



Hexagonal Rare Earth-Iron Mixed Oxides (REFeO₃): Crystal Structure, Synthesis, and Catalytic Properties

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The rare earth-iron mixed oxide (REFeO₃) is an attractive material in fields such as electronic, magnetic, and catalytic research. Generally, orthorhombic REFeO₃ (*o*-REFeO₃) with a perovskite structure is better known than hexagonal REFeO₃ (*h*-REFeO₃), because *o*-REFeO₃ is thermodynamically stable for all RE elements. However, *h*-REFeO₃ has a very interesting crystal structure in which a RE and Fe layer are alternately stacked along the *c*-axis in the unit cell; nevertheless, synthesis of the *h*-REFeO₃ belonging to metastable phase can be problematic. Fortunately, solution-based synthetic methods like solvothermal or coprecipitation synthesis have recently enabled the selective synthesis of *h*-REFeO₃ and *o*-REFeO₃ with comparative ease. Although the electronic and magnetic properties of *h*-REFeO₃ have typically been evaluated, recent research has also revealed excellent catalytic properties that enable environmental cleanup reactions such as hydrocarbon or CO oxidation. This mini-review introduces a synthetic method for controlling the crystal structure between orthorhombic and hexagonal REFeO₃ and the catalytic performance of *h*-REFeO₃-based materials.

Keywords: solvothermal method, coprecipitation method, catalyst, perovskite structure, hexagonal structure

OPEN ACCESS

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Specialty section:

This article was submitted to
Inorganic Chemistry,
a section of the journal
Frontiers in Chemistry

Received: 19 July 2018

Accepted: 07 January 2019

Published: 28 January 2019

Citation:

Hosokawa S (2019) Hexagonal Rare Earth-Iron Mixed Oxides (REFeO₃): Crystal Structure, Synthesis, and Catalytic Properties. *Front. Chem.* 7:8. doi: 10.3389/fchem.2019.00008

INTRODUCTION

REFeO₃ (RE: rare earth) with a RE/Fe ratio of 1 are largely relevant to the perovskite structure, a structure in which RE ions are basically replaced with 1/4 of cubic close-packed oxygen ions, and Fe ions occupy all octahedral gaps formed from the remaining oxygen ions. REFeO₃ having a perovskite structure have been applied in various fields from electronic devices to catalysts. On the other hand, hexagonal REFeO₃ is known to exist as a metastable phase, but the synthetic method is very complex. Interestingly, the crystal structure has a unique coordination state for Fe³⁺ ion and is different from that of the perovskite-type REFeO₃; that is, Fe³⁺ ions in hexagonal structure have trigonal bipyramidal coordination, although Fe³⁺ ions in α -Fe₂O₃, Fe₃O₄, or perovskite-type REFeO₃ generally prefer octahedral or tetrahedral coordination. Therefore, hexagonal structure has a potential which provokes an interesting property for the above applied fields. In particular, novel catalysts composed on abundant base metal as Fe ion have been recently desired to replace the use of precious metals, such as Pt or Pd; the catalyst design based on a unique crystal structure is considered to be necessary to dramatically improve the catalytic performance of Fe-based material.

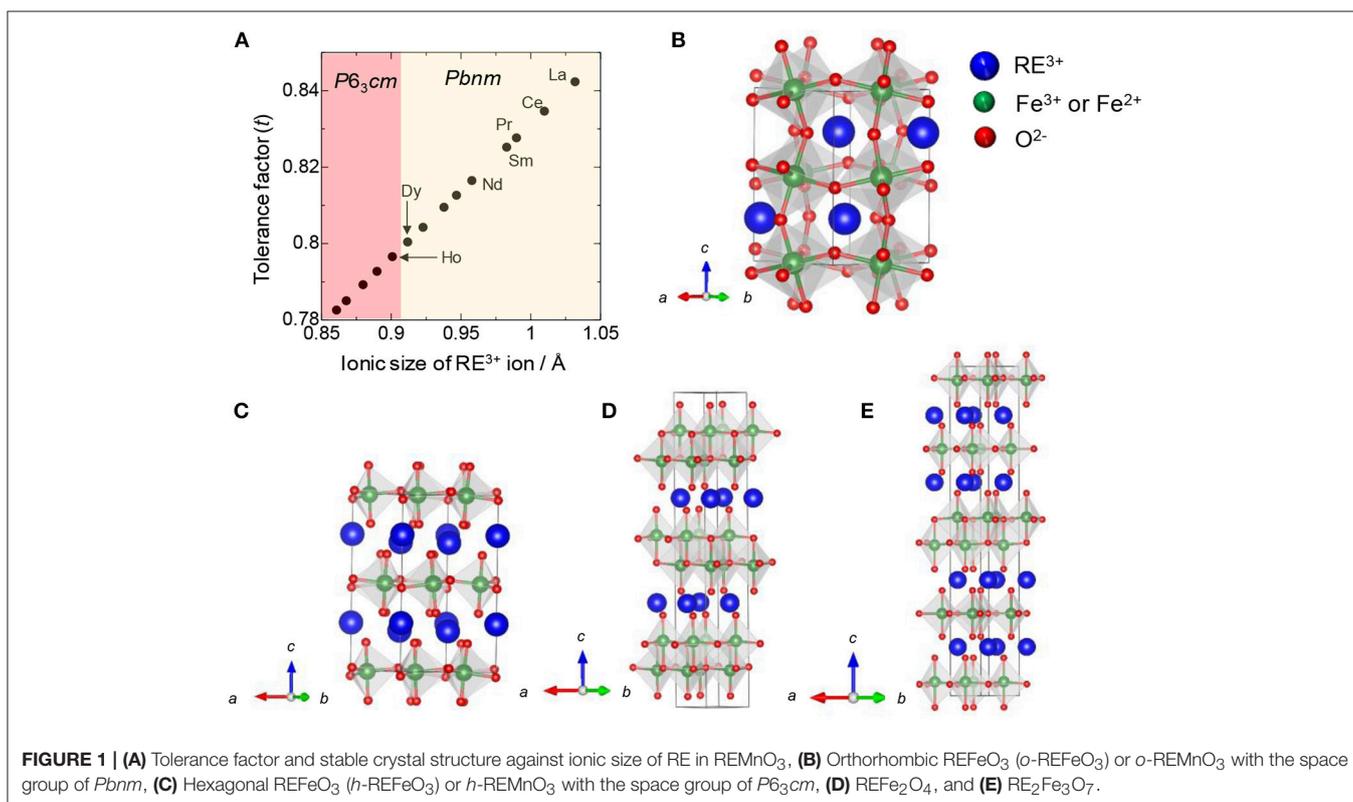
First, the relationship between RE elements and hexagonal structure is introduced, based on a general perovskite structure. Considering that each ion is in contact within the perovskite structure, the following equation is true: $(r_A + r_O) = \sqrt{2}(r_B + r_O)$, where r_A , r_B , and r_O represent the ionic radii of the A cation as RE ion, B cation as Fe ion, and oxygen ion, respectively. Therefore, the perovskite structure is generally considered to be a stable phase, when the tolerance factor,

$t = [(r_A + r_O)]/[\sqrt{2}(r_B + r_O)]$ is close to 1 (Schneider et al., 1961; Woodward, 1997; Li et al., 2004). Regarding the relationship between RE elements and transition metal ions, the tolerance factor decreases with decreasing ionic radius of the RE element (Kumar et al., 2011); that is, the perovskite structure becomes less stable. However, for REFeO_3 , the orthorhombic phase is thermodynamically stable for all RE elements, and the trend is different from a general trend observed in REMnO_3 (Figure 1A); orthorhombic REMnO_3 (*o*- REMnO_3) with a perovskite structure and the space group of $Pbnm$ is preferentially formed for RE elements with large ionic sizes (La–Dy), while hexagonal REMnO_3 (*h*- REMnO_3) with $P6_3cm$ is obtained for RE elements with small ionic sizes (Ho–Lu and Y) (Figures 1B,C). As the ionic size of an Fe^{3+} ion is almost the same as that of an Mn^{3+} ion, the difference in the electronic configuration of d orbitals between Fe^{3+} and Mn^{3+} ions may contribute to the stability of the hexagonal phase. In other words, because *h*- REFeO_3 is a thermodynamically unstable phase, it is relatively poorly studied compared with *o*- REFeO_3 .

By controlling the synthetic route, *h*- REFeO_3 composed from RE ions with a smaller ionic radius than Er or Y have been obtained. The space group of *h*- REFeO_3 has been reported as $P6_3cm$ with a YMnO_3 structure type or $P6_3/mmc$ with a YAlO_3 structure type (Li et al., 2008; Kumar et al., 2009; Magome et al., 2010). The crystal structure belonging to $P6_3cm$ is very similar to that to $P6_3/mmc$, except for a slightly more distorted crystal structure in the former than in the latter. Actually, the oxygen layer has a zigzag structure in the $P6_3cm$ structure. In either space

group, *h*- REFeO_3 has a unique crystal structure other than the coordination state of Fe^{3+} ion; RE and Fe layers are alternately stacked along the *c*-axis. REFe_2O_4 or $\text{RE}_2\text{Fe}_3\text{O}_7$, represented by the chemical formula $\text{RE}_n\text{Fe}_{n+1}\text{O}_{(3n+1)}$, are known as hexagonal phase-related materials (Malaman et al., 1976; Qin et al., 2009; Bourgeois et al., 2012; Lafuerza et al., 2014), and the coordination environment of Fe ions is a trigonal bipyramidal structure similar to the structure of *h*- REFeO_3 . REFe_2O_4 has a hexagonal layer structure with the space group of $R\bar{3}m$, which is formed by the alternate stacking of two layers with compositions of $\text{REO}_{3/2}$ and $\text{Fe}^{2+}\text{Fe}^{3+}\text{O}_{5/2}$ (Figure 1D). The Fe layer consists of two triangular sheets of corner-sharing FeO_5 trigonal bipyramids. $\text{RE}_2\text{Fe}_3\text{O}_7$ can be transcribed to $\text{REFe}_2\text{O}_4 \bullet (\text{REFeO}_3)$, and the structures of the $\text{REFe}_2\text{O}_4 \bullet (\text{REFeO}_3)_n$ phases are described by alternately stacking REFe_2O_4 and hexagonal REFeO_3 blocks along the *c*-axis direction (Figure 1E).

When *h*- REFeO_3 is viewed as an applied material, its layered structure composed of RE and Fe layers along the *c*-axis is very attractive for multiple purposes, from electric to catalytic applications. In fact, $\text{LuFe}_2\text{O}_{4+x}$ has shown excellent oxygen storage properties because its hexagonal-related structure has unique structural flexibility accompanied by “topotactic transition” during the oxygen intercalation/de-intercalation process (Hervieu et al., 2014). In this transformation, the original cation ordering in the hexagonal structure is maintained without any intermixing between RE and Fe ions. This mini-review therefore presents the method for controlling the crystal structure of *h*- REFeO_3 and *o*- REFeO_3 and discusses the catalytic properties of *h*- REFeO_3 .



SOLVOTHERMAL METHOD

Because h -REFeO₃ is a metastable phase, a unique synthesis method is typically required. Among existing methods, a solvothermal method is effective for controlling the hexagonal and orthorhombic phases. In this method, synthesis of inorganic material is achieved by reaction in a liquid medium at high temperatures in a closed vessel (autoclave) (Demazeau, 1999; Cushing et al., 2004). Therefore, the traditional solvothermal method is a hydrothermal method in which water is used as the solvent. Since the last three decades, alcohol or glycol has been used as a solvent in the solvothermal method (Fanelli and Burlaw, 1986; Das et al., 2008), with which various metal oxides or mixed oxides with unique morphology or ultrafine nanoparticles have been reported.

Inoue et al. found that h -REFeO₃ nanoparticles composed of RE with a smaller ionic radius than Er can be obtained through a non-aqueous solvothermal reaction of RE acetate with Fe acetylacetonate in 1,4-butanediol at 300°C (Figure 2; Inoue et al., 1997). It should be noted that crystal growth in the c -axis direction in h -REFeO₃ is drastically suppressed during solvothermal synthesis, resulting in the formation of nanoparticles with a particle size of approximately 20 nm and a well-formed hexagonal plate-like morphology. It was found that h -YbFeO₃ and o -YbFeO₃ can be controlled by the choice of reaction conditions and the starting material for the solvothermal reaction (Hosokawa et al., 2009). Interestingly, when RE chloride (RE = Sm-Yb) and Fe acetylacetonate are used for the solvothermal reaction in 1,4-butanediol in the presence of hexamethylenediamine, monodisperse particles of o -REFeO₃ (crystallite size: about 80 nm) are formed. It is suggested that o -YbFeO₃ has a larger crystallite size than solvothermally-synthesized h -YbFeO₃, which indicates that crystal nucleation is more difficult for o -YbFeO₃ than h -YbFeO₃.

High-resolution transmission electron microscopy (TEM) of Yb₃Fe₄O₁₀ revealed that three or more YbFeO₃ layers are inserted between the YbFe₂O₄ layers (Matsui et al., 1979),

suggesting that the REFe₂O₄ phase with Fe³⁺ and Fe²⁺ species may act as a nucleus for h -REFeO₃. The result indicates that the existence of Fe²⁺ ions plays an important role in the formation of h -REFeO₃. The solvothermal reaction in 1,4-butanediol causes reductive conditions because of the reducing ability of glycol; that is, Fe²⁺ species formed in the reaction system seem to contribute to the formation of h -REFeO₃. On the other hand, because the incorporation of amine into the solvothermal reaction suppresses the reduction from Fe³⁺ to Fe²⁺ ions owing to the chelating ability of hexamethylenediamine, o -YbFeO₃ must be obtained. In addition, the reducibility of Fe³⁺ species is unsurprisingly also considered to depend on whether the ligand of the starting material is acetate or chloride.

This non-aqueous solvothermal method enables the crystallization of REFeO₃ nanoparticles below 100 nm without calcination. Therefore, it is promising to control the crystal structure, shape, and particle size by adjusting the additives and solvent in the solvothermal system.

COPRECIPITATION AND SOL-GEL METHOD

General synthetic routes such as the coprecipitation method inevitably involve a calcination process for the synthesis of metal oxide materials, and it is difficult to synthesize the metastable phase. Therefore, h -REFeO₃ is often synthesized by optimizing the crystallization process. For example, h -REFeO₃ is synthesized by introducing solutions containing metal salts into a high-temperature inductively coupled plasma (ICP) (Mizoguchi et al., 1996). An instant crystallization under the ICP atmosphere yields h -REFeO₃ nanoparticles sized 20–50 nm. Kumar et al. reported that the hexagonal phase is synthesized by rapidly cooling a melt of the composition REFeO₃ under controlled oxygen pressure (Vijaya Kumar et al., 2008). This method requires special equipment in which the precursor is suspended on a nozzle fitted to an oxygen gas jet, thereby preventing heterogeneous

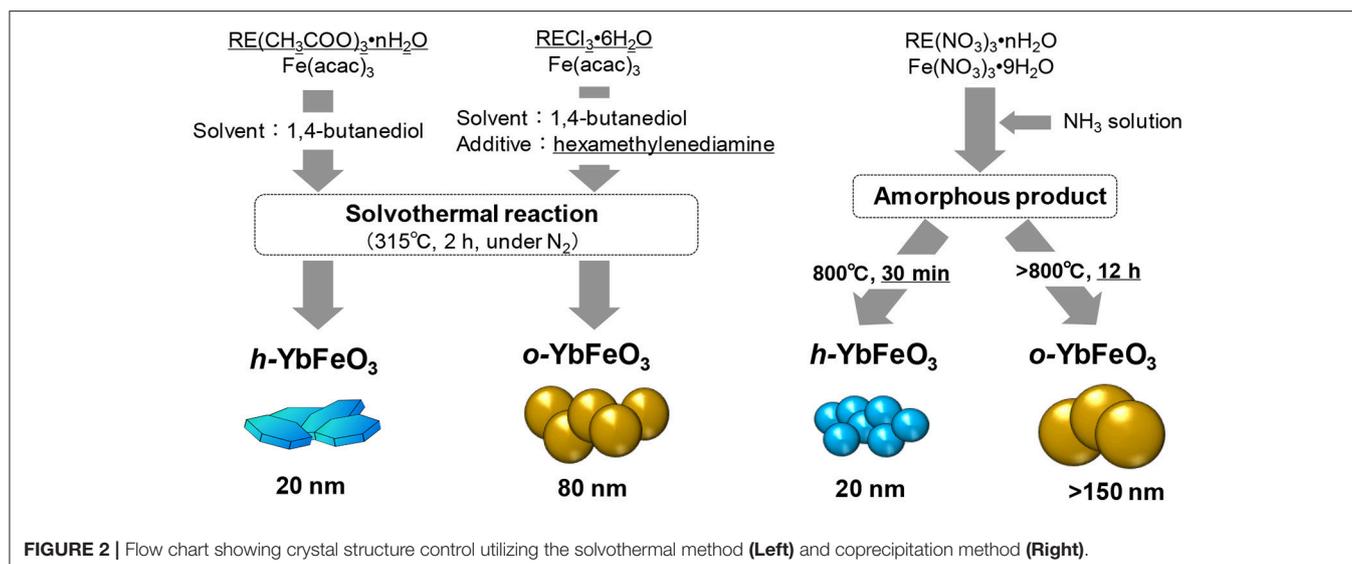


FIGURE 2 | Flow chart showing crystal structure control utilizing the solvothermal method (Left) and coprecipitation method (Right).

nucleation that occurs on the walls of the container. As a result, *h*-LuFeO₃ with high crystallinity is obtained under an oxygen partial pressure of 1×10^5 Pa.

On the other hand, in the case of *h*-REFeO₃ synthesis from an amorphous precursor obtained by coprecipitation method in which ammonia water is added immediately to an aqueous solution containing RE and Fe ions (Nishimura et al., 2013), *h*-REFeO₃ for RE ions with a smaller ionic radius than Er can be easily obtained under precisely controlled calcination conditions. For an amorphous precursor with the composition of YbFeO₃, an exothermic peak without weight change is observed in the temperature range slightly below 800°C, by thermal gravimetric-differential thermal analysis. Therefore, the sample calcined in air at 700°C for 30 min is amorphous, and the formation of pure-phase *h*-YbFeO₃ is confirmed by calcining the amorphous product at 800°C for 30 min (Figure 2). Note that, when the retention time at 800°C is extended to 12 h, *o*-YbFeO₃ is obtained as the main product. These results strongly suggest that the exothermic peak is attributed not only to crystallization from an amorphous to hexagonal structure but also a phase transition from a hexagonal structure to orthorhombic structure. In other words, the hexagonal and orthorhombic phase can be kinetically classified by adjusting the heat retention time in the calcination process. In this manner, because a subtle change in calcination conditions leads to the formation of *h*-REFeO₃ from an amorphous product, the synthesis of *h*-REFeO₃ is much more difficult than that of *o*-REFeO₃.

Similar crystallization behavior is also observed for a precursor containing organic species synthesized by a citric acid-assisted sol-gel process (Zhang et al., 2012). For an amorphous precursor with the composition of YFeO₃, the crystallization temperature of *h*-YFeO₃ is 700°C. This is lower than that of *h*-YbFeO₃ (800°C); therefore, the crystallization temperature depends on the ionic radius of RE ions. Interestingly, doping Pd on *h*-YFeO₃ via the sol-gel method stabilizes the hexagonal phase, and the phase transformation to the orthorhombic phase hardly proceeds even by calcination at 1,000°C (Li et al., 2008).

h-REFeO₃, which is obtained by the calcination of a precursor synthesized by the solution method, often comprises fine particles with a crystallite diameter below 50 nm. On the other hand, *o*-REFeO₃, which is obtained by phase transition from *h*-REFeO₃, has a much larger particle size than *h*-REFeO₃. For example, the particle size of *h*-YbFeO₃ synthesized by the coprecipitation method is approximately 20 nm, whereas that of *o*-YbFeO₃ is above 150 nm. A nucleation and growth mechanisms has been reported to proceed in a phase transition from γ -Al₂O₃ or θ -Al₂O₃ to α -Al₂O₃ (Dynys and Halloran, 1982; Bagwell et al., 2001): that is, rapid crystal growth of α -Al₂O₃ simultaneously progresses with the formation of crystal nuclei of α -Al₂O₃, resulting in the formation of α -Al₂O₃ with a very large particle size. Similar to the phenomena for α -Al₂O₃, crystal nucleation and rapid crystal growth of *o*-REFeO₃ must proceed during the phase transition from *h*-REFeO₃ to *o*-REFeO₃. These results imply that *h*-REFeO₃ nanoparticles can be synthesized by the coprecipitation or sol-gel method, but *o*-REFeO₃ with a particle size below 100 nm is difficult to synthesize for RE ions with a smaller ionic radius than Er.

CATALYTIC PERFORMANCE OF *H*-REFE₃O₃

o-REFeO₃ has been applied as a catalyst material in various fields including the purification of volatile organic compound etc. (Ciambelli et al., 2001; Barbero et al., 2006). Applications of *h*-REFeO₃ have been rare, except for in magnetic or electronic fields, until about 15 years ago. However, recent applications have emerged in the field of catalysts (Kurzman et al., 2011; Ismael et al., 2017). For example, *h*-YFeO₃ has been reported to show a higher catalytic activity than *o*-YFeO₃ for the photodecomposition of methyl orange under visible light irradiation (> 420 nm) (Zhang et al., 2012). As *h*-YFeO₃ (1.94 eV) has a narrower band gap than *o*-YFeO₃ (2.43 eV), the band structure of *h*-YFeO₃ may be contributed to the high catalytic activity. *h*-YFeO₃ with the unique band structure is also demonstrated to be suitable as a photoanode for solar water splitting (Guo et al., 2017).

The catalytic performance of *h*-REFeO₃ as an oxidation catalyst has actively been investigated. When CH₄ oxidations over *h*-YbFeO₃ and *o*-YbFeO₃ obtained by the solvothermal reaction are evaluated (Hosokawa et al., 2011), the *h*-YbFeO₃ catalyst shows extremely high combustion activity compared with *o*-YbFeO₃. The T_{50} value, at which the catalyst exhibits 50% CH₄ conversion, is 475°C for *h*-YbFeO₃, while that for *o*-YbFeO₃ is 550°C. The surface area of the *o*-YbFeO₃ catalyst significantly decreases during calcination at 800°C in catalyst preparation; that is, the surface area of *o*-YbFeO₃ synthesized by the solvothermal method is $26 \text{ m}^2\text{g}^{-1}$ and that of *o*-YbFeO₃ after calcination is $6 \text{ m}^2\text{g}^{-1}$. Interestingly, the surface area of the *h*-YbFeO₃ catalyst (approximately $30 \text{ m}^2\text{g}^{-1}$) does not change significantly during the calcination, and the well-formed hexagonal plate shape is maintained. This result suggests that the surface energy of *o*-YbFeO₃ is higher than that of *h*-YbFeO₃. In other words, because *h*-YbFeO₃ synthesized by the solvothermal method has high thermal stability, high catalytic activity must be achieved.

The *h*-YFe_{1-x}Pd_xO_{3- δ catalyst synthesized by the sol-gel method has been reported to show high catalytic activity ($T_{50} = 100^\circ\text{C}$) for CO oxidation under excess O₂ concentration (1,000 ppm CO and 10% O₂), comparable to that of a Pd/Al₂O₃ catalyst with high surface area (Li et al., 2008). The ionic Pd species in the hexagonal lattice contributes to the catalytic activity. Lu et al. also reported that a Pd catalyst supported on *h*-YFeO₃ is more effective for CH₄ oxidation than Pd/*h*-YMnO₃ or Pd/*o*-LaFeO₃, and that the Pd/YFeO₃ catalyst maintains a high catalytic activity for CH₄ oxidation even after aging treatment at 900°C despite the phase transformation to *o*-YFeO₃ (Lu et al., 2014a,b, 2015). In these cases, as the Pd species is adequately anchored with the *h*-YFeO₃ support, the catalyst seems to have high catalytic activity.}

Furthermore, to develop a noble-metal free *h*-YbFeO₃-based catalyst with high catalytic activity, transition metal-modified *h*-YbFeO₃ catalysts are synthesized by solvothermal methods (Hosokawa et al., 2016). Mn modification by the solvothermal method dramatically improves the catalytic activity of *h*-YbFeO₃ itself for CO oxidation in which a reaction gas composed of 5,000 ppm CO and 5,000 ppm O₂ is introduced on catalyst bed.

The catalytic activity ($T_{50} = 120^{\circ}\text{C}$) of Mn-modified h -YbFeO₃ (Mn- h -YbFeO₃) with the composition of YbFe_{0.6}Mn_{0.4}O₃ exceeds that ($T_{50} = 134^{\circ}\text{C}$) of the noble metal Pd/Al₂O₃ catalyst.

CONCLUSION

Conventionally, a special method has been required for the synthesis of h -REFeO₃ due to its metastable nature; however, h -REFeO₃ can now be easily synthesized by precisely controlling the calcination process even when employing the coprecipitation or sol-gel methods. h -REFeO₃-based materials have been demonstrated to be applicable for catalyst materials, as well as magnetic or electronic materials. I believe that excellent catalyst

materials will evolve from catalyst designs focusing on the unique crystal structure of h -REFeO₃ or hexagonal-related materials (RE_{*n*}Fe_{*n*+1}O_(3*n*+1)).

AUTHOR CONTRIBUTIONS

The author confirms being the sole contributor of this work and has approved it for publication.

ACKNOWLEDGMENTS

The author sincerely thanks Masashi Inoue, Professor Emeritus at Kyoto University, for his invaluable discussion on hexagonal REFeO₃ materials.

REFERENCES

- Bagwell, R. B., Messing, G. L., and Howell, P. R. (2001). The formation of α -Al₂O₃ from θ -Al₂O₃: the relevance of a “critical size” and: diffusional nucleation or “synchro-shear”? *J. Mater. Sci.* 36, 1833–1841. doi: 10.1023/A:1017545213590
- Barbero, B. P., Gamboa, J. A., and Cadus, L. E. (2006). Synthesis and characterization of La_{1-x}Ca_xFeO₃ perovskite-type oxide for total oxidation of volatile organic compound. *Appl. Catal. B Environ.* 65, 21–30. doi: 10.1016/j.apcatb.2005.11.018
- Bourgeois, J., Hevieu, M., Poienar, M., Abakumov, A. M., Elkaim, E., Sougrati, M. T., et al. (2012). Evidence of oxygen-dependent modulation in LuFe₂O₄. *Phys. Rev. B* 85:064102. doi: 10.1103/PhysRevB.85.064102
- Ciambelli, P., Cimino, S., Rossi, S., Lisi, L., Minelli, G., Porta, P., et al. (2001). AFeO₃ (A = La, Nd, Sm) and LaFe_{1-x}Mg_xO₃ perovskites as methane combustion and CO oxidation catalysts: structural, redox and catalytic properties. *Appl. Catal. B Environ.* 29, 239–250. doi: 10.1016/S0926-3373(00)00215-0
- Cushing, B. L., Kolesnichenko, V. L., and O'Connor, C. J. (2004). Recent advances in liquid-phase syntheses of inorganic nanoparticles. *Chem. Rev.* 104, 3893–3946. doi: 10.1021/cr030027b
- Das, S., Chaudhuri, S., and Maji, S. (2008). Ethanol-water mediated solvothermal synthesis of cube and pyramid shaped nanostructured tin oxide. *J. Phys. Chem. C* 112, 6213–6219. doi: 10.1021/jp800612v
- Demazeau, G. (1999). Solvothermal processes: a route to the stabilization of new materials. *J. Mater. Chem.* 9, 15–18. doi: 10.1039/a805536j
- Dynys, F. W., and Halloran, J. W. (1982). Alpha-alumina formation in alum-derived gamma-alumina. *J. Am. Ceram. Soc.* 65, 442–448. doi: 10.1111/j.1151-2916.1982.tb10511.x
- Fanelli, A. J., and Burlew, J. (1986). Preparation of fine alumina powder in alcohol. *J. Am. Ceram. Soc.* 69, C174–C175. doi: 10.1111/j.1151-2916.1986.tb04828.x
- Guo, Y., Zhang, N., Huang, H., Li, Z., and Zou, Z. (2017). A novel wide-spectrum response hexagonal YFeO₃ photoanode for solar water splitting. *RSC Adv.* 7, 18418–18420. doi: 10.1039/C6RA28390J
- Hervieu, M., Guesdon, A., Bourgeois, J., Elkaim, E., Poienar, M., Damay, F., et al. (2014). Oxygen storage capacity and structural flexibility of LuFe₂O_{4+x} (0 ≤ x ≤ 0.5). *Nat. Mater.* 13, 74–80. doi: 10.1038/nmat3809
- Hosokawa, S., Jeon, H.-J., and Inoue, M. (2011). Thermal stabilities of hexagonal and orthorhombic YbFeO₃ synthesized by solvothermal method and their catalytic activities for methane combustion. *Res. Chem. Intermed.* 37, 291–296. doi: 10.1007/s11164-011-0251-9
- Hosokawa, S., Jeon, H.-J., Iwamoto, S., and Inoue, M. (2009). Synthesis of rare earth iron-mixed oxide nanoparticles by solvothermal methods. *J. Am. Ceram. Soc.* 92, 2847–2853. doi: 10.1111/j.1551-2916.2009.03295.x
- Hosokawa, S., Tada, R., Shibano, T., Matsumoto, S., Teramura, K., and Tanaka, T. (2016). Promoter effect of Pd species on Mn oxide catalysts supported on rare-earth-iron mixed oxide. *Catal. Sci. Technol.* 6, 7868–7874. doi: 10.1039/C6CY01462C
- Inoue, M., Nishikawa, T., Nakamura, T., and Inui, T. (1997). Glycolthermal reaction of rare-earth acetate and iron acetylacetonate: formation of hexagonal REFeO₃. *J. Am. Ceram. Soc.* 80, 2157–2160. doi: 10.1111/j.1151-2916.1997.tb03103.x
- Ismael, M., Elhaddad, E., Taffa, D., and Wark, M. (2017). Synthesis of phase pure hexagonal YFeO₃ perovskite as efficient visible light active photocatalyst. *Catalysts* 7:326. doi: 10.3390/catal7110326
- Kumar, M. S. V., Higaki, N., Kuribayashi, K., Hibiya, T., and Yoda, S. (2011). Formation of orthorhombic and multiferroic hexagonal phases from an undercooled RMnO₃ (R=Rare-Earth Element) melt using a containerless technique. *J. Am. Ceram. Soc.* 94, 281–288. doi: 10.1111/j.1551-2916.2010.04042.x
- Kumar, M. S. V., Kuribayashi, K., and Kitazono, K. (2009). Effect of oxygen partial pressure on the formation of metastable phases from an undercooled YbFeO₃ melt using an aerodynamic levitator. *J. Am. Ceram. Soc.* 92, 903–910. doi: 10.1111/j.1551-2916.2009.02974.x
- Kurzman, J. A., Li, J., Schladt, T. D., Parra, C. R., Ouyang, X., Davis, R., et al. (2011). Pd²⁺/Pd⁰ redox cycling in hexagonal YMn_{0.5}Fe_{0.5}O₃: implications for catalysis by PGM-substituted complex oxides. *Inorg. Chem.* 50, 8073–8084. doi: 10.1021/ic200455a
- Lafuerza, S., García, J., Subías, G., Blasco, J., and Cuartero, V. (2014). Strong local lattice instability in hexagonal ferrites RFe₂O₄ (R= Lu, Y, Yb) revealed by x-ray absorption spectroscopy. *Phys. Rev. B* 89:045129. doi: 10.1103/PhysRevB.89.045129
- Li, C., Soh, K. C. K., and Wu, P. (2004). Formability of ABO₃ perovskites. *J. Alloys Compd.* 372, 40–48. doi: 10.1016/j.jallcom.2003.10.017
- Li, J., Singh, U. G., Schladt, T. D., Stalick, J. K., Scott, S. L., and Seshadri, R. (2008). Hexagonal YFe_{1-x}Pd_xO_{3-δ}: nonperovskite host compounds for Pd²⁺ and their catalytic activity for CO oxidation. *Chem. Mater.* 20, 6567–6576. doi: 10.1021/cm801534a
- Lu, Y., Keav, S., Maegli, A. E., Weidenkaff, A., and Ferri, D. (2015). Pd loading and structure of flame-made Pd/YFeO_{3±δ}. *Top. Catal.* 58, 910–918. doi: 10.1007/s11244-015-0459-9
- Lu, Y., Keav, S., Marchionni, V., Chiarello, G. L., Pappacena, A., Di Michiel, M., et al. (2014a). Ageing induced improvement of methane oxidation activity of Pd/YFeO₃. *Catal. Sci. Technol.* 4, 2919–2931. doi: 10.1039/C4CY00289J
- Lu, Y., Michalow, K. A., Matam, S. K., Winkler, A., Maegli, A. E., Yoon, S., et al. (2014b). Methane abatement under stoichiometric conditions on perovskite-supported palladium catalysts prepared by flame spray synthesis. *Appl. Catal. B Environ.* 144, 631–643. doi: 10.1016/j.apcatb.2013.08.001
- Magome, E., Moriyoshi, C., Kuroiwa, Y., Masuno, A., and Inoue, H. (2010). Noncentrosymmetric structure of LuFeO₃ in metastable state. *Jpn. J. Appl. Phys.* 49:09ME06. doi: 10.1143/JJAP.49.09ME06
- Malaman, B., Tanniere, N., Courtois, A., and Protas, J. (1976). Structure cristalline de la phase Yb₂Fe₃O₇. *Acta Cryst. B* 32, 749–752. doi: 10.1107/S0567740876003919

- Matsui, Y., Kato, K., Kimizuka, N., and Horiuchi, S. (1979). Structure image of $\text{Yb}_3\text{Fe}_4\text{O}_{10}$ by a 1 MV high-resolution electron microscope. *Acta Cryst. B* 35, 561–564. doi: 10.1107/S0567740879004155
- Mizoguchi, Y., Onodera, H., Yamauchi, H., Kagawa, M., Syono, Y., and Hirai, T. (1996). Mossbauer spectra and magnetic susceptibilities of ultrafine hexagonal RFeO_3 (R = Eu, Yb) particles formed by the spray inductively coupled plasma technique. *Mater. Sci. Eng. A* 217/218, 164–166. doi: 10.1016/S0921-5093(96)10339-7
- Nishimura, T., Hosokawa, S., Masuda, Y., Wada, K., and Inoue, M. (2013). Synthesis of metastable rare-earth-iron mixed oxide with the hexagonal crystal structure. *J. Solid State Chem.* 197, 402–407. doi: 10.1016/j.jssc.2012.08.056
- Qin, Y. B., Yang, H. X., Zhang, Y., Tian, H. F., Ma, C., Zhao, Y. G., et al. (2009). The effect of Mg doping on the structural and physical properties of LuFe_2O_4 and $\text{Lu}_2\text{Fe}_3\text{O}_7$. *J. Phys. Condens. Matter.* 21:015401. doi: 10.1088/0953-8984/21/1/015401
- Schneider, S. J., Roth, R. S., and Waring, J. L. (1961). Solid state reactions involving oxides of trivalent cations. *J. Res. Nat. Bur. Stand. A* 65, 345–374. doi: 10.6028/jres.065A.037
- Vijaya Kumar, M. S., Nagashio, K., Hibiya, T., and Kuribayashi, K. (2008). Formation of hexagonal metastable phases from an undercooled LuFeO_3 melt in an atmosphere with low oxygen partial pressure. *J. Am. Ceram. Soc.* 91, 806–812. doi: 10.1111/j.1551-2916.2007.02200.x
- Woodward, P. M. (1997). Octahedral tilting in perovskites. II. structure stabilizing forces. *Acta Cryst. B* 53, 44–46.
- Zhang, Y., Yang, J., Xu, J., Gao, Q., and Hong, Z. (2012). Controllable synthesis of hexagonal and orthorhombic YFeO_3 and their visible-light photocatalytic activities. *Mater. Lett.* 81, 1–4. doi: 10.1016/j.matlet.2012.04.080

Conflict of Interest Statement: The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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