Theoretical investigation of effects of spin contamination error on DFT calculations for core-shell catalyst models

Kohei Tada,[a,*] **Hiroaki Koga,**[b] **Yoshinori Ato,**[c] **Akihide Hayashi,**[c] **Mitsutaka Okumura,**[b,c] **Shingo Tanaka**[a]

[a]*Research Institute of Electrochemical Energy, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan*

[b]*Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University, 1-30 Goryo Ohara, Nishikyo, Kyoto, Kyoto 615-8245, Japan*

cDepartment of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan

**Corresponding author: +81-72-751-9714, k-tada@aist.go.jp*

Abstract: Using density functional theory, the activation barrier of catalytic NO reduction by TiO_2/Ag and ZrO_2/Cu core-shell catalyst models were calculated with correction of spin contamination error. The estimated barrier of the TiO_2/Ag system is increased, whereas that of ZrO_2/Cu system is decreased by the correction of spin contamination. The difference between two systems are caused by the difference of surface structure of these systems. Additionally, the rate-determining step of ZrO_2/Cu was changed by the correction. These results show the importance of the correction of spin contamination error for the detailed investigation of catalytic reaction by heterogeneous catalysts.

Keywords: core-shell catalyst (TiO_2/Ag and ZrO_2/Cu), NO_x reduction, density functional theory.

1. Introduction

Vehicle emissions include toxic gases, such as NOx, CO, and hydrocarbons. For inhibiting environmental pollution, three-way catalysts based on Pt, Pd, and Rh metals are used [1]. However, these metals are extensive and rare; therefore, replacing them with a more inexpensive and universal material is desired. In particular, the reduction of NO molecule relies on Rh metal, which is the most expensive metal among Pt, Pd, and Rh. Accordingly, the reaction mechanism analysis of NO reduction is necessary to develop design guidelines for new materials. The investigation of electronic structure using the first-principle calculation is an effective method for the analysis.

For catalytic reactions, spin-polarized states participate in reactions of open-shell molecules, e.g. O_2, NO, and so on.; therefore, spin-polarized DFT calculations with plane-wave basis (SDFT/PW) are usually carried out to investigate the catalytic mechanism of heterogeneous catalysts. However, such spin-polarized calculations include spin contamination errors [2-4], and the errors on activation barriers estimated by SDFT/PW method have not been investigated, and the effects of the error are still unclear.

In the present work, we have estimated the spin contamination errors on the activation barriers of catalytic reduction by TiO_2/Ag [5] and ZrO_2/Cu [6] core-shell catalyst models, which are metal cores (Ag and Cu) covered with metal oxide thin films (TiO_2 and ZrO_2). The results of two systems have been compared, and the effects of spin contamination error on surface catalytic reactions have been investigated.

2. Theoretical

SDFT/PW calculations were performed, and the spin contamination errors were estimated by the approximate spin projection (AP) method [3]. The application scheme of the AP method to plane-wave calculation was discussed in our recent work [4]. The GGA-PBE exchange-functional was used, and the PAW scheme was used for the treatment of the core region. The correlation of the on-site Coulomb to the Ti 3d orbital was adopted (U = 2.0 eV). The cut-off energy for the wavefunction is 400 eV. The mesh of k-points sampling is 2×2×1. The program package for the DFT calculation was VASP.

3. Results and discussion

The catalytic NO reduction mechanisms by TiO_2/Ag and ZrO_2/Cu models have been reported in our previous works [5,6]. The reactions are multiple, and the elementary reactions are shown in equations (1–3).

$$2NO(a) \rightarrow N_2O_2(a) \rightarrow N_2O + O(a) \quad (1)$$

$$N_2O \rightarrow N_2 + O(a) \quad (2)$$

$$O(a) + CO \rightarrow CO_2 \quad (3)$$

Here, (a) indicates the adsorbed state. The spin contamination error only affects reaction (1) because only NO has an open-shell electronic structure. Figure 1 shows the energy diagrams of reaction (1). Table 1 summarizes the activation barriers of elementary reactions with and without correction.

In the TiO_2/Ag system, a spin contamination error of 0.03 eV (destabilization) occurs in the initial structure of reaction (1); therefore, the activation barrier was increased by correcting the error. In contrast, in ZrO_2/Cu system, a spin contamination error of 0.04 eV (destabilization) occurs in the transition structure of reaction (1); therefore, the activation barrier was decreased by the correction, and the rate-determining step was changed.

The metal cation distance in TiO_2 is in the region where the spin contamination becomes large in the gas-phase NO dimerization; however, the distance in ZrO_2 is larger than the maximum value of the region. Additionally, the NO distances in the TS structures become shorter than those in IS structures. Consequently, in the TiO_2/Ag system, the spin contamination error mainly affects in the IS, while in the ZrO_2/Cu system, it only affects in the TS.

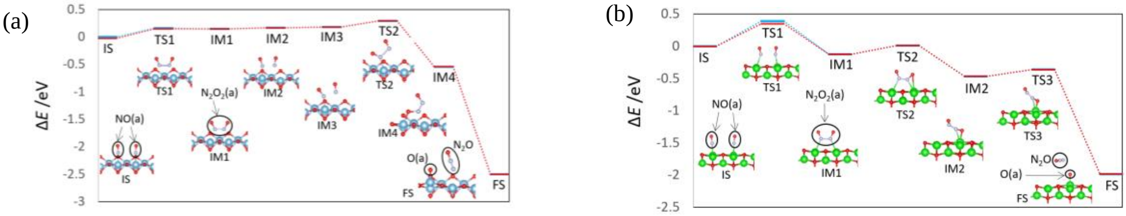

Figure 1. Energy diagrams of reaction (1) catalysed by TiO_2/Ag (a) and ZrO_2/Cu (b). blue and red lines represent the results without and with correction of spin contamination error, respectively.

Table 1. Activation energies of elementary reactions (1–3) with and without correction of spin contamination errors.

elementary reaction	TiO_2/Ag		ZrO_2/Cu	
	without correction	with correction	without correction	with correction
reac. (1)	0.29 eV	0.32 eV	0.39 eV	0.35 eV
reac. (2)	0.38 eV	0.38 eV	0.06 eV	0.06 eV
reac. (2)	0.51 eV	0.51 eV	0.36 eV	0.36 eV

4. Conclusions

Using the AP method [5,6], the effects of spin contamination errors on catalytic reduction by TiO_2/Ag and ZrO_2/Cu core-shell model structures were investigated. The results clearly show that the activation barriers were affected by the error. Especially, the rate-determining step of ZrO_2/Cu system was changed. Hence, it is better to investigate the effect of spin contamination error when the surface catalytic reactions are investigated using SDFT/PW calculations.

References

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