Catalysis Today 139 (2008) 37–42

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Preparation of alumina-supported $LaFeO_3$ catalysts and their catalytic activity for propane combustion

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ARTICLE INFO

Article history:
Available online 23 September 2008

Keywords:
Perovskite
Supported catalyst
Propane combustion

ABSTRACT

Supported $LaFeO_3$ catalysts on alumina were prepared and their catalytic activities for propane oxidation were investigated. Perovskite oxides were selectively deposited in or outside the pore of alumina support (intra- or extra-pore deposition) by using reverse homogeneous precipitation (RHP) and incipient wetness (IW) methods. X-ray diffraction and Raman spectroscopic studies confirmed the formation of the perovskite structure on the alumina support, and revealed that the dispersion of $LaFeO_3$ on alumina strongly depended on preparation methods. The catalytic activity for propane oxidation also depended on preparation methods, and perovskite catalysts deposited in the intra-pore of alumina showed higher activity than those deposited on the extra-pore of alumina. The activity of $LaFeO_3/Al_2O_3$ with the intra-pore deposition by the IW method hardly changed up to the calcination temperature of 1000 °C.

1. Introduction

Perovskite-type oxides containing transition metals show the high catalytic activity for complete oxidation of hydrocarbons and NO_x removal. These oxides have been extensively studied because of the possibility that they can be substituted for precious metal catalysts in many reactions [1–5].

So far, two kinds of processes have been mainly used for the preparation of perovskite oxides. The one is the solid-state reaction process and the other includes chemical solution processes (wet-processing). The former process needs high calcination temperatures usually higher than 1000 °C for the preparation of perovskite oxides [6], which gives rise to the formation of oxides with low surface areas and large particle sizes. Therefore, much attention has been focused on the chemical solution processes including co-precipitation, sol–gel, and complexing methods to obtain perovskite oxides with high surface areas [7–11]. These methods were effective in obtaining perovskite nano-particles at lower calcination temperatures. In some cases, however, the processes are complicated and a large quantity of organic solvents is necessary. From the standpoint of greener preparation method, simple methods are required for the preparation of perovskite oxide catalysts. We have reported that the reverse homogeneous precipitation (RHP) method gives homogeneous hydroxide precursors, which are transformed to perovskite particles at low calcination temperature as compared with conventional co-precipitation processes [12].

We have been investigating the development of preparation methods of not only nano-sized perovskite oxides but also supported perovskite catalysts with high activity and thermal stability. RHP method seems to be suitable for the preparation of γ-alumina-supported catalysts because γ-alumina loses it high surface area by heat treatment at high temperatures. We also herein attempted application of incipient wetness (IW) method, which have been conventionally used for preparation of supported noble metal catalyst, for preparation of supported perovskite catalyst [13,14]. The method utilizes pore of support material for preparation of perovskite. In this paper, we report that perovskite $LaFeO_3$ oxide can be selectively deposited in or outside the pore of alumina support by using RHP and incipient wetness methods. This finding can enable us to compare the catalytic properties of perovskite oxides in the pore with those on the outside of the pore. The present study has revealed that the deposition of perovskite oxides inside the pore of alumina support is useful for the preparation of supported perovskite catalysts with high activities for propane oxidation and high thermal stability up to 1000 °C.

2. Experimental

2.1. Materials

Catalyst supports, γ-Al_2O_3 (Japan Reference Catalyst (JRC) ALO-1 and ALO-8) were obtained from Catalysis Society of Japan and

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doi:10.1016/j.cattod.2008.08.006

used after calcination at 850 °C for 5 h in air. The specific surface area and pore volume were 118 and 0.58 mL g^{-1} for JRC-ALO-1 and 142 and 1.05 mL g^{-1} for JRC-ALO-8, respectively. The alumina support used was JRC-ALO-1 unless stated otherwise. $La(NO_3)_3 \cdot 6H_2O$ (purity: >97%) and $Fe(NO_3)_3 \cdot 9H_2O$ (>99%) of analytical reagent grade were obtained from Kishida Chemical Co., Ltd.

2.2. Preparation of alumina-supported $LaFeO_3$ catalysts

Fig. 1 shows the preparation procedures of alumina-supported $LaFeO_3$ catalysts. Four processes were used for the catalyst preparation, namely, mechanical mixing (MM), impregnation of RHP-prepared hydroxide precursor (I-RHP), RHP in pore (P-RHP), and incipient wetness.

2.2.1. Mechanical mixing method

Hydroxide precursors of the targeted perovskite were prepared by RHP method according to the method described elsewhere [12]. A mixed aqueous solution of La and Fe nitrates was dropped into aqueous ammonia (19%, 300 mL) at a rate of 1.5 mL min^{-1} under vigorous stirring. Then the RHP-prepared precursor was calcined at 750 °C for 5 h in air. The obtained oxide was then mixed with alumina by grinding for 10 min in an agate mortar. The MM-prepared catalyst was used as a reference catalyst to discuss the property of the other supported catalysts.

2.2.2. Impregnation of RHP-prepared hydroxide precursor method

The appropriate amount of the RHP-prepared hydroxide precursor was mixed well in distilled water (300 mL) with alumina by ultrasonication, and then evaporated to dryness under vigorous stirring (wet-impregnation), followed by grinding and calcination at 750 °C for 5 h in air. The water content of the hydroxide precursor was measured by thermogravimetry (Rigaku TG8120) prior to the impregnation.

2.2.3. RHP in pore method

The hydroxide precursor was prepared in the pore of alumina support by applying RHP technique. Aqueous ammonia (28%) and mixed aqueous nitrates of La and Fe were successively dry-impregnated to alumina; the volume of each solution was the same as a half of pore volume of alumina. The dry-impregnation was completed by wrapping impregnated alumina with PVC film and crumpling by the palm of the hands. The catalyst was calcined at 750 °C for 5 h in air.

2.2.4. Incipient wetness method

Mixed aqueous solution of metal nitrates, the quantity of which was equal to 50–75% pore volume of alumina, was dry-impregnated in alumina pore. The obtained samples were then calcined at 750 °C for 5 h in air. For the catalyst with 20 wt% loading, the cycle of dry-impregnation and drying was repeated twice.

2.3. Characterization of the supported catalysts and support material

The crystal structure of catalysts was examined by X-ray diffractometer (Rigaku RINT2200) using Cu Kα radiation. The Raman spectra were recorded at room temperature with 514.5 nm Ar^+ laser (Jasco NRS-2100). The colloidal particle size of RHP-prepared hydroxide precursor was measured by laser light scatting technique (Otsuka electronics ELS-8000QW). Nitrogen adsorption/desorption isotherms were measured at 77 K (Quantachrome NOVA2000). The specific surface area was determined by the BET method, and the pore size distribution was calculated from the adsorption branch of isotherms using the Barrett–Joyner–Halenda (BJH) formula. The pore volume of the samples was calculated by the integration of pore size distribution curve.

2.4. Catalytic activity measurement

Propane oxidation was carried out with a fixed-bed flow reactor by feeding He-balanced C_3H_8 (0.8%)–O_2 (25.5%) with a contact time (catalyst weight/flow rate) of 0.2 or 0.4 g s cm^{-3}. The granulated catalysts with 22–60 mesh (0.2 or 0.1 g) were placed in a U-shaped quartz-glass reactor under the reaction gas flow of 30 mL min^{-1}. The outlet gas was analyzed by an online TCD gas chromatograph (Shimazu GC-8A) equipped with a Molecular Sieve 5A column. Catalytic activity was evaluated by temperature for 50% conversion

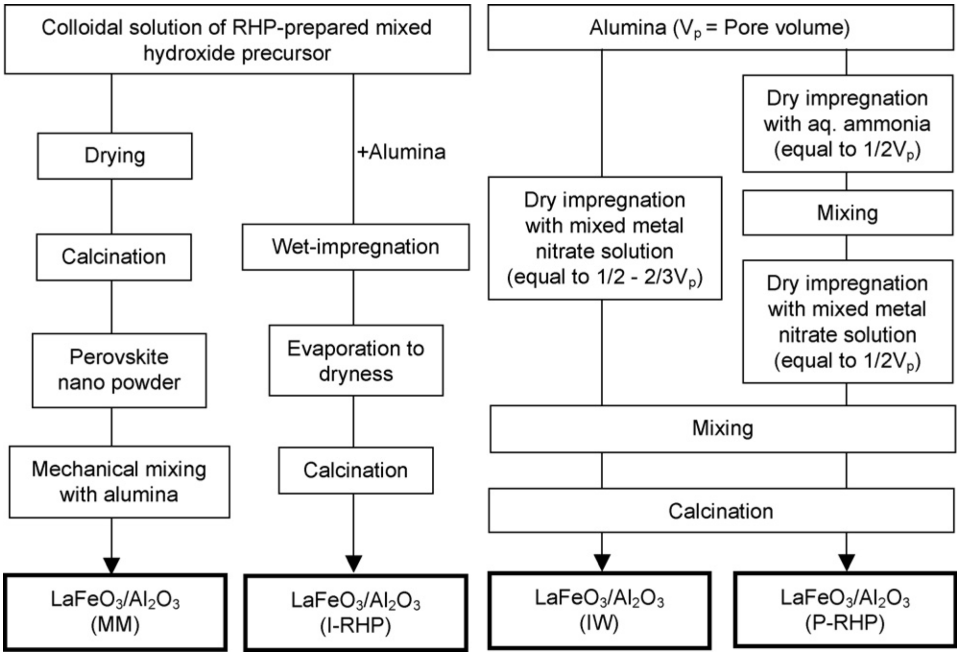

Fig. 1. Preparation procedures of alumina-supported $LaFeO_3$ catalysts.

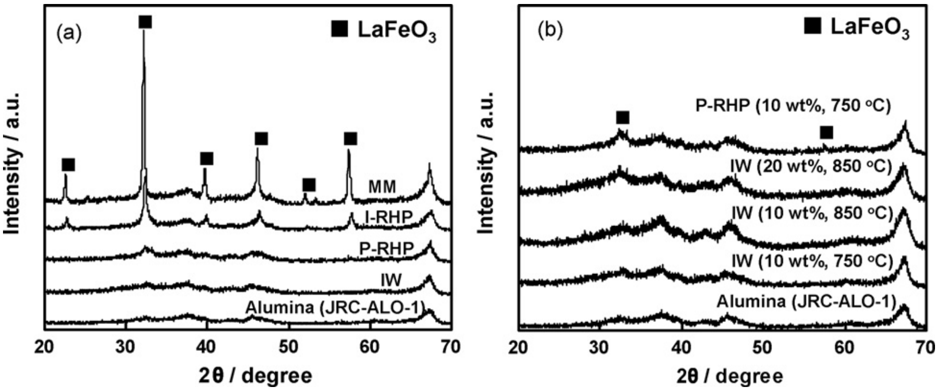

Fig. 2. XRD patterns of γ-alumina and $LaFeO_3/Al_2O_3$: (a) 10 wt% $LaFeO_3/Al_2O_3$ prepared by various methods and calcination at 750 °C; (b) IW- and P-RHP-prepared $LaFeO_3/Al_2O_3$. Preparation methods (a) and loading and the calcination temperature (b) are shown in figures.

(T_{50}) and the pseudo-first-order rate constants normalized to catalyst weight (k_w). It was confirmed that the propane oxidation reaction under the present experimental condition could be analyzed by the pseudo-first-order reaction to the concentration of propane.

3. Results

3.1. Structural characterization of IW-, P-RHP-, I-RHP- and MM-prepared catalysts

Fig. 2 shows the XRD patterns of $LaFeO_3/Al_2O_3$ catalysts prepared by the different methods. The diffraction peaks due to perovskite structure were clearly detected for MM- and I-RHP-prepared catalysts when they were calcined at 750 °C (Fig. 2(a)). The peak intensities became stronger when the calcination temperature was raised to 850 °C (data are not shown) due to the growth of the particle size. The diffraction peaks of I-RHP-prepared catalysts were broader than those of MM-prepared catalysts, indicating that the crystallite size of $LaFeO_3$ in the I-RHP-prepared catalyst was smaller than in the MM-prepared catalyst. Since the same hydroxide precursor was used for both preparations, the growth of $LaFeO_3$ particles during the calcination might be suppressed on the alumina support.

Fig. 3(a) shows the distribution of colloidal particle sizes of the hydroxide precursor prepared by RHP method. The particle sizes distributed from ca. 200 to 500 nm. Fig. 3(b) shows the pore size distribution of alumina support used (JRC-ALO-1). The pore sizes ranged from 2 to 120 nm with a maximum at 20 nm. Thus, the sizes of RHP-prepared hydroxide precursors were larger than those of alumina pores. This is a reason why the perovskite oxide in the I-RHP-prepared catalyst deposited outside of alumina pore and gave the stronger XRD peaks than those in P-PHP- and IW-prepared catalysts (see below).

Fig. 2(b) shows expanded XRD patterns of P-PHP- and IW-prepared $LaFeO_3/Al_2O_3$ catalysts. Since the strongest peak from the perovskite phase at around 33° is overlapped with a broad peak from γ-Al_2O_3, the identification of the perovskite phase was difficult. From careful analysis of XRD patterns, however, the formation of the perovskite oxide in 10 wt% $LaFeO_3/Al_2O_3$ calcined at 750 °C was confirmed in the P-RHP-prepared catalyst but not in the IW-prepared one. For IW-prepared catalysts, no obvious diffraction peaks due to perovskite structure were detected even after the calcination temperature was raised up to 850 °C and the loading level was increased to 20 wt%.

Fig. 4 shows the Raman spectra of 20 wt% $LaFeO_3/Al_2O_3$ prepared by IW method together with reference materials of $LaFeO_3$, Fe_2O_3 and Al_2O_3. The bands appeared at 234, 297 and 410 cm^{-1} for Fe_2O_3, while $LaFeO_3$ perovskite oxides showed the bands at 165 and 450 cm^{-1} [15,16]. $LaFeO_3/Al_2O_3$ gave two weak signals around 170 and 460 cm^{-1}, and this pattern was similar to that of $LaFeO_3$. From the results of Raman spectroscopic investigation and XRD, it can be concluded that the perovskite phase is formed in the IW-prepared catalyst but the size of the perovskite is too small to be detected by XRD. All the results of the catalyst characterization clearly show that the dispersion state of perovskite oxide on the alumina support was very much dependent on the preparation methods (Table 1).

3.2. Catalytic activity of alumina-supported $LaFeO_3$ catalysts for propane oxidation

Fig. 5 shows the catalytic activity for propane oxidation over 10 wt% $LaFeO_3/Al_2O_3$ catalysts prepared by IW, I-RHP and P-RHP methods and calcined at 750 °C. The catalytic activity depended on

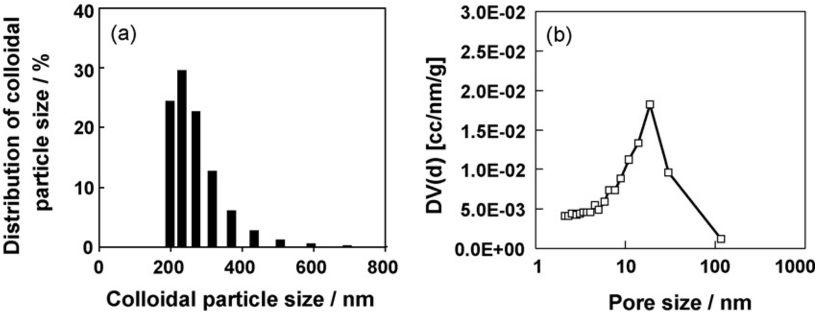

Fig. 3. (a) Colloidal particle size distribution of RHP-prepared hydroxide precursor and (b) BJH pore size distribution of Al_2O_3 calcined at 850 °C.

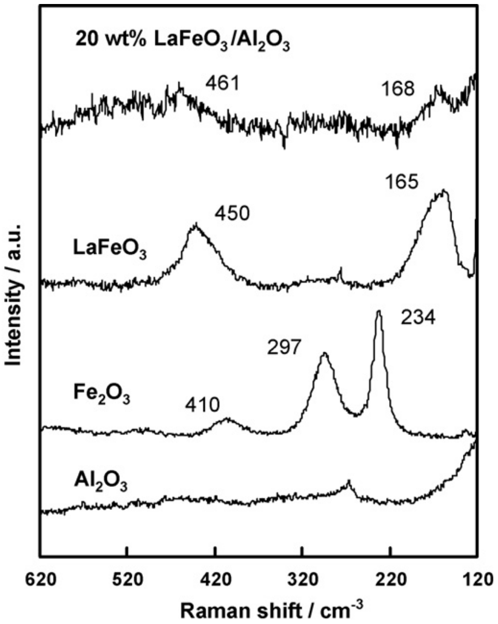

Fig. 4. Raman spectra of 20 wt% $LaFeO_3/Al_2O_3$ calcined at 850 °C and reference samples of $LaFeO_3$, Fe_2O_3 and Al_2O_3.

the preparation method and decreased in the order: IW > P-RHP > I-RHP method. Table 2 summarizes the rate constant for propane oxidation over 10 wt% $LaFeO_3/Al_2O_3$ catalysts prepared by different methods. Rate constants of IW-, P-RHP- and I-RHP-prepared catalysts were 5.6, 4.1 and 3.3 times higher, respectively, than that of the MM-prepared catalyst.

Fig. 6 compares catalytic activities for propane oxidation at 450 °C of 10 wt% $LaFeO_3/Al_2O_3$ and FeO_x/Al_2O_3 catalysts; for the latter catalyst, crystalline phase of any iron oxide was not detected by XRD at calcination temperatures of 650 and 750 °C, but Fe_2O_3 was observed at calcination temperature of 850 °C. Here, the catalysts were prepared by the IW method and the loading amount of Fe in both catalysts was the same. The rate constant for $LaFeO_3/Al_2O_3$ catalysts normalized by catalyst weight was 2.2–3.4 times higher than that of FeO_x/Al_2O_3 catalysts at any given calcination temperatures.

Fig. 7 shows the effect of calcination temperature on the catalytic activity for propane oxidation of 10 wt% $LaFeO_3$ supported on Al_2O_3 (JRC-ALO-8) prepared by the IW method. The propane oxidation activities were almost unchanged when the catalysts were calcined at the temperature 650–1000 °C (Fig. 7(a)). On the other hand, the activity greatly deteriorated after the calcination at 1200 and 1300 °C. Fig. 8 shows XRD patterns of $LaFeO_3/Al_2O_3$ calcined between 650 and 1300 °C. As stated above, no peaks other than those of γ-Al_2O_3 was observed when the calcination temperature was 850 °C and lower. The peaks due to the perovskite structure were not detected by XRD in all the temperature range examined. Very small peaks due to θ-Al_2O_3 phase appeared after the calcination at 1000 °C. After calcination at 1200 and 1300 °C, diffraction peaks ascribable to $LaAl_{11}O_{18}$ and α-Al_2O_3 newly appeared. This suggests the occurrence of not only the phase transition of alumina from γ to α modifications but also the solid-state reaction of alumina with $LaFeO_3$ to give $LaAl_{11}O_{18}$; the latter event undoubtedly accompanies the decomposition of the perovskite phase. The specific surface area of IW-prepared 10 wt% $LaFeO_3/Al_2O_3$ was shown in Fig. 7(b) as a function of calcination temperature. With increasing calcination temperature, the specific surface area decreased gently and greatly below and above 1000 °C, respectively.

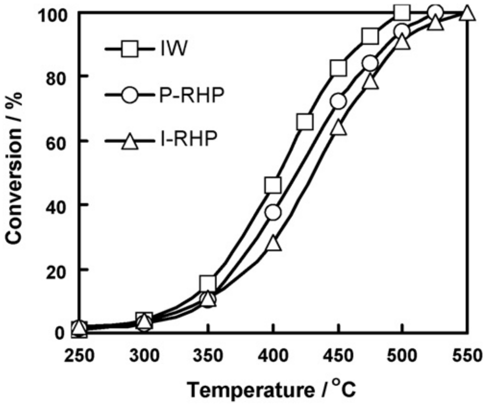

Fig. 5. Comparison of catalytic activity for propane oxidation over IW-, P-RHP- and I-RHP-prepared 10 wt% $LaFeO_3/Al_2O_3$ catalysts calcined at 750 °C: $W/F = 0.4\ g\ s\ cm^{-3}$.

4. Discussion

It has been reported that reverse homogeneous precipitation method is effective for the preparation of perovskite-type oxides with high surface area [12]. In this process, hydroxide precursors of the oxides were prepared at first, and then calcined at a temperature of 650 °C or above to form single-phase perovskite oxides. This study revealed that this preparation method was also useful for the preparation of alumina-supported $LaFeO_3$ perovskite oxide catalysts along with incipient wetness method. By using these techniques, perovskite oxides were selectively deposited in (intra-pore deposition) or outside the pore of alumina support (extra-pore deposition).

The extra-pore deposition was realized by the I-RHP method. In this method, the hydroxide precursor of the perovskite was prepared by the RHP method before its deposition on the alumina support. The precursors can be selectively deposited outside the pore of alumina support because the colloidal particle size of the RHP-prepared hydroxide precursor was larger than the pore size of alumina (Fig. 3). The hydroxide precursors on the alumina support were transformed to perovskite-type oxide by calcination at 750 °C.

Perovskite oxides were selectively deposited in the pore of alumina by IW and P-RHP methods, because these methods utilize alumina pore as the reaction space of perovskite synthesis. Especially in the IW method, perovskite oxides can be highly

Table 1
Summary of XRD results and specific surface area of prepared $LaFeO_3/Al_2O_3$ catalysts

Preparation method	Catalyst	Calcination temperature (°C)	SBET ($m^2\ g^{-1}$)	Crystal phase detected by XRD
IW	20 wt% $LaFeO_3/Al_2O_3$	850	83	γ-Alumina
IW	10 wt% $LaFeO_3/Al_2O_3$	850	105	γ-Alumina
IW	10 wt% $LaFeO_3/Al_2O_3$	750	103	γ-Alumina
P-RHP	10 wt% $LaFeO_3/Al_2O_3$	750	101	γ-Alumina, $LaFeO_3$
I-RHP	10 wt% $LaFeO_3/Al_2O_3$	750	117	γ-Alumina, $LaFeO_3$
MM	10 wt% $LaFeO_3/Al_2O_3$	750	107	γ-Alumina, $LaFeO_3$

Table 2
Pseudo-first-order rate constant per catalyst weight (k_w) for propane oxidation over 10 wt% $LaFeO_3/Al_2O_3$ catalysts prepared at 750 °C

Preparation method	k_w ($\times 10^{-9}$ m^3-C_3H_8 g^{-1} s^{-1})
IW	35.1
P-RHP	25.7
I-RHP	20.6
MM	6.3

Reaction conditions: $[C_3H_8] = 0.8\%$, $[O_2] = 25.5\%$, He balance, 450 °C and $W/F = 0.4$ g s cm^{-3}.

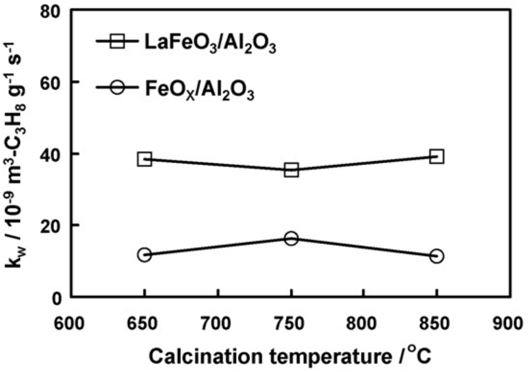

Fig. 6. Pseudo-first-order rate constant per catalyst weight for propane oxidation over 10 wt% $LaFeO_3/Al_2O_3$ and FeO_x/Al_2O_3 catalysts. Reaction temperature = 450 °C and $W/F = 0.4$ g s cm^{-3}.

dispersed in the pore of alumina and the oxide structure was not detected by XRD even after calcination at 850 °C and higher loading level (20 wt%). It has been reported that the constituent metals react with support materials to form impurity phases [17]. In the case of $LaFeO_3/Al_2O_3$, however, the reaction of perovskite with alumina was not observed when they were calcined at 850 °C and below (Fig. 2). In case of a Co-containing catalyst, it is well known that the reaction between alumina and Co to give a spinel-type oxide easily occur. The formation of $LaFeO_3$ perovskite may take priority over the formation of the Fe–Al spinel due to the moderate reactivity between alumina and Fe. The formation of perovskite-type oxides was confirmed by catalytic activity measurements and Raman spectroscopic studies. $LaFeO_3/Al_2O_3$ catalysts showed higher activities than FeO_x/Al_2O_3 catalysts (Fig. 6). This result suggests the presence of $LaFeO_3$ perovskite, because it is reported to be more active than an iron oxide (Fe_2O_3) [2]. Moreover, Raman spectra confirmed the formation of perovskite structure for the $LaFeO_3/Al_2O_3$ catalyst prepared by IW method and calcined at 850 °C (Fig. 4). For the P-RHP-prepared catalyst, on the other hand, the perovskite formation was confirmed by XRD, indicating that the crystalline size was large as compared with the IW-prepared catalyst.

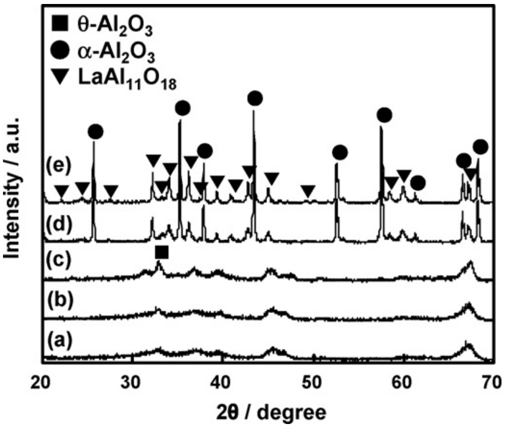

Fig. 8. XRD patterns of 10 wt% $LaFeO_3/Al_2O_3$ calcined at (a) 650 °C, (b) 850 °C, (c) 1000 °C, (d) 1200 °C and (e) 1300 °C.

The catalytic activities for the propane oxidation depended on the dispersion of perovskite oxides on alumina. The catalyst prepared by mechanical mixing of $LaFeO_3$ and alumina showed lower dispersion and much lower activity than the catalysts prepared by impregnation methods (IW, P-RHP and I-RHP methods). The perovskite oxides deposited in the alumina pore (IW and P-RHP methods) showed higher activities than that deposited outside the pore (I-RHP method). Especially, high activity of IW-prepared catalyst is ascribed to the high dispersion of perovskite oxides in the pore of alumina as compared with P-RHP-prepared catalyst. The MM catalyst was prepared by simple mixing of alumina support and $LaFeO_3$ powder that was prepared by the RHP method and the calcination temperature of 750 °C. The specific surface area of thus-prepared $LaFeO_3$ was 10.8 m^2 g^{-1}. Provided that the specific activity of $LaFeO_3$ per surface area is the same for unsupported and alumina-supported catalysts, the specific surface area of $LaFeO_3$ formed on alumina support can be calculated to be 60.5, 44.3 and 35.6 m^2 g^{-1} for IW-, P-RHP- and I-RHP-prepared catalysts, respectively, from the experimental result of specific activity per weight (Table 2).

The deposition of perovskite oxides in the pore of alumina by the IW method was also effective in improving thermal stability of the catalysts. It has been reported that unsupported perovskite oxides decrease in their activities with the increase in calcination temperature due to the decrease of their surface areas [18]. On the other hand, $LaFeO_3/Al_2O_3$ catalysts prepared by the IW method showed improved thermal stability: the surface area was gently decreased and crystalline perovskite oxides were not observed

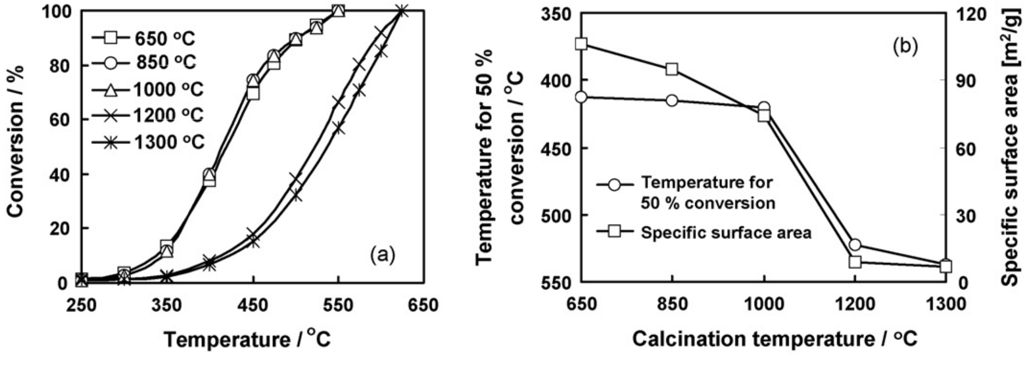

Fig. 7. Effect of calcination temperature on catalytic activity for propane oxidation and specific surface area of 10 wt% $LaFeO_3/Al_2O_3$: $W/F = 0.2$ g s cm^{-3}.

with increasing the calcination temperature up to 1000 °C. It is likely that the sintering and/or agglomeration of perovskite hardly occur and the high dispersion of perovskite remained up to 1000 °C, probably due to strong interaction between $LaFeO_3$ and Al_2O_3. However, the catalyst surface area significantly decreased and the perovskite structure was decomposed due to the reaction of La with alumina support to form $LaAl_{11}O_{18}$ phase, which is the reason for the catalyst deactivation at temperatures over 1000 °C.

5. Conclusion

In this study, we prepared alumina-supported ferrite perovskites ($LaFeO_3/Al_2O_3$) catalysts and investigated their activities for propane oxidation. Perovskite oxides were selectively deposited in or outside the pore of alumina (intra- or extra-pore deposition) by using reverse homogeneous precipitation and incipient wetness methods. X-ray diffraction study and Raman spectroscopy analysis confirmed the formation of perovskite structure on the alumina support, and revealed that the dispersion of $LaFeO_3$ on alumina strongly depended on the preparation methods. The perovskite catalysts deposited in the alumina pore showed higher activity than those selectively deposited outside the pore, and the activity did not change by heat treatment up to 1000 °C, probably due to high dispersion of perovskite and strong interaction between perovskite and alumina. The present results clearly show that the formation of perovskite in alumina pore is very powerful in preparing active supported perovskite catalysts with thermal stability.

Acknowledgements

This work was partially supported by “Nano-structured Catalysts and Materials” Research Area, CREST, JST (Japan Science and Technology Agency).

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