Hexagonal YbFeO$_3$ ($h$-YbFeO$_3$) were prepared by solvothermal and Pechini methods. Although the morphology of $h$-YbFeO$_3$ synthesized by solvothermal method was hexagonal plate, $h$-YbFeO$_3$ synthesized by the Pechini method was composed of large aggregates of irregularly-shaped fine particles. Activities of Ru catalysts supported on $h$-YbFeO$_3$ for combustion reaction of propane or propene were investigated. For the support of the Ru catalyst, $h$-YbFeO$_3$ 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 $h$-YbFeO$_3$ showed higher activity than the catalyst supported on an amorphous product having a large surface area.

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Key-words : YbFeO$_3$, Hexagonal phase, Perovskite, Catalyst, Morphology, Combustion, XAFS, Solvothermal method

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[Fe(NO$_3$)$_3$]•9H$_2$O, 10 mmol) and ytterbium carbonate hydrate [Yb$_2$(CO$_3$)$_3$]•nH$_2$O, 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 $h$-YbFeO$_3$(PC-$yy$), in which $yy$ is the calcination temperature.

Supported catalysts were prepared by the 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/Al$_2$O$_3$ catalyst was prepared by the same impregnation method. Commercial Al$_2$O$_3$ (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% O$_2$, 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 3.0 GeV. 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 $I_0$ [100] and I [75% Ar diluted with Kr] ion chambers or in a fluorescence mode using an I$_0$ ion chamber [100% Ar] and a Lytel 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 $h$-YbFeO$_3$ 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 $h$-YbFeO$_3$ were 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 $h$-YbFeO$_3$ sample decreased, while the crystallite size as well as the aspect ratio ($D_{300}/D_{200}$) of the sample increased (Table 1). The last result indicates that the crystal growth along the $a$ 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 morphology of $h$-YbFeO$_3$(ST-315) was hexagonal plate, as reported in previous works,[13,14] while $h$-YbFeO$_3$(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 $h$-YbFeO$_3$ was crystallized by calcination at 800°C. Although the crystallite size of $h$-YbFeO$_3$(PC-800) was smaller than that of $h$-YbFeO$_3$(ST-315), the BET surface area of the former sample was smaller than that of the latter, indicating that the particles of $h$-YbFeO$_3$(PC-800) were severely aggregated. Actually, the TEM images of $h$-YbFeO$_3$(PC-800) showed that this product was composed of large aggregates of irregularly-shaped particles. The aspect ratio of $h$-YbFeO$_3$(PC-800) was much smaller than that of $h$-YbFeO$_3$(ST-315).

3.2 Combustion activities of noble metal catalysts supported on $h$-YbFeO$_3$

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 $h$-YbFeO$_3$.
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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>C₃H₈ α)</th>
<th>C₃H₆ β)</th>
<th>S_{BET}/m²g⁻¹</th>
<th>Crystal size/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>T_{50°C}/°C</td>
<td>T_{90°C}/°C</td>
<td>T_{50°C}/°C</td>
<td>T_{90°C}/°C</td>
</tr>
<tr>
<td>1</td>
<td>h-YbFeO₃(ST-315)</td>
<td>407</td>
<td>473</td>
<td>396</td>
<td>423</td>
</tr>
<tr>
<td>2</td>
<td>Pd/h-YbFeO₃(ST-315)</td>
<td>284</td>
<td>322</td>
<td>187</td>
<td>197</td>
</tr>
<tr>
<td>3</td>
<td>Rh/h-YbFeO₃(ST-315)</td>
<td>232</td>
<td>262</td>
<td>242</td>
<td>268</td>
</tr>
<tr>
<td>4</td>
<td>Ru/h-YbFeO₃(ST-315)</td>
<td>214</td>
<td>256</td>
<td>201</td>
<td>220</td>
</tr>
<tr>
<td>5</td>
<td>Ru/o-YbFeO₃</td>
<td>267</td>
<td>298</td>
<td>233</td>
<td>264</td>
</tr>
<tr>
<td>6</td>
<td>Ru/Al₂O₃</td>
<td>246</td>
<td>285</td>
<td>234</td>
<td>247</td>
</tr>
<tr>
<td>7</td>
<td>Ru/h-YbFeO₃(PC-800)</td>
<td>239</td>
<td>286</td>
<td>207</td>
<td>223</td>
</tr>
<tr>
<td>8</td>
<td>Ru/YbFeO₃(ST-230)</td>
<td>247</td>
<td>314</td>
<td>192</td>
<td>218</td>
</tr>
<tr>
<td>9</td>
<td>Ru/h-YbFeO₃(ST-250)</td>
<td>210</td>
<td>254</td>
<td>176</td>
<td>195</td>
</tr>
<tr>
<td>10</td>
<td>Ru/h-YbFeO₃(PC-800)</td>
<td>201</td>
<td>241</td>
<td>185</td>
<td>217</td>
</tr>
</tbody>
</table>

α) Reaction conditions: C₃H₈, 0.3%; O₂, 17%, He balance; W/F = 0.3 g s ml⁻¹.
β) Reaction conditions: C₃H₈, 0.3%; O₂, 14%, He balance; W/F = 0.3 g s ml⁻¹.
γ) Temperature at which the catalyst attained 50% conversion of hydrocarbons.
δ) 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-YbFeO$_3$(ST-315) was superior to that of Ru/Al$_2$O$_3$, 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-YbFeO$_3$ upon the catalytic activity. Ru/h-YbFeO$_3(ST-250)$ and Ru/h-YbFeO$_3(ST-285)$ had essentially identical activities with that of Ru/h-YbFeO$_3(ST-315)$ for the propane combustion reaction, while Ru/YbFeO$_3(ST-230)$ had a much lower catalytic activity. In propene combustion reaction, the catalytic activity of Ru/h-YbFeO$_3$ slightly increased with the decrease in solvothermal temperature from 315°C to 250°C, while Ru/h-YbFeO$_3(ST-250)$ showed a low activity. These results suggest the crystallized h-YbFeO$_3$ 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 K-edge XANES spectra of Ru/h-YbFeO$_3(ST-315)$ and Ru/h-YbFeO$_3(PC-800)$ catalysts were essentially identical with that of the RuO$_2$ standard, indicating that the Ru species in these catalysts have a RuO$_2$-like structure. The XANES spectra of Ru/h-YbFeO$_3(ST-250)$ and Ru/YbFeO$_3(ST-230)$ were different from that of the RuO$_2$ standard in that the intensities of the peak at around 22125 eV of the former samples were weaker than that of the RuO$_2$ standard. Moreover, Ru/h-YbFeO$_3(ST-250)$ and Ru/h-YbFeO$_3(ST-230)$ 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, suggesting that the distorted Ru species were formed on h-YbFeO$_3$(ST-250) and YbFeO$_3$(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-YbFeO$_3(ST-315)$ and Ru/h-YbFeO$_3(PC-800)$, and the oscillation and the feature of the FT spectra were essentially identical with those of the RuO$_2$ standard, indicating that the major part of Ru species was loaded as RuO$_2$. On the other hand, the intensity of the peaks due to the second shell of the Ru species of the Ru/h-YbFeO$_3$ catalyst decreased with the decrease in the solvothermal temperature for the synthesis of the h-YbFeO$_3$ phase, suggesting that the particle size of the RuO$_2$-like phase decreased with the increase in the surface area of the support. The second shell for Ru/h-YbFeO$_3(ST-250)$ or Ru/YbFeO$_3(ST-230)$ was not observed in the FT of the EXAFS spectra, indicating that the Ru species were highly dispersed on the surface of h-YbFeO$_3(ST-250)$ or YbFeO$_3(ST-230)$ because of strong interaction with the support.

Although the dispersion state of Ru species on h-YbFeO$_3(ST-250)$ was significantly different from that on h-YbFeO$_3(ST-315)$, the catalytic activity of Ru/YbFeO$_3(ST-250)$ for propane combustion was essentially identical with that of Ru/h-YbFeO$_3(ST-315)$. 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-YbFeO$_3$. 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.
4. Conclusions

Crystallized $h$-YbFeO$_3$ 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. $h$-YbFeO$_3$ 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 $h$-YbFeO$_3$, the Ru catalyst showed the highest activity for propane combustion reaction, and Ru/$h$-YbFeO$_3$(ST-315) had a higher activity than Ru/$h$-YbFeO$_3$(PC-800), Ru/$\alpha$-YbFeO$_3$ or Ru/Al$_2$O$_3$ for both the propane and propene combustion reactions. The Ru catalyst supported on crystallized $h$-YbFeO$_3$(ST-250) showed higher activity than the Ru catalyst supported on an amorphous product [YbFeO$_3$(ST-230)] having a large surface area. Although the dispersion of Ru species on $h$-YbFeO$_3$ 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 $h$-YbFeO$_3$. 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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