Effects of Transition Metal Doping to Cerium-Oxides in Thermal Reduction Reaction

Takaki Nishimura,¹ Yuki Tsutsumi,¹ Tomohiko Ishii,¹ Tatsuya Kodama,² and Genta Sakane³

¹ Department of Advanced Materials Science, Graduate School of Engineering, Kagawa University, 2217-20 Hayashi-cho, Takamatsu, Kagawa 761-0396, Japan
² Faculty of Engineering, Niigata University, 8050 Ikarashi 2 nocho, Nishi-ku, Niigata, 950-2181, Japan
³ Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1 Ridaicho, Kita-ku, Okayama 700-0005, Japan

E-mail: s18g576@stu.kagawa-u.ac.jp

Abstract. Considering our lives, novel energy production is so required, and many scientists have been investigated this problem from a lot of views. One of the ways for the new energy productions is the solar power thermochemical production by an oxidation-reduction reaction of the ceramics CeO₂ (ceria). In this research, the ceria is used for obtaining an H₂ gas in vapor reaction in high-temperature thermal equipment which has a heat production system consisting by focused sun light. Nowadays technology has been also developed to keep a human living, not to harm the Earth environment. From these points, it is realized that how important the H₂ gas is for our lives, so we are trying to improve the thermochemical H₂ gas production by means of a ceria as a catalyst. Our purpose in this study is, to point out what effects occur in doped ceria’s thermal reduction (TR) reaction by using DV-Xα method. Comparing the models between the pure ceria and the Mn doped ceria, we have realized the difference by the reaction. In this appearance, one of the considerations is a view from p-DOSs (partial-Density of States), in which there are different O-2p DOSs by different crystal structures. From this view, we considered that the ceria structure would become more stable to keep the stable cyclic thermal reaction in Mn doped ceria.

1. Introduction
1.1. How to solve the energy problem and get H₂ gas?
We face a big problem. It is an energy problem and we have to sustain energy production even using the limited rare resources such as petroleum and natural gas. Considering our lives, a novel energy production is so required, and many scientists have been investigated this problem from lots of views. One of the ways for the new energy productions is the solar power thermochemical production by an oxidation-reduction reaction of the ceramics CeO₂ (ceria). This thermal oxidation-reduction reacting mechanism is shown in figure 1, there is two-step reaction. The first step is the thermal reduction reaction called TR reaction, the oxygen atoms are reduced from CeO₂ in 1500 ℃. The second step is the water decomposition reaction, which is also called WD reaction. As its name, the vaporized water is decomposed to the H₂ gas around 1000 ℃, it will be decomposed to the O₂ gas completely after the TR
reaction. The redox cerium reaction is the cycle reaction consisted of two step-reactions, the continuous reaction makes it possible to efficiently produce H\textsubscript{2} gas.

![Figure 1. Scheme of the thermal oxidation-reduction reaction. (Left figure)](image1)

![Figure 2. Floor plan of solar reactor concept for a circulating reaction measure. (Right figure)](image2)

In this research, the ceria is used for obtaining the H\textsubscript{2} gas in high-temperature thermal equipment which has heat production systems consisting of focused sunlight. The system is shown in figure 2.

1.2. The advantages of the H\textsubscript{2} gas utility.

The advantages of the producing H\textsubscript{2} gas system are mainly mentioned at three points, which are listed below.

(i) The first point is that it is very suitable for producing H\textsubscript{2} gas in an environment where abundant sunlight can be obtained (called as the sunbelt zone). In this matter, if the solar light can be supplied stably, the thermal redox reaction can be continued. More H\textsubscript{2} gas production is expected well in such areas where have the amount of sunlight irradiation.

(ii) The second point is that H\textsubscript{2} gas can be stored and transported. It is applicable for supplying H\textsubscript{2} gas to countries with poor energy resources such as Japan. Moreover, it has the advantage of being able to store sustainable "solar energy" which can be poured from the sun to the earth as the form of "hydrogen energy". It could be the hope of the energy problem solution in the world.

(iii) The third point is the fact that H\textsubscript{2} gas can be an important resource to support our lives. When H\textsubscript{2} gas is used as energy, it is possible to suppress the emission of harmful substances and produce more electric power energy in the thermal power generation.

From these points, it is realized that how important the H\textsubscript{2} gas is for our lives, we are trying to improve the thermochemical H\textsubscript{2} gas production by means of a ceria as a catalyst. "Hydrogen production using the cyclic thermochemical reaction of cerium oxide" is one of the researches conducted by Kodama et al. in Niigata University.

![Figure 3. Scheme of the image in each advantage of the H\textsubscript{2} gas utility.](image3)

2. The purpose of this study

Our purpose in this study is to point out what effects occur in doped ceria’s TR reaction by using Discrete Variational-X\textalpha{} molecular orbital calculation. The cycle reaction used the manganese (Mn) doped ceria has been reported the high efficiency in the experimental by Kodama et al., and much higher efficiency is also required. We have investigated to solve the mechanism of the ceria’s cycle reaction to get higher efficiency.
It has been also pointed out that there are some extra crystal structures in the CeO$_2$ after TR reaction from the views of XRD peak patterns. However, it has been confirmed that there is no extra crystal structure in the Mn-doped ceria. This difference is the key point of whether keeping the cycle reaction or not. As the results of our simulation, it was suggested that the crystal of Ce$_2$O$_3$ is formed after TR reaction, the crystal structure of the about 30% ceria has been changed from Fm-3m (#225, CeO$_2$) to Ia-3 (#206, Ce$_2$O$_3$) space groups, respectively. So, the amount of the cerium oxide available for cycle reaction is reduced, which may well reduce the reaction efficiency. In other words, by suppressing the collapse of the crystal, it is possible to explain the efficiency improvement of the cycle reaction, and further efficiency improvement can be aimed at by considering the factor of the peak.

### 3. Calculation models

We prepared 6 types of the calculation models, the center atom is the metal atoms (Ce or Mn) and oxygen atoms coordinated around the center metal. It was divided for some groups by the types of pure cerium or Mn-doped and CeO$_2$ or Ce$_2$O$_3$. And the 6 prepared calculation models, in which Coulomb potential (Madelung potential) of atoms surrounding the central metal and the oxygen atoms are taken into considerations. However, considering the environment of oxygen atoms around the central metal, there are one kind of environment for CeO$_2$ and two kinds of environment for Ce$_2$O$_3$. For this reason, a total of three models were prepared from the difference of coordination environments, the experimental facts were reproduced by changing the central metals (Ce or Mn) in order to consider the doping effect on ceria. Since cerium atoms with different coordination environments exist in the Ce$_2$O$_3$ crystal, they are named as Ce1 and Ce2, respectively, and the Ce$_2$O$_3$ crystal structure has cerium atoms consisted of Ce1 : Ce2 = 3 : 1.

### 4. Considerations

Comparing the models between the pure ceria and the Mn-doped ceria, we have realized the difference by the TR reaction (after TR reaction : CeO$_2$ 100% changes into CeO$_2$ 70% and Ce$_2$O$_3$ 30%), which are mentioned below.

#### 4.1 The states of electrons.

At first, We want to introduce how the electrons states are in each model to explain well why the Ce$_2$O$_3$ structure is formed in pure cerium after TR reaction, also why the Mn-doped model does not have the Ce$_2$O$_3$ structure.

![Figure 4. Scheme of the electronic state of each crystal structure.](image_url)

**4.1.1 In the CeO$_2$ structure.**

First of explanations, explaining the pure CeO$_2$ structure. The electrons state (CeO$_2$) is shown in figure 4 (left). The energy gap is 2.593 eV from LUMO (Lowest Unoccupied Molecular Orbital) to HOMO (Highest Occupied Molecular Orbital) levels. The electrons in the HOMO levels are fully occupied on the three-generation orbitals, it would be occupied for LUMO levels beyond for the 2.593 eV gap when adding more electrons into the CeO$_2$ structure. This means that the CeO$_2$ structure is reduced by oxygen defects, electrons caused by oxygen defects would not be easily captured in the HOMO levels of the CeO$_2$ structure.
4.1.2 In the Mn-doped CeO$_2$ structure.

On the other hand, the electrons state of Mn-doped CeO$_2$ is shown in figure. 4 (middle). The energy gap is 1.069 eV from LUMO to HOMO levels, the value of the bandgap is lower than the pure CeO$_2$ model. The electrons in the LUMO levels are not fully occupied on the two-generation orbitals, it would be occupied for LUMO levels beyond 0 eV when adding more electrons. Even if adding more electrons to the Mn-doped structure at the fully occupied on the HOMO levels, the electrons move to the LUMO levels beyond for the 1.069 eV gap. Compared between the Mn-doped CeO$_2$ structure and pure CeO$_2$, electrons caused by oxygen deficiency would be captured easily in hybrid orbitals than the CeO$_2$ structure. From the viewpoint of electron acceptability of ceria, we have studied the behaviour of electrons provided by oxygen defects and we have found that electrons are more acceptable in the Mn-doped ceria.

4.1.3 In the Ce$_2$O$_3$ structure.

We are also to explain the Ce$_2$O$_3$ structure. The electrons states of Ce1 and Ce2 in Ce$_2$O$_3$ are shown in figure. 4 (right) and it is one of the models after TR reaction. The energy gap of each structure is 0.00004 eV in Ce1 model and, 0.050 eV in Ce2 model. The electrons in the LUMO levels are not fully occupied in an orbital in both models, it appears the characteristics like the Mn-doped CeO$_2$ model. Moreover, there is almost no energy difference, which shows it is so easy to be occupied in LUMO levels too.

From the views of electron’s behaviour in the orbitals, the CeO$_2$ crystal structure is difficult to receive electrons, which makes it difficult to reduce the CeO$_2$. So, it is sufficiently considered that Ce$_2$O$_3$ is formed along with oxygen defects due to the TR reaction and electrons are supplied into the Ce$_2$O$_3$ structure. Since Mn-doped CeO$_2$ is regarded as a pseudo-Ce$_2$O$_3$ when Mn is doped into CeO$_2$, it is concluded that the need to newly form Ce$_2$O$_3$ by the TR reaction is eliminated as the amount of Mn-doped increases.

4.2 Density of states in oxygen 2p orbitals.

Figure 5 shows the p-DOS (partial-Density of States), in which there are different O-2p DOS figures by each different crystal structures. In figure. 5, the upper three figures and lower three figures are the results of the p-DOSs in the cases of pure cerias (upper) and the Mn-doped cerias (lower), respectively. And left column, and center and right columns are the results in the case before (left) and after (center and right) the TR reaction. It is mentioned in the above column that there are different coordination environments to the Ce atom (Ce1 and Ce2) though they are belonged to the same crystal structures.

![Image of Figure 5](image_url)

**Figure 5.** Six characteristic graphs show the O-2p DOS, in which each graph’s upper right indicate the state of oxygen atoms coordination. The vertical axis is the energy levels (eV), the horizontal axis shows what ratio is : DOS (1eV/ atom). The left figures belong the crystal structure (#225), both center and right crystal structure (#206). Bottom figure’s models are Mn-doped but upper figures are not doped.
The 0 eV on the vertical axis in figure. 5 means that it is the HOMO levels in each crystal structure. The DOS peaks in the O-2p orbitals is lower along with changing the CeO$_2$ structure in the pure ceria model, but in the Mn-doped model, it can be seen that the energy level itself of the DOS peaks at relatively high energy levels are not changed so much. It is considered that O-2p DOS peaks is observed in the vicinity of the energy level below lower the HOMO level means that the stability of the oxygen atom becomes higher. This indicates that, in pure ceria crystals, the stability of oxygen atoms due to the structural change (CeO$_2$ to Ce$_2$O$_3$) is enhanced as the result of the TR reaction. And with the changed Ce$_2$O$_3$ crystal structure, oxygen atoms would have a lower elimination reaction of oxygen. On the other hand, in the Mn-doped CeO$_2$, the overall DOS peaks shift downward compared to the pure CeO$_2$ model. In the initial state of Mn doping (Mn-doped CeO$_2$), there is a tendency that the oxygen atoms around the Mn-doped ceria are stable and there is a tendency not to break its crystal structure along with oxygen defects more than the pure ceria. Even if the structure is changed by the TR reaction from this state (Mn-doped CeO$_2$), the DOS peaks shift is not observed, so that the stability of oxygen is lower than that of pure ceria, and the necessity of the structure change by the TR reaction would be lower in Mn-doped ceria, too. From the view of O-2p DOS, it can also be explained that the formation of Ce$_2$O$_3$ is difficult when Mn is doped and no peak is observed after the TR reaction.

5. Conclusion

Based on the above conclusion, the TR reaction requires an environment in which electrons are easy to donate, and the environment is such that the bandgap is small and the electrons on the LUMO are not full. The CeO$_2$ achieves this by changing its own crystal system, but it can also be created by artificial manipulation (Mn doping). From the view of O-2p DOS, it can be explained that the formation of Ce$_2$O$_3$ is difficult when Mn is doped and no peak is observed after the TR reaction. We concluded that the reasons for the XRD peak difference between the pure ceria and Mn-doped ceria are given for us by these theories.

Reference

[1] Steffen Gríeshammer, 2017 J. Phys. Chem. C 121 15078-15084.
[2] Nobuyuki Gokon, Toshinori Sudab, Tatsuya Kodama 2015 Thermochimica Acta 617 179-190.
[3] Nobuyuki Gokon, Toshinori Sudah, Tatsuya Kodama 2015 Energy 90 1280-1289.
[4] Roger Jocot, Ren Mor, Ronald Michalsky, Aldo Steinfeld, and Greta R. Patzke, J. Mater. 2017 Chem. A 5 19901.