Electronic state calculation of NO-CO reaction on rhodium surface

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The three-way catalysts equipped in cars contain noble metals such as platinum, rhodium and palladium. A detailed understanding of the reaction processes on the noble metals to purge the exhaust gas is important with respect to not only reduction of the noble metals but also development of new catalysts. The catalytic reactions on noble metals have been widely studied, but the details remain incompletely understood. In the experimental study[1], when NO adsorbs at fcc-hollow site on Rh(111) surface, and CO adsorbs at other hollow site, N_2 is produced from two N atoms of dissociated two NO's, and CO_2 is produced from O atom of dissociated NO and CO. We focused on the experimental result and investigated the energy profile of NO-CO reaction by using DFT (Density Functional Theory) calculations.

In this paper, we assume that the NO-CO reaction is composed of seven elementary steps as NO adsorption, CO adsorption, NO dissociation, CO+O association, CO_2 desorption, N+N association, and N_2 desorption. (see Fig. 1) The mark of * in the figure means the adsorbed state. We consider the model of five-layered Rh(111)(3×3) slab. All calculations are performed by using the Vienna *Ab-initio* Simulation Package[2,3] with the Perdew-Burke-Ernzerhof functional[4] and the Projector Augmented Wave method[5]. The number of *k*-points is chosen as 5×5×1 and the cut-off energy of the plane wave is 400 eV. We used the Nudged Elastic Band (NEB) method[6] to calculate the reaction path.

As the results, the total adsorption energy of four molecules (two NO's and two CO's) is -8.69 eV. In order to find the intermediate stable state of CO+O association, we calculate the potential surface, as the rough estimation, for O atom from dissociated NO: The O atom is moved on the *xy* plane at the various heights from the surface with fixed the position of all other atoms. The potential surface for N atom from dissociated NO is estimated by the similar way. We decide intermediate stable states of NO dissociation, CO+O association, CO_2 desorption, N+N association, and N_2 desorption by the calculations with relaxing the structure and energy. The reaction path is investigated by the NEB method. In Fig. 1, we show the energy profile of 2NO-2CO reaction. There are reaction barriers for NO dissociation, N+N association, and N_2 desorption. Each heights of barrier are about 4.7 eV, 3.0 eV, and 1.9 eV, respectively. Note that there is no barrier for CO_2 desorption. This indicates that N_2 can adsorb stable on Rh(111) surface, but CO_2 cannot adsorb on the surface. The highest barrier in the reaction path corresponds to the NO dissociation, that is, the rate-determining step of NO-CO reaction is the NO dissociation process.

The barrier height for NO dissociation depends on the environment of adsorbed NO molecule: If one NO molecule is adsorbed only at the hcp-hollow site of Rh(111) surface, for example, the reaction barrier for NO dissociation is 1.7 eV. We will present the reaction path for various cases in the symposium.

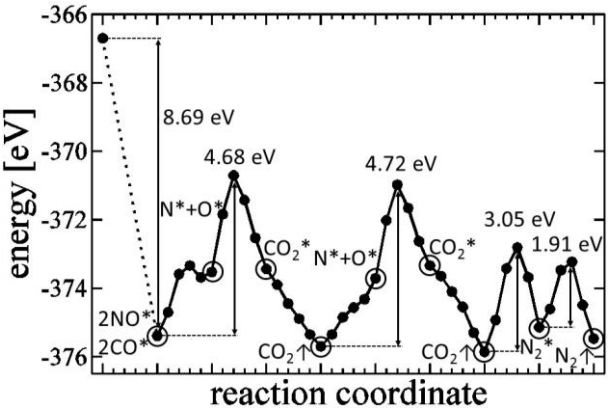

Fig.1 Energy profile of $2NO+2CO \rightarrow N_2+2CO_2$.

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