. A Si(311) two crystal monochromator was used. Ru K-edge XAFS spectra were measured in a transmission mode using I₀ [100% Ar] and I [75% Ar diluted with Kr] ion chambers or in a fluorescence mode using an I₀ ion chamber [100% Ar] and a Lytle detector [100% Kr]. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) data were analyzed using the REX2000 program (ver. 2.5; Rigaku Corp.).

3. Results and discussion

3.1 Syntheses of *h*-YbFeO₃ by solvothermal and Pechini methods

Figure 1 shows the XRD patterns of the products as-synthesized by solvothermal reactions at various temperatures. The diffraction peaks due to *h*-YbFeO₃ were clearly observed for the products as-synthesized at above 250°C. On the other hand, the product obtained by the solvothermal reaction at 230°C exhibited the diffraction peaks with significantly low intensities, indicating that this product was essentially amorphous.

With the increase in the solvothermal temperature, the BET surface area of the *h*-YbFeO₃ sample decreased, while the crystallite size as well as the aspect ratio (*D*₃₀₀/*D*₀₀₂) of the sample increased (**Table 1**). The last result indicates that the crystal growth along the *ab* plane proceeded preferentially over the growth toward the *c* axis direction, the preferential growth becoming more significant with the increase in the solvothermal temperature. The TEM observation (**Fig. 2**) revealed that the

Fig. 1. XRD patterns of the products as-synthesized by the solvothermal and Pechini methods: (a), YbFeO₃(ST-230); (b), *h*-YbFeO₃(ST-250); (c), *h*-YbFeO₃(ST-285); (d), *h*-YbFeO₃(ST-315); (e), YbFeO₃(PC-700); (f), *h*-YbFeO₃(PC-800).

Table 1. BET surface areas and crystallite sizes of *h*-YbFeO₃ samples as-synthesized by the solvothermal method at various temperatures and by Pechini method

Entry	Sample	Crystallite size/nm		<i>D</i> ₃₀₀ / <i>D</i> ₀₀₂	<i>S</i> _{BET} /m ² g ⁻¹	<i>S</i> _G /m ² g ⁻¹
		<i>D</i> ₃₀₀	<i>D</i> ₀₀₂			
1	YbFeO ₃ (ST-230)	—	—	—	155	—
2	<i>h</i> -YbFeO ₃ (ST-250)	8	7	1.1	72	86 ^{a)}
3	<i>h</i> -YbFeO ₃ (ST-285)	25	10	2.5	54	52 ^{b)}
4	<i>h</i> -YbFeO ₃ (ST-315)	58	18	3.2	26	26 ^{b)}
5	<i>h</i> -YbFeO ₃ (PC-800)	19	12	1.6	30	55 ^{b)}

a) Geometric surface area calculated on the assumption that each *h*-YbFeO₃ particle is spherical with a diameter of 7 nm.

b) Geometric surface area calculated on the assumption that each *h*-YbFeO₃ particle is a hexagonal plate with a thickness of *D*₀₀₂ and a width of *D*₃₀₀.

morphology of *h*-YbFeO₃(ST-315) was hexagonal plate, as reported in previous works,^{13),14)} while *h*-YbFeO₃(ST-250) was composed of nanoparticles with the sizes of 10 nm. These results agreed well with the aspect ratio determined by XRD analyses.

As for the Pechini method, the product obtained by calcination at 700°C was essentially amorphous, while *h*-YbFeO₃ was crystallized by calcination at 800°C. Although the crystallite size of *h*-YbFeO₃(PC-800) was smaller than that of *h*-YbFeO₃(ST-315), the BET surface area of the former sample was smaller than that of the latter, indicating that the particles of *h*-YbFeO₃(PC-800) were severely aggregated. Actually, the TEM images of *h*-YbFeO₃(PC-800) showed that this product was composed of large aggregates of irregularly-shaped particles. The aspect ratio of *h*-YbFeO₃(PC-800) was much smaller than that of *h*-YbFeO₃(ST-315).

3.2 Combustion activities of noble metal catalysts supported on *h*-YbFeO₃

Figure 3 shows the XRD patterns of the Ru catalysts obtained by calcination at 500°C after impregnation of Ru(acac)₃. The peaks due to Ru species were not observed, and the patterns were essentially identical with those of the as-synthesized *h*-YbFeO₃.

Fig. 2. TEM images of the products as-synthesized by the solvothermal and Pechini methods: (a), *h*-YbFeO₃(ST-250); (b), *h*-YbFeO₃(ST-315); (c), *h*-YbFeO₃(PC-800).

Fig. 3. XRD patterns of Ru catalysts obtained by calcination at 500°C after impregnation method of Ru(acac)₃: (a), Ru/YbFeO₃(ST-230); (b), Ru/*h*-YbFeO₃(ST-250); (c), Ru/*h*-YbFeO₃(ST-285); (d), Ru/*h*-YbFeO₃(ST-315); (e), Ru/*h*-YbFeO₃(PC-800).

samples shown in Fig. 1. Although the BET surface area of Ru/YbFeO₃(ST-230) drastically decreased by calcination at 500°C after the impregnation of Ru(acac)₃, both the BET surface areas of the Ru catalysts and crystallite sizes of the *h*-YbFeO₃ phase (Table 2) were essentially identical with those of the corresponding as-synthesized *h*-YbFeO₃ samples (Table 1), indicating that the sintering of *h*-YbFeO₃ scarcely occurred by calcination at 500°C. This result is consistent with the previously reported result that the hexagonal-plate morphology of *h*-YbFeO₃ synthesized by the solvothermal method was maintained during calcination until the phase transformation into the thermodynamically stable *o*-YbFeO₃ occurred at ~950°C.^{8),14)}

Table 2 shows that the activities of the *h*-YbFeO₃-supported noble metal catalysts for combustion reactions. Of the noble metal catalysts supported on *h*-YbFeO₃(ST-315), the Ru catalyst showed the highest activity for propane combustion, while the Pd catalyst had a higher activity than the Ru catalyst for propene combustion. The Ru/*h*-YbFeO₃(ST-315) had a higher activity than Ru/*o*-YbFeO₃ or Ru/*h*-YbFeO₃(PC-800) for both the propane and propene combustions, suggesting that the catalytic activity was affected on the crystal structure and/or morphology of the support particles. The catalytic activity of

Table 2. Combustion activities, BET surface areas and crystallite sizes of noble metal catalysts obtained by calcination at 500°C after impregnation method

Entry	Catalyst	C ₃ H ₈ ^{a)}		C ₃ H ₆ ^{b)}		<i>S</i> _{BET} /m ² g ⁻¹	Crystallite size/nm	
		<i>T</i> ₅₀ ^{c)} /°C	<i>T</i> ₉₀ ^{d)} /°C	<i>T</i> ₅₀ ^{c)} /°C	<i>T</i> ₉₀ ^{d)} /°C		<i>D</i> ₃₀₀	<i>D</i> ₀₀₂
1	<i>h</i> -YbFeO ₃ (ST-315) ^{e)}	407	473	366	423	26	47	18
2	Pd/ <i>h</i> -YbFeO ₃ (ST-315)	284	322	187	197	—	—	—
3	Rh/ <i>h</i> -YbFeO ₃ (ST-315)	232	262	242	268	—	—	—
4	Ru/ <i>h</i> -YbFeO ₃ (ST-315)	214	256	201	220	32	40	15
5	Ru/ <i>o</i> -YbFeO ₃ ^{f)}	267	298	233	264	20	—	—
6	Ru/Al ₂ O ₃	246	285	234	247	148	—	—
7	Ru/ <i>h</i> -YbFeO ₃ (PC-800)	239	286	207	223	36	22	6
8	Ru/YbFeO ₃ (ST-230)	247	314	192	218	93	—	—
9	Ru/ <i>h</i> -YbFeO ₃ (ST-250)	210	254	176	195	72	11	6
10	Ru/ <i>h</i> -YbFeO ₃ (ST-285)	201	241	185	217	47	18	10

a) Reaction conditions: C₃H₈, 0.3%; O₂, 17%, He balance; *W*/*F* = 0.3 g s ml⁻¹.

b) Reaction conditions: C₃H₆, 0.3%; O₂, 14%, He balance; *W*/*F* = 0.3 g s ml⁻¹.

c) Temperature at which the catalyst attained 50% conversion of hydrocarbons.

d) Temperature at which the catalyst attained 90% conversion of hydrocarbons.

e) The sample was calcined at 500°C.

f) *o*-YbFeO₃ was synthesized by a solvothermal method.¹²⁾

Ru/*h*-YbFeO₃(ST-315) was superior to that of Ru/Al₂O₃, even though the latter catalyst had a large surface area.

Entries 8–10 of Table 2 examined the effect of the temperature of solvothermal reaction for the synthesis of *h*-YbFeO₃ upon the catalytic activity. Ru/*h*-YbFeO₃(ST-250) and Ru/*h*-YbFeO₃(ST-285) had essentially identical activities with that of Ru/*h*-YbFeO₃(ST-315) for the propane combustion reaction, while Ru/YbFeO₃(ST-230) had a much lower catalytic activity. In propene combustion reaction, the catalytic activity of Ru/*h*-YbFeO₃ slightly increased with the decrease in solvothermal temperature from 315°C to 250°C, while Ru/*h*-YbFeO₃(ST-230) showed a low activity. These results suggest the crystallized *h*-YbFeO₃ was effective as catalyst support for the combustion reaction.

The states of Ru species on the supports were investigated by Ru K-edge XAFS analyses. As shown in Fig. 4, the Ru

Fig. 4. XANES spectra of: (a), Ru/YbFeO₃(ST-230); (b), Ru/*h*-YbFeO₃(ST-250); (c), Ru/*h*-YbFeO₃(ST-285); (d), Ru/*h*-YbFeO₃(ST-315); (e), Ru/*h*-YbFeO₃(PC-800); (f), RuO₂.

K-edge XANES spectra of Ru/*h*-YbFeO₃(ST-315) and Ru/*h*-YbFeO₃(PC-800) catalysts were essentially identical with that of the RuO₂ standard, indicating that the Ru species in these catalysts have a RuO₂-like structure. The XANES spectra of Ru/*h*-YbFeO₃(ST-250) and Ru/YbFeO₃(ST-230) were different from that of the RuO₂ standard in that the intensities of the peak at around 22125 eV of the former samples were weaker than that of the RuO₂ standard. Moreover, Ru/*h*-YbFeO₃(ST-250) and Ru/*h*-YbFeO₃(ST-230) exhibited a pre-edge peak at around 22110 eV. The existence of the pre-edge peak implies that the Ru species is distorted from the octahedral symmetry,^{15),16)} suggesting that the distorted Ru species were formed on *h*-YbFeO₃(ST-250) and YbFeO₃(ST-230).

In the Fourier transforms (FT) of Ru K-edge EXAFS spectra (Fig. 5), the peaks at 2.0–4.0 Å were observed for Ru/*h*-YbFeO₃(ST-315) and Ru/*h*-YbFeO₃(PC-800), and the oscillation and the feature of the FT spectra were essentially identical with those of the RuO₂ standard, indicating that the major part of Ru species was loaded as RuO₂. On the other hand, the intensity of the peaks due to the second shell of the Ru species of the Ru/*h*-YbFeO₃ catalyst decreased with the decrease in the solvothermal temperature for the synthesis of the *h*-YbFeO₃ phase, suggesting that the particle size of the RuO₂-like phase decreased with the increase in the surface area of the support. The second shell for Ru/*h*-YbFeO₃(ST-250) or Ru/YbFeO₃(ST-230) was not observed in the FT of the EXAFS spectra, indicating that the Ru species were highly dispersed on the surface of *h*-YbFeO₃(ST-250) or YbFeO₃(ST-230) because of strong interaction with the support.

Although the dispersion state of Ru species on *h*-YbFeO₃(ST-250) was significantly different from that on *h*-YbFeO₃(ST-315), the catalytic activity of Ru/YbFeO₃(ST-250) for propane combustion was essentially identical with that of Ru/*h*-YbFeO₃(ST-315). On the other hand, the catalytic activity for propene combustion increased with the increase in the dispersion of Ru species when they were supported on crystallized *h*-YbFeO₃. This result suggests that the nature of Ru species affected the catalytic activity in combustion of propene possessing both allylic hydrogen atoms having high reactivity and an unsaturated C=C bond having high coordination ability to the catalyst.

Fig. 5. Ru K-edge EXAFS (A) and FT (B) spectra of: (a), Ru/YbFeO₃(ST-230); (b), Ru/*h*-YbFeO₃(ST-250); (c), Ru/*h*-YbFeO₃(ST-285); (d), Ru/*h*-YbFeO₃(ST-315); (e), Ru/*h*-YbFeO₃(PC-800); (f), RuO₂.

4. Conclusions

Crystallized *h*-YbFeO₃ was directly obtained by solvothermal reaction of ytterbium acetate and iron acetylacetonate at above 250°C, while the product obtained by the reaction at 230°C was amorphous. *h*-YbFeO₃ synthesized by solvothermal reaction was composed of hexagonal-plate particles. On the other hand, irregularly-shaped particles were obtained by the Pechini method.

Of the noble metal catalysts supported on *h*-YbFeO₃, the Ru catalyst showed the highest activity for propane combustion reaction, and Ru/*h*-YbFeO₃(ST-315) had a higher activity than Ru/*h*-YbFeO₃(PC-800), Ru/*o*-YbFeO₃ or Ru/Al₂O₃ for both the propane and propene combustion reactions. The Ru catalyst supported on crystallized *h*-YbFeO₃(ST-250) showed higher activity than the Ru catalyst supported on an amorphous product [YbFeO₃(ST-230)] having a large surface area. The dispersion of Ru species on *h*-YbFeO₃ increased with the increase in the surface areas of the support which, in turn, increased with the decrease in the solvothermal temperature for the synthesis of *h*-YbFeO₃. Although the dispersion of Ru species affected the catalytic activity for propene combustion, the catalytic activity for propane combustion did not depend on the dispersion of Ru species.

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