

Reduction process of Pd-containing La-Fe perovskite-type oxides by in-situ Dispersive X-ray absorption spectroscopy

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Abstract. Reduction process of Pd-containing La-Fe perovskites was investigated by in-situ Pd K-edge dispersive X-ray absorption fine structure as well as mass spectroscopy. The prepared perovskite was characterized by a conventional X-ray absorption spectra to confirm the incorporation of cationic Pd into perovskite matrix. Under the reductive atmosphere (5 vol%H₂/He), we found the presence of three reduction processes of Pd cations in perovskite structure. The segregation of Pd metal particles was observed from 200-400 °C although the cationic Pd species remained at 700 °C due to the strong metal-support interaction.

1. Introduction

Over the past years, many researchers have investigated the catalytic properties of Palladium-supported/incorporated perovskite-type oxides for three-way catalytic reaction to remove pollutants in automobile emission [1]. Nishihata et al. reported LaFe_{0.95}Pd_{0.05}O₃ perovskite, which achieved incorporation of Pd into the perovskite matrix (B-site) as ionic state of Pdⁿ⁺ (n≥2) [2]. In this catalyst, Pd can segregate out of and reintegrate in the perovskite lattice under reductive and oxidative atmospheres, respectively. This self-regenerating property prevents Pd particles from sintering and enables to maintain their high catalytic activity with high metal dispersion. This research clearly indicates that the redox properties are one of the most important factors to determine the activity of three-way catalyst. Temperature-programmed reduction (TPR) techniques are commonly used to investigate the redox properties of metal oxides. H₂-TPR can be easily applied for a simple system like MO_x/Al₂O₃ (M = metal cation) because only one metal cation contributes to the reduction behavior. However, the results always become more difficult in a mixed metal oxide system since we cannot distinguish which cations were reduced based on the conventional TPR. Therefore, it is of great interest to investigate the redox properties for a particular element in the sample. X-ray absorption fine structure (XAFS) technique is one of the candidates for solving the problem as it can obtain



information on local structure and electronic states of the target element at the same time. Here, we investigated the reduction process of Pd-containing LaFe perovskites by simultaneously conducting Pd K-edge XAFS and H₂-TPR with mass spectrometer. Dispersive XAFS (DXAFS) mode was applied for high speed observation.

2. Experimental

Pd-containing La-Fe perovskites (LaFe_{0.95}Pd_{0.05}O₃) were prepared by the amorphous citrate method. The aqueous solution of the metal nitrates and citric acid (chemicals and purity; La(NO₃)₃·6H₂O > 95.0 %, Fe(NO₃)₃·9H₂O > 99.0 %, 5%Pd(NO₃)₂ aq.solution, citric acid > 99 %) in a molar ratio of La: Fe: Pd: citric acid = 1:0.95:0.05:3 were evaporated to dryness under stirring, followed by the calcination in air at 600 °C for 2 h. XRD patterns of the as-prepared perovskites (labeled as LaFePdO₃) were indexed with orthorhombic structure and no impurities were detected. Incorporation of Pd was also preliminarily confirmed by a conventional XAFS (Quick XAFS) at BL01B1 of SPring-8 using Si(311) for Pd, La K-edge and BL06 of SAGA-LS using Si(111) for Fe K-edge. In-situ Pd K-edge DXAFS experiments were carried out at BL28B2 of SPring-8[6]. DXAFS spectra were collected by a Si(422) bent crystal with the Laue-configuration polychromator and a position sensitive CCD detector (Hamamatsu Photonics K.K., 656(X) x 178(Y) pixels were used for our experiment). The intensities of the vertical (Y) direction were summed to produce a spectrum and those of the horizontal (X) direction were used for calibration plots to convert pixel into energy. The calibration plots were produced by comparing a conventional XAFS and DXAFS spectrum using Pd foil. The energy region that we have acquired was from 24.10 keV to 25.24 keV. A single frame was acquired at the exposure time of 240 ms. A spectrum used for analysis was obtained by accumulating 10 frames to improve counting statistics (2.4 s/spectrum). The samples were preliminarily treated at 350 °C for 10 min in 20 vol.%O₂/He and cooled to 60 °C under the same atmosphere. H₂-TPR were carried out from 60 to 700 °C at 10 °C/min using 5 vol.%H₂/He at 30 mL/min. The data analysis was processed by using ATHENA and ARTEMIS, a suite of IFEFFIT software programs[7].

3. Results and discussion

3.1. Incorporation of Pd into perovskite structure

The local structure of Pd in the prepared material was analysed by a conventional Q-XAFS before starting DXAFS measurement. **Figure 1.** shows normalized Pd K-edge XANES spectra of LaFePdO₃ perovskites. The shoulder (24.340-24.345 keV) was clearly observed for PdO, confirming that Pd²⁺ ions are in square planar coordination. For LaFePdO₃, XANES spectra couldn't be expressed on the basis of both Pd foil and PdO contributions, indicating the disappearance of PdO on LaFePdO₃. In contrast, peak in 24.367 keV (post-edge region) exhibited the formation of a Pd-containing oxide phase because the peak could also be observed for LaPdO₃[3]. In addition, the XANES spectra of

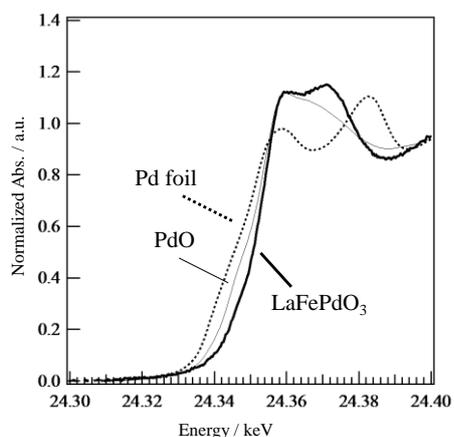


Figure 1. Pd K-edge XANES of LaFePdO₃

LaPdO₃ and LaFePdO₃ were very similar reflecting the similar structure of both materials[3]. These results suggested that Pd-LaFeO₃ solid solutions were successfully achieved in LaFePdO₃ and Pd occupied distorted octahedral sites (Fe site) of LaFeO₃.

Furthermore, we compared EXAFS oscillations among the three cationic ions (La, Fe, Pd) in LaFePdO₃. The non-phase shift corrected *k*³-weighted EXAFS spectra and their Fourier transformation for LaFePdO₃ were presented in **Figure 2**(A) and (B), respectively. EXAFS oscillations of PdO and LaFePdO₃ (@La K-edge, (c)) were completely different in both their amplitude and period from that of LaFePdO₃ (@Pd K-edge, (a)). On the other hand, LaFePdO₃ (@Pd K-edge, (a)) shared several oscillation features in LaFePdO₃ (@Fe K-

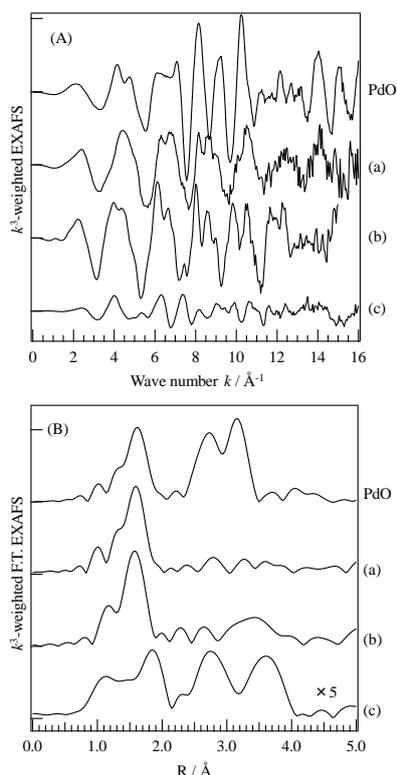


Figure 2. k^3 -weighted Pd K-edge EXAFS (A) and their Fourier transformation (B) for PdO@Pd K-edge, (a) LaFePdO₃@Pd K-edge, (b) LaFePdO₃@Fe K-edge and (c) LaFePdO₃@La K-edge. F.T. range was fixed to 3-15 Å for all EXAFS.

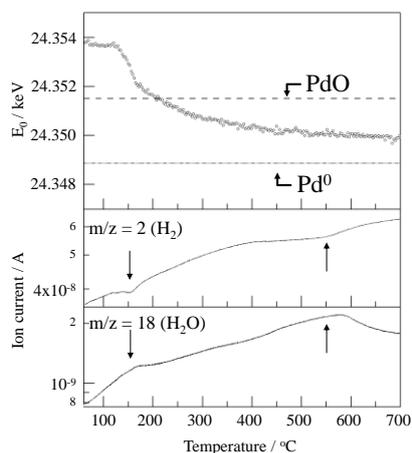


Figure 3. Temperature-dependent change of E_0 and mass spectrometer signal profile of LaFePdO₃ during reduction by hydrogen from 60 °C to 700 °C

EXAFS by curve fitting. We conducted R -space fitting using F.T. EXAFS (R range of 1-3.5 Å) with two shell model (Pd-O, Pd-Pd). The reaction with the host material such as alloying of Pd with Fe could not be observed in La-Fe-Pd perovskite system[4]. The fitting results were shown in Figure 4. for Pd-O and Pd-Pd shells. Due to the strong correlation between coordination number (C.N.) and thermal factor, Pd-Pd shell slightly under estimate the values. However, it was observed from 200 °C

edge, (b)) even though each oscillation period was slightly different due to the difference of phase shift and bond length.

As a result, LaFePdO₃ showed similar F.T. EXAFS in Pd K-edge (a) and Fe K-edge (b), reflecting the same local structure of these materials. As a consequence, we confirmed that cationic Pd of LaFePdO₃ occupies B-site of La-Fe perovskites.

3.2. Reduction behaviour of Pd under 5 vol.%H₂/He

The reduction process of LaFePdO₃ was investigated by dispersive XAFS measurements. The dispersive Pd K-edge XANES spectra of LaFePdO₃ didn't show any shift after changing atmosphere from pretreatment gas (O₂) into H₂ at 60 °C. Therefore, most of cationic Pd species maintained the state and local structure even in this condition. **Figure 3** shows temperature dependence of XANES spectra and the absorption edge energy (E_0) change on LaFePdO₃ under 5 vol.%H₂/He. The ion current of mass spectrometer (H₂ ($m/z = 2$), H₂O ($m/z = 18$)) against the temperature were also included. The figure indicated that E_0 was stable under 120 °C while a remarkable decrease was observed from 120-200 °C. Then, the position of E_0 exhibited between that of PdO and Pd⁰ the entire temperature from 200 °C to 700 °C. This result means that a part of cationic Pd is still in perovskite lattice, and Pd⁰ particles, which strongly interacting with support, were formed on the perovskite[4]. In terms of mass signals (H₂, H₂O), they showed the H₂ consumption (negative) and H₂O evolution (positive) peaks at around 120-200 °C and 400-550 °C. The former reduction was coincided with the behavior of E_0 while the latter one was not. Even though the slow reduction was confirmed at around 550 °C in E_0 , it might be difficult to observe as a peak, considering the variation of E_0 . These results suggest that the reduction at around 400-550 °C is originated from the reduction of Fe³⁺ in perovskite[3]. In particular, the reduction rate both cationic Fe and Pd became quite small and the total reaction seemed to be stopped over 550 °C. This caused the decrease of water production and the absence of negative peak in H₂.

Figure 4 shows non-phase shift corrected k^2 -weighted DXAFS (a) and their Fourier transformation (k range 3-10 Å) (b) for LaFePdO₃ under H₂-TPR. The EXAFS oscillations exhibited shift of the peak and its amplitude became small as the temperature increased due to the structural change and thermal factor. The peak at 1.5 Å in F.T. EXAFS corresponds to Pd-O shell. It remained over the whole temperature range, which had an agreement with XANES results. On the contrary, Pd-Pd shell at 2.5 Å was observed above 180 °C. In order to understand the structural changes, the local structure of Pd was estimated from

and became almost constant over 400 °C, whose temperature coincided with the end of a remarkable decrease E_0 . This suggested that the supply of Pd from the bulk has stopped and particle growth was suppressed by strong metal-support interaction[4]. Besides, C.N. of Pd-O shell showed the constant values until Pd-Pd shell was appeared at 200 °C. This temperature was just under the reduction peak in mass signal at 120-200 °C and the temperature at the intersection of E_0 for LaFePdO₃ and PdO (Pd²⁺) is just around 200 °C. Thus, the reduction at this temperature range was not the reduction of cationic Pd into Pd metal particles but into stable Pd²⁺ species. Moreover, the constant C.N. in Pd-O indicated that LaFePdO₃ perovskite structure around Pd is stable below 200 °C in this condition even if the cationic Pd was reduced or segregated out from the lattice.

Considering these results, the reduction process of Pd species in Pd-incorporated La-Fe perovskites can be expected to show three reduction reactions; I (120-200 °C) Reduction of Pdⁿ⁺ (n = 3 or 4) into Pd²⁺ species in perovskite matrix or PdO particles, II (200-400 °C) the simultaneous reduction of cationic Pd and Fe in perovskite structure (decomposition), III (550-700 °C) the reduction of Pd²⁺ species and Fe in perovskite were almost ended.

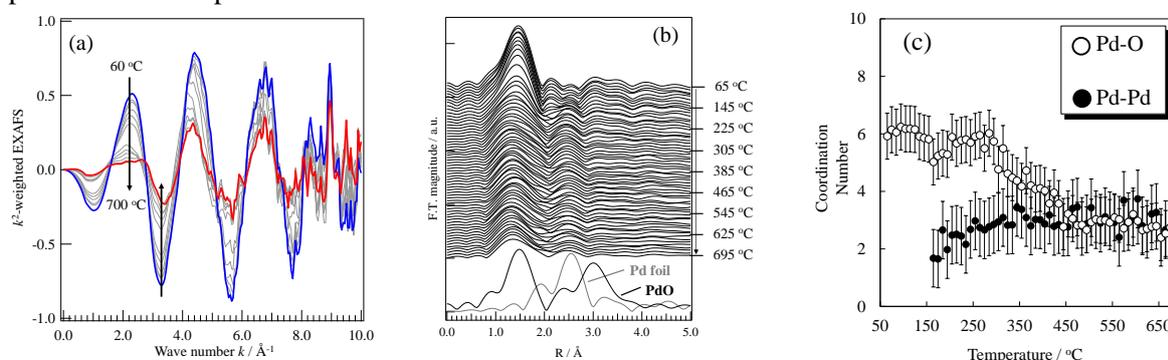


Figure 4. Temperature-dependent change of k^2 -weighted Pd K-edge EXAFS, their Fourier transformation (B) and coordination number of Pd-O and Pd-Pd.

4. Conclusion

In-situ Pd K-edge DXAFS and mass spectrometry techniques enabled the simultaneous investigation on XAFS and TPR study. We identified the presence of three reduction processes of Pd on Pd-containing LaFe perovskites. Under 5 vol.%H₂/He, the segregation of Pd metal particles observed and Pd couldn't be completely reduced due to the strong metal-support interaction.

Acknowledgements

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References

- [1] Li X, Chen C, Liu C, Xian H, Guo L, Lv J, Jiang Z, Vernoux P 2013 *ACS Catalysis* **3**(6) 1071
- [2] Nishihata Y, Mizuki J, Akao T, Tanaka H, Uenishi M, Kimura M, Okamoto T and Hamada 2002 *Nature* **418** 164
- [3] Eyssler A, Mandaliev P, Winkler A, Hug P, Safonova O, Figi R, Weidenkaff A, Ferri D 2010 *Journal of Physical Chemistry C* **114**(10) 4584
- [4] Katz M B, Graham G W, Duan Y, Liu H, Adamo C, Schlom D G, PAN X 2011 *Journal of the American Chemical Society* **133**(45) 18090
- [5] Kato K, Uruga T, Tanida H, Yokota S, Okumura K, Imai Y, Irie T and Yamakata Y 2007 *AIP Conference Proceedings* **879** 1214
- [6] Ravel B, Newville M 2005 *Journal of Synchrotron Radiation* **12** 537