Spinodal nano decomposition in perovskite three-way catalysts: First-principles calculations and Monte Carlo simulations ☆

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ABSTRACT

We show that self-forming perovskite three-way catalysts might occur fluctuation distribution of precious metal concentrations owing to spinodal nano-decomposition (SND). We perform *ab initio* calculations to evaluate the free energy of $La(Fe_{1-x},Pd_x)O_3$ and $La(Fe_{1-x},Rh_x)O_3$. In addition the fluctuation distribution is simulated by applying the Monte Carlo method mapped to the Ising model with realistic *ab initio* chemical pair interactions between precious metal impurities in perovskite catalysts. It is found that the SND inherently occurs in $La(Fe_{1-x},Pd_x)O_3$, but not in $La(Fe_{1-x},Rh_x)O_3$. Calculated inhomogeneous distributions of Pd atoms in $La(Fe_{1-x},Pd_x)O_3$ are consistent with the high-resolution X-ray energy dispersive spectroscopy measurements.

1. Introduction

A lot of researchers are of much interest in self-forming Pd-, Rh-, and Pt-doped perovskite catalysts for automotive emissions control due to their unique functionalities [1–15]. In a conventional catalyst made of fine precious metal particles supported on a solid like an alumina, agglomeration of the metal particles is inevitable under high temperature conditions in the redox environment. This is main reason for deterioration of automotive three-way catalysts. In the self-forming perovskite catalysts, however, the deterioration is strongly suppressed. Therefore, consumption of the precious metal is greatly reduced, providing a highly efficient solution for supply problems. The reason for non-deterioration is thought to be reformation of a precious metal doped perovskite lattice in the NO_x-reduction environment from segregated nano-particles of precious metal created in the CO- and C_xH_y-oxidation environment. According to Nishihata et al., in this self-forming model, precious metal atoms are assumed to move into and out of the perovskite host matrix. Thus, growth of precious metal grains is suppressed due to this repeated motion of precious metal atoms between a solid solution and metallic nano-particles during three-way catalytic reactions [2]. In some doped perovskite structures, it is known that

diffusion of oxygen happens rather frequently. At the same time, we may expect motion of metal atoms via a process exchanging metallic atoms. The process would be enhanced, if oxygen vacancies are created in the perovskite host crystal. This scenario might support the above model of self-forming perovskite catalysts. However, recently it has been reported by Katz et al. that the processes proposed by Nishihata et al. occur to a very limited extent, the predominant mode is the localized reaction that occurs between Pd particles situated on the surface and the perovskite support under oxidizing conditions [12]. In addition to this indication, they observed that the Pd particles have sunk partially into the $LaFeO_3$ and the presence of some Pd within the film by means of energy dispersive spectroscopy (EDS) mapping, as shown in Figure 1. As expected from the work of Nishihata et al. [2], regions with Pd as indicated in the Figure 1 are also regions of relatively low Fe concentration, since Pd is known to take the place of Fe in the perovskite lattice. In addition, we find that Pd (or Fe) atoms show concentration fluctuations in the Figure 1 of EDS mappings as indicated by red dashed lines.

2. Purpose

In order to investigate a possibility of inhomogeneous distributions of Pd atoms in the perovskite film we propose an idea employed a new model based on spinodal nano-decomposition (SND) [16]. Here we define that SND means a nanoscale fluctuation of an impurity concentration after a quenching process. When SND happens, spatial inhomogeneity in distribution of precious metal atoms occurs but the crystal structure itself is maintained. In the
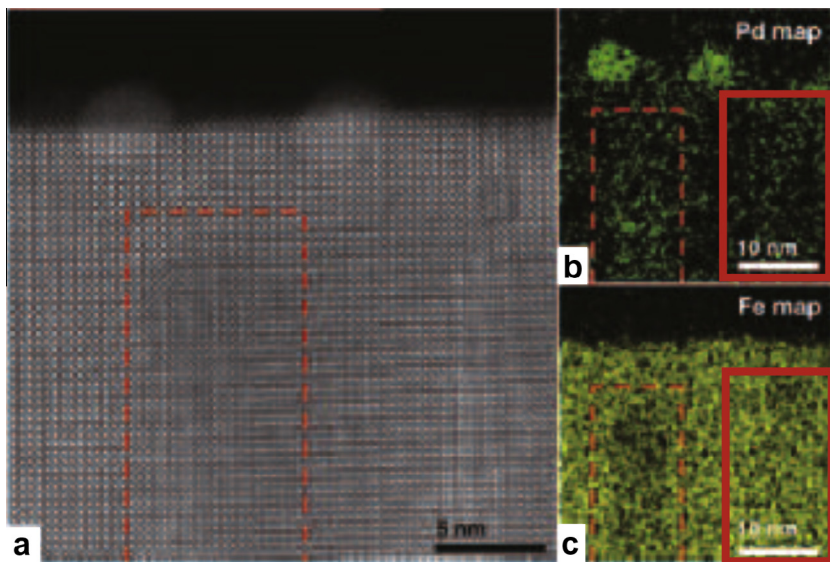
Figure 1. Experimental data of Katz et al. [12](a) HAADF-STEM image of a region of the oxidized Pd/LaFeO$_3$ PLD thin film with a visibly distorted lattice, together with corresponding (b) Pd and (c) Fe EDS maps. The indicated areas contain Pd (at levels estimated to be approximately 20% of Fe) within the oxide. We add the concentration fluctuated area by red solid lines in (b) and (c). (For interpretation of the references to colour in this figure caption, the reader is referred to the web version of this article.)

SND model, thus we can naturally explain stability of the catalysts found in the experiment [17]. In this letter, we show calculated mixing free energies of between LaFeO$_3$ and LaPdO$_3$ and that of between LaFeO$_3$ and LaRhO$_3$ with taking a lattice relaxation effect into consideration as an extended result from the previous report [16]. In addition we also show *ab initio* calculations for such inhomogeneous disordered systems. For the sake of simplicity cubic structure is assumed.

3. Calculation method

We consider La(Fe$_{1-x}$,Pd$_x$)O$_3$ (LFPO) as the typical perovskite catalyst. In order to investigate a material dependence, La(Fe$_{1-x}$,Rh$_x$)O$_3$ (LFRO) is also considered. The position of doped precious metal is known to be at the B site of the perovskite structure [2,7,12,18]. Our calculations are obtained by using Korringa–Kohn–Rostoker (KKR) method within local density approximation (LDA). Pd or Rh atoms are substituted for Fe atoms randomly in the crystals. A homogeneous distribution of Pd or Rh atoms in the host matrices is assumed. This kind of random substitutional disorder is well described by the coherent potential approximation (CPA). We actually use the MACHIKANEYAMA package developed by Akai [19].

The mixing energy ΔE is given for LFPO as $\Delta E(x) = E(\text{La}(\text{Fe}_{1-x}\text{Pd}_x)\text{O}_3) - \{(1-x)E(\text{LaFeO}_3) + xE(\text{LaPdO}_3)\}$, where $E(\text{M})$ is the total energy of a material M. If ΔE is positive, the system has a tendency toward spinodal decomposition (or phase separation), while negative ΔE suggests that the system favors a homogeneous mixing. In this case we perform a lattice relaxation in terms of Vegard's law. The lattice of LaFeO$_3$ and LaPdO$_3$ is relaxed respectively as a first step. Secondly we employ the Vegard's law for some Pd concentration. In order to describe the temperature dependence, we introduce the mixing entropy to have a free energy as $F = \Delta E(x) - TS$ with $S = -k_\text{B}[x\log x + (1-x)\log(1-x)]$.

In order to investigate the concentration fluctuation based on SND we perform a simulation by using Monte Carlo method. Generally speaking, this kind of calculations is difficult owing to no method to approach. Sato et al., however, has established the methods by taking a very simplified way in dilute magnetic semiconductor systems [20,21]. The calculation procedure consists of four steps, i.e., (i) Calculation of the electronic structure for homo-

geneous system with a random distribution of impurities, (ii) Calculation of the chemical pair interactions of two impurities in such an effective homogeneous medium based on KKR–CPA–LDA calculation, (iii) Simulation of the SND using Monte Carlo method and (iv) Estimation of the SND phase.

The first part of our calculation procedure is to evaluate the effective chemical pair interactions between Pd or Rh atoms. Prescriptions formulated by Ducastelle and Gautier [22] are employed. The theory assumes a CPA effective medium as a reference and calculates the effective interactions in the medium. In this case chemical pair interactions V_{ij} between Pd or Rh atoms at sites i and j are energy difference between Pd–Pd (or Rh–Rh) and Fe–Fe pairs and two Pd–Fe (or Rh–Fe) pairs in the effective medium, i.e., $V_{ij} = V_{ij}^{\text{Pd–Pd(or Rh–Rh)}} + V_{ij}^{\text{Fe–Fe}} - 2V_{ij}^{\text{Pd–Fe(or Rh–Fe)}}$ where $V_{ij}^{\text{A–B}}$ is the potential energy when sites i and j are occupied by A and B atoms, respectively. As is well known in this approach, positive V_{ij} means effective repulsive interaction between Pd (or Rh) atoms, while negative V_{ij} means effective attractive interaction.

The second part is to generate the SND phase by using Monte Carlo method. The systems are described by the Ising model which Hamiltonian is defined as $H = -\frac{1}{2}\sum_{i \neq j} V_{ij}\sigma_i\sigma_j$, where V_{ij} is effective pair interaction between impurities at site i and j, σ_i is occupation number of impurity at site i. V_{ij} values are calculated from *ab initio* by using prescription explained previously. The V_{ij} up to 15th neighbors are taken into consideration through the simulations. We perform the simulations at scaled temperature of $k_\text{B}T/V_{01} = 0.2690$ and 51.4810 for LFPO and LFRO, respectively. This means that real temperature T corresponds to 1000 K for both materials with 5% Pd or Rh, respectively. Starting from complete random distribution, configuration at $T = \infty$, first we choose one impurity site, then try to move the impurity to one of the nearest neighbor sites which is chosen randomly. By obeying the Monte Carlo criterion, energy difference between original position and trial position decides if this trial is accepted or rejected. Visiting every impurity site counts one Monte Carlo step. Schematic substitution process of LFPO is shown in Figure 4.

After starting Monte Carlo loop, the system is relaxed towards the thermal equilibrium. We are not interested in the full relaxed thermal equilibrium Pd or Rh configuration but in a quenched and frozen in phase as a non-equilibrium transient state. Therefore we interrupt the Monte Carlo sequence after 500 steps.