Theoretical investigation for the cause and role of surface oxidation of the nickel oxide / gold core-shell catalysts

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Abstract: The cause and role of surface oxidation of the Au@NiO core-shell catalyst was clarified by DFT calculations. The oxidized state of NiO ($Ni_{1-x}O$) is stabilized by the interaction with the gold core. Specifically, electrons from the NiO/Au interface fill the holes created by Ni vacancies and O_2 adsorption. The oxidized surface has basic sites that dehydrogenate the reaction intermediate of MMA synthesis.

Keywords: Heterojunction system, Oxide/metal core shell structure, theoretical calculation.

1. Introduction

The Au@NiO core-shell cluster is renowned as a catalyst for aerobic oxidative esterification of methacrolein in methanol to methyl methacrylate (MMA).[1] The NiO surface of the catalyst is highly oxidized, and this oxidized state ($Ni_{1-x}O$) is thought to be important for its catalytic activity. However, the detailed mechanism behind this is yet to be revealed. So we have investigated the surface oxidation of Au@NiO, as well as the reaction mechanism (Figure 1) using DFT calculation.

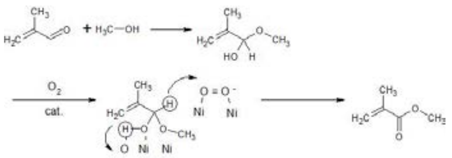

Figure 1. MMA synthesis scheme

2. Theoretical

The Au@NiO catalyst was simulated by a slab model in which two or three NiO(001) layers were supported on two or three Au(001) layers (Figure 2a). At the interface of this model, each Au was directly bonded to each O of NiO(001). As the oxidized state of NiO, we examined models with a Ni vacancy (Figure 2b) and an O_2 adsorbate (Figure 2c). Ni vacancies were introduced in several layers. For comparison, an unsupported NiO(001) bilayer was also calculated. In the DFT calculations of this work, the PBE functional was used as exchange correlation functional. The Brillouin zone was sampled by a 3x3x1 Monkhorst-Pack *k*-point mesh. The formation energy of a Ni vacancy is defined as $\Delta E = E_{def} - E_{sts}$, where E_{sts} is the total energy of the stoichiometric system and E_{def} that of a system with a vacancy. The O_2 adsorption energy is defined as $\Delta E = E_{ads} - E_{sts} - E_{O2}$, where E_{sts} is the total energy of the stoichiometric system, E_{ads} that of a system with O_2 adsorption, and E_{O2} that of molecular oxygen.

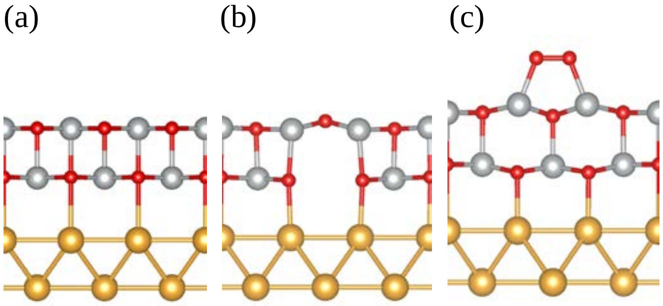

Figure 2.
Examples of (a) Calculated stoichiometric model (b) Caluculated Ni deficiency model (c) Calculated O2 adsorption model

3. Results and discussion

Figure 3 presents the Ni vacancy energies in several layers for the NiO/Au and NiO models. It shows that Ni vacancies were stabilized more than 1 eV by joining Au to NiO. This implies that Au@NiO catalysts have much more Ni vacancies than usual NiO nanoparticles. Figure 4 presents the O_2 adsorption energies for the NiO/Au and NiO models. It shows that O_2 adsorption is also stabilized by the NiO/Au interactions.

Figure 5 depicts the spin density distribution around the Ni vacancy. The spin density on O2p orbitals indicates the holes created by Ni deficiency. Figure 5 also depicts the variation in the charge density due to joining NiO and Au. It indicates charge transfer from the NiO/Au interface to oxygen around the vacancy. Figure 6 shows spin densities for O_2/NiO and O_2/NiO/Au models. Both π^* orbitals of O_2 are spin polarized in O_2/NiO, while only one is polarized in O_2/NiO/Au. This indicates charge transfer from the interface to the other π^* orbital of O_2.

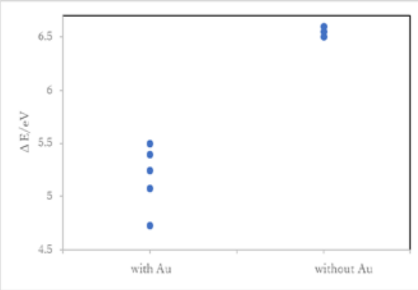

Figure 3. Ni deficiency energy(eV)

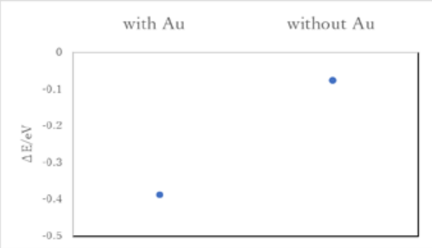

Figure 4.
Oxygen adsorption energy(eV)

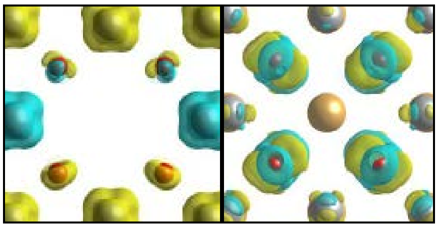

Figure 5. spin density (left) and charge difference distribution (right) around nickel deficiency

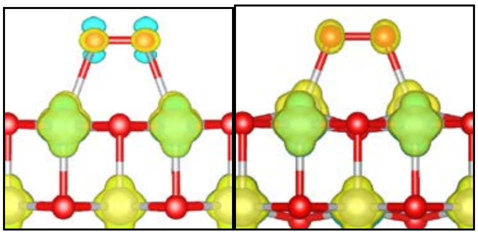

Figure 6. spin density without Au (left) and with Au (right)

4. Conclusions

To examine the surface oxidation of the Au@NiO catalyst, we performed DFT calculations on the NiO/Au slab models with Ni vacancy and O_2 adsorbate. The calculation results suggest that both oxidized states are stabilized by the interaction with the Au core. This is because the electrons from the NiO/Au interface fill the holes created by the oxidation of NiO. This charge transfer is induced by the antibonding interaction between Au and O at the interface. Thus, the direct Au–O contact plays an important role in promoting the surface oxidation.

References

1. K. Suzuki, T Yamaguchi, K Matsushita, C Iitsuka, J Miura, T Akaogi and H Ishida *ACS. Catal.*, **3**, 2013 p. 1845.