La-Fe-Pd 系ペロブスカイト型酸化物の Pd K-, L_3-edge による XAFS 化学状態分析

Characterization of mechanochemically synthesized Pd-containing La-Fe perovskites by Pd K- and L_3-edge X-Ray Absorption Spectroscopy

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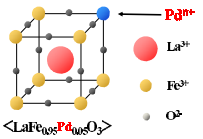
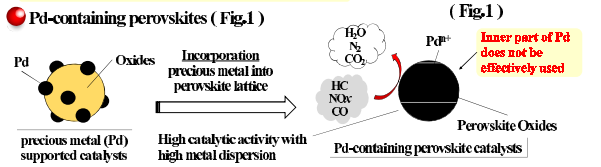
Introduction

- Conventional three-way-catalyst
  - use of extra precious metals
  - Strengthening of emission regulations
  - Drastic world wide increase of vehicle possession
- Conservation of precious metals is required.
- Pd-containing perovskites (Fig.1)



(Fig.1)

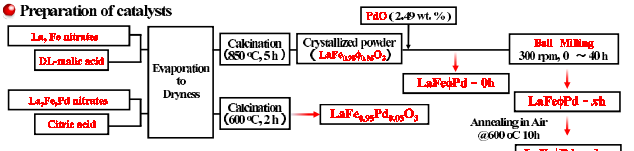


Purpose of this study

- To investigate the effect of milling time on the state of Pd and incorporation of Pd into the perovskite structure by means of Pd K- and L_3-edge XAFS spectra.

Experimental

- Preparation of catalysts



- Characterization
  - Structural analysis
    - Powder X-ray diffraction (XRD)
  - Quantitative analysis of Pd
    - Inductively coupled plasma (ICP)
  - Surface analysis
    - X-Ray photoelectron spectroscopy (XPS)
  - Local structural analysis of Palladium
    - X-ray absorption fine structure (XAFS)

SPring-8 BL-01B1	Si (3 1 1) double crystal Rh-coated mirror
Pd K-edge	Transmission mode (Q-XAFS)
SAGA-LS BL-06	Si (1 1 1) double crystal Rh-coated mirror
Pd L_3-edge	Fluorescence Yield (Step Scan)

Summary

- Pd K-edge XAFS spectrum suggested that PdO reacted with La-Fe perovskites to form solid solution by ball-milling.
- Pd L_3-edge XAFS spectrum suggested that the existence of Pd^{2+} and Pd^{4+} in La-Fe-Pd perovskites and the presence of isosbestic point in the milling time dependence showed interconverting Pd species(2+⇔4+).
- The local structure and chemical bonding of Pd can be extracted from Pd K-edge XAFS while Pd L_3-edge XAFS can distinguish the difference oxidation state of Pd between 2+ and 4+.

Results and Discussion

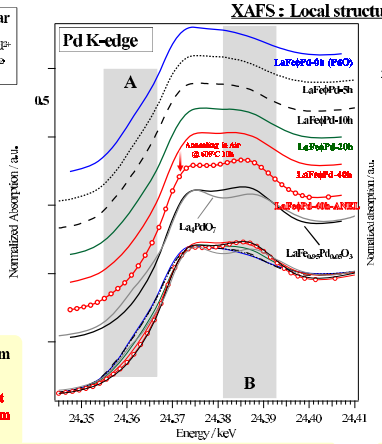
- Shoulder A observed for LaFe/Pd-0h, confirms Pd^{2+} (PdO) in square planar coordination.

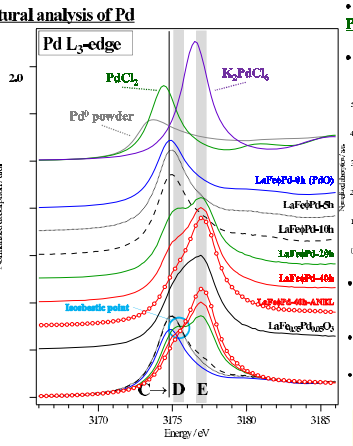
- Peak B appeared and Shoulder A disappeared in the spectra of LaFe/Pd-20,40h.
- Peak B is characteristic of Pd^{3+} ($LaFe_{0.95}Pd_{0.05}O_3$) occupying octahedral sites.
- La_4PdO_7 (Pd^{2+}, sq. planar) also showed the peaks in the range of B though its position was slightly different from $LaFe_{0.95}Pd_{0.05}O_3$.

The peaks in the range of B merely confirm the formation of Lanthanum palladates.

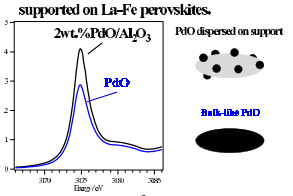
Pd K-edge XAFS spectrum suggested that PdO reacted with La-Fe perovskites to form solid solution by ball-milling.

XAFS : Local structural analysis of Pd





- Chemical shift of reference samples
  $PdCl_2$ (Pd^{2+}) < PdO (Pd^{2+}) < K_2PdCl_6 (Pd^{4+})
  Chloride < Oxide
- The white line intensity of peak C increased for 5 h, which indicates that PdO was supported on La-Fe perovskites.



- The spectrum of PdO shifts to higher energy range and eventually doublet peaks of D and E.
- Peak D is originated from Pd^{2+}, incorporated into La-Fe perovskite lattice.
- Peak E appeared higher energy than K_2PdCl_6 (Pd^{4+}).

Peak D and E can be assigned to Pd^{2+} incorporated into La-Fe perovskite lattice.

The difference oxidation state of Pd between 2+ and 4+ cannot be distinguished each other by Pd K-edge XAFS while Pd L_3-edge XAFS can confirm the existence of Pd^{2+} and Pd^{4+}.

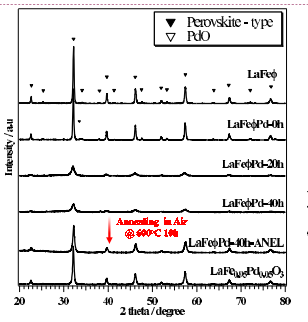
⇔

The existence of Pd^{2+} and Pd^{4+} are confirmed by Pd L_3-edge XAFS.
The presence of isosbestic point in the milling time dependence showed interconverting Pd species(2+⇔4+).

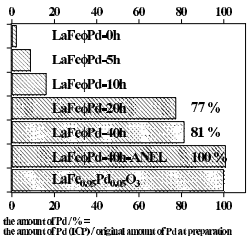
XRD : structural analysis of perovskites

- All samples were orthorhombic perovskites
- Broadening of peaks in ball-milled samples

Introduction of lattice distortion and Decrease of crystalline size



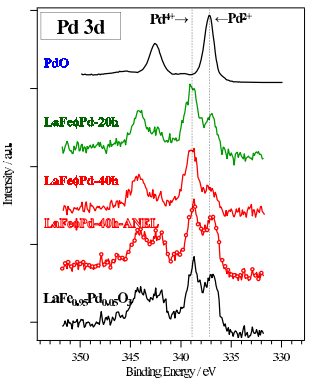
ICP : Quantitative analysis of Pd



- The amount of Pd incorporated into the perovskite increased with increasing milling time.

Pd was incorporated into perovskite by milling

XPS : Surface analysis



- XPS peak of 338.9 eV and 337.1 eV of Pd $3d_{5/2}$ can be attributed to Pd^{4+} and Pd^{2+} respectively.
- The intensity of Pd^{2+} (PdO) were decreased with increasing milling time.

Consistent with the results of Pd L_3-edge XAFS that the existence of mixed valence state of Pd.