Theoretical Investigation of Surface Oxidation of NiO/Au Core-Shell Catalyst

Akihide Hayashi† and Yoshinori Ato
Department of Chemistry, Graduate School of Science, Osaka University,
1-32 Machikaneyama, Toyonaka, Osaka 563-0043, Japan

Kohei Tada
Department of Energy and Environment, National Institute of Advanced Industrial Science and Technology (AIST),
1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

Hiroaki Koga
Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University,
1-30 Goryo Ohara, Nishikyo, Kyoto, Kyoto 615-8245, Japan

Takashi Kawakami and Shusuke Yamanaka
Department of Chemistry, Graduate School of Science, Osaka University,
1-32 Machikaneyama, Toyonaka, Osaka 563-0043, Japan

Mitsutaka Okumura
Department of Chemistry, Graduate School of Science, Osaka University,
1-32 Machikaneyama, Toyonaka, Osaka 563-0043, Japan and
Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University,
1-30 Goryo Ohara, Nishikyo, Kyoto, Kyoto 615-8245, Japan

(Received 9 January 2018; Accepted 24 April 2018; Published 7 June 2018)

The surface oxidation of a Au@NiO core-shell catalyst is the key to its catalytic activity. In this density functional theory (DFT) study, we explain why the Au core promotes the oxidation of the NiO shell. The Au@NiO catalyst is represented by a slab model in which NiO(001) layers are placed on Au(001) substrates (NiO/Au). Ni vacancy and oxygen adsorption are examined as the surface oxidized state. Spin density analysis, as well as differential charge density analysis, shows that the oxidation of NiO/Au depletes the electrons in the Au{O antibonding orbitals at the interface, instead of creating holes in NiO. Thus, the highly-oxidized state of the NiO shell is stabilized by its interaction with the Au core. [DOI: 10.1380/ejssnt.2018.242]

Keywords: Density functional calculations; Oxidation; Gold; Nickel oxides; Heterojunctions

I. INTRODUCTION

With high transparency and rigidity, polymethyl methacrylate (PMMA) is sometimes called the Queen of Plastics [1]. From an industrial point of view, it is very important to synthesize its monomer, methyl methacrylate (MMA), at low cost. In the usual scheme, aldehydes are oxidized to form carboxylic acids, which are reacted with alcohols to undergo dehydration condensation. A much more efficient process is aerobic oxidative esterification, in which oxidation and condensation occur simultaneously using oxygen from air. The reaction mechanism of aerobic oxidative esterification with Au@NiO core-shell catalyst is shown in Fig. 1. For aldehydes other than α,β-unsaturated aldehydes, several aerobic oxidative esterification methods have been developed, e.g., an organometallic chemical reaction with Pd [2, 3]. However, it is very difficult to carry out the direct reaction on α,β-unsaturated aldehydes, including methacrolein, because side reactions such as CO desorption significantly decreases the selectivity of the target compound [1, 4]. Currently, practical catalysts that are capable of the direct synthesis of MMA are limited to PdPb [1] and Au nanoparticles wrapped with NiO (Au@NiO) [5]. The Au@NiO core-shell catalysts also have appealing characteristics such as high durability because Au, which is easily sintered, is completely covered with NiO. Therefore, Au@NiO is an excellent practical catalyst for the MMA synthesis.

It has been experimentally shown that NiO, not Au, is exposed on the surface of the Au@NiO catalysts. In addition, the NiO shell is nonstoichiometric, containing more oxygen than Ni. This oxygen-rich state is important to the special catalytic activity of this catalyst [5]. It is known that the O-rich state is realized because of the Au core, but the underlying mechanism is unclear. It is also unclear how the O-rich state influences the ac-

* This paper was presented at the 8th International Symposium on Surface Science, Tsukuba International Congress Center, Tsukuba, Japan, October 22-26, 2017.
† Corresponding author: hayashia15@chem.sci.osaka-u.ac.jp

FIG. 1. Reaction mechanism of aerobic oxidative esterification with Au@NiO core-shell catalyst.
In order to handle core electrons, we used the PAW method. A plane-wave basis set was used as the basis functions. In the calculations, we used PBE [22] as an exchange correlation functional, and a plane-wave basis set was used as the basis functions. In order to handle core electrons, we used the PAW method [23, 24]. To correctly calculate NiO, which is a strongly correlated material, we used DFT + U [25]. The parameter of $U - J = 5$ eV was adopted [9]. For integration over the reciprocal space, we used a $3 \times 3 \times 1 k$-point mesh with horizontal shifts, as well as Gaussian smearing with $\sigma = 0.05$ eV.

![Diagram](image_url)

**FIG. 2.** Examples of calculated stoichiometric models. Top view (a) and side views (b–e). Au$_{32}$Ni$_{32}$O$_{32}$(b), Au$_{32}$Ni$_{32}$O$_{48}$ (c), Ni$_{32}$O$_{32}$(d), Ni$_{32}$O$_{48}$(e). Numbers next to NiO indicates the layer numbers counted from NiO/Au interface or the NiO surface. Gold ball represents Au, silver ball represents Ni, and red ball represents O.

NiO(001), Au(001), and NiO(001) supported Au(001) surface models were investigated. For the surface models investigated, the $2\sqrt{2} \times 2\sqrt{2}$ cells were used in all calculations. In NiO and Au cells, there are 16 O and 16 Ni atoms in a NiO layer and 16 Au atoms in a gold layer, respectively. In the following sections, we denote $n$ layer NiO as Ni$_{16n}$O$_{16n}$ and $n$ layer Au as Au$_{16n}$. When a Ni vacancy is introduced in $m$-th layer counting from Au layer, we denote this model as Ni$_{16m-1}$O$_{16m-1}$. We also denote O$_2$ adsorption model as Ni$_{16n}$O$_{16n+2}$.

Four types of models were calculated: (1) a NiO(001) bilayer supported on a Au(001) bilayer (Au$_{32}$Ni$_{32}$O$_{32}$, Au$_{32}$Ni$_{31}$O$_{32}$-1, Au$_{32}$Ni$_{31}$O$_{32}$-2, Au$_{32}$Ni$_{32}$O$_{31}$), (2) a NiO(001) trilayer supported on a Au(001) trilayer (Au$_{48}$Ni$_{48}$O$_{48}$, Au$_{48}$Ni$_{47}$O$_{48}$-1, Au$_{48}$Ni$_{47}$O$_{48}$-2, Au$_{48}$Ni$_{47}$O$_{48}$-3), (3) an unsupported NiO(001) bilayer (Ni$_{32}$O$_{32}$, Ni$_{31}$O$_{32}$-1, Ni$_{31}$O$_{32}$-2, Ni$_{31}$O$_{32}$-3), (4) an unsupported NiO(001) trilayer (Ni$_{48}$O$_{48}$-1, Ni$_{47}$O$_{48}$-2). To mimic bulk Au, two Au layers at the bottom were fixed if NiO are supported on Au. Calculated stoichiometric models are shown in Fig. 2. There was a sufficient distance in the $z$ direction. In all models, Au and O are directly bonded at the (001) interface, as was found earlier [9].

### III. Results and Discussion

#### A. Ni vacancy energy

First, we compared the stability of a Ni vacancy in unsupported NiO and NiO/Au. The relative stability was evaluated using the following formulae:

$$\Delta E(LnDm \text{ without Au}) = E(Ni_{16n-1}O_{16n-1}) - E(Ni_{16n}O_{16n})$$

$$\Delta E(LnDm \text{ with Au}) = E(Au_{16n}Ni_{16n-1}O_{16n-1}) - E(Au_{16n}Ni_{16n}O_{16n})$$

Figure 3 shows the calculation results that were obtained. It can be seen that the Ni vacancy is stabilized more stable than 1 eV by joining NiO to Au. Moreover, it was revealed that the Ni vacancy is more stable in the layer closer to Au. These results indicate that there are many more Ni vacancies in this catalyst than in ordinary NiO. In particular, Ni vacancies are more likely to be found in the layer closer to the Au core. In addition, the opti-
mized structure in Fig. 4(a) shows that when a Ni vacancy is present in the layer immediately below the surface, the O above the vacancy rises 0.3 Å. This protruded O may contribute to the reaction as a strong base site.

B. $O_2$ adsorption energy

We calculated the adsorption energy of $O_2$ on NiO/Au and that on unsupported NiO using the following formulae:

$$\Delta E(\text{with Au}) = E(Au_{32}Ni_{32}O_{34}) - E(Au_{32}Ni_{32}O_{32}) - E(O_2)$$

$$\Delta E(\text{without Au}) = E(Ni_{32}O_{34}) - E(Ni_{32}O_{32}) - E(O_2)$$

Here, $O_2$ is adsorbed side-on to unsupported NiO, whereas $O_2$ bridges two Ni sites on NiO/Au. The adsorption energies were calculated to be $-0.08$ eV (to unsupported NiO) and $-0.39$ eV (to NiO/Au). Thus, this indicates that oxygen is more easily adsorbed to Au@NiO than it is to the usual NiO.

C. Electronic structure

In order to understand the reason for which the oxidation of NiO is stabilized only when it is supported on Au, we prepared spin-density distribution plots and differential charge-density plots. The latter were obtained by calculating $\rho(NiO/Au) - \rho(NiO) - \rho(Au)$. Here, $\rho(NiO/Au)$ is the charge density of a model obtained by optimizing the structure of a NiO/Au heterojunction. $\rho(NiO)$ is the charge density obtained by extracting only NiO from the structure of NiO/Au, and fixing the coordinates of all nuclei. In the same way, $\rho(Au)$ is the calculated charge density obtained by extracting only Au and fixing the coordinates of all the nuclei. Figure 5 shows the spin-density distribution plot of unsupported NiO with a Ni vacancy. When Ni$^{2+}$ is reduced and extracted as a neutral species, the p orbitals of the surrounding O are depleted of electronic charge. In other words, when Ni vacancies are present, the surrounding oxygen becomes radical-like. This result is consistent with earlier result [26].

Figure 6 shows the differential charge-density distribution plots around the Ni vacancy. From this figure, it is understood that the charge density of the orbitals of oxygen, which has become radical, is increased by the presence of Au. In contrast, it can be seen that the charge density of the orbital of Au and O in the $z$ direction decreases at the junction interface. Because the Au–O distance at the interface decreases by 0.3 Å when Ni vacancies are introduced, the orbital in which the charge decreases is considered as the antibonding orbital of O and Au. The system is stabilized by the charge transfer from Au–O antibonding orbitals to the radical orbitals generated by Ni vacancy.

Figure 7 shows the spin density of bridging $O_2$ on unsupported NiO and that on NiO/Au. When the Au layer is absent, there are two radical orbitals of oxygen. However, when the Au layer is present, there is only one radical orbital. The O–O bond length of 1.34 Å, together with the spin disappearance, indicates a super-oxo state created by charge transfer to the $\pi^*$ orbital. Figure 8 shows the differential charge density for $O_2/NiO/Au$. From this figure, it can be seen that the charge density of the $\pi^*$ orbital of adsorbed oxygen increases when the Au layer is present. In addition, it is understood that the sources of
FIG. 8. Differential charge distribution around adsorbed O$_2$ for interacting and non-interacting NiO/Au. Yellow zone is charge-increasing zone. Blue zone is charge-decreasing zone.

FIG. 9. Wavefunctions at the Γ point under the Fermi level. Energies based on the Fermi level are $-0.08245$ eV (a), $0.08513$ eV (b), $-0.08565$ eV (c), and $-0.08962$ eV (d). These are anti-bonding orbitals between Au and O.

IV. CONCLUSION

Using DFT calculation, we studied about the mechanism of the surface oxidation of Au@NiO core-shell catalyst. When Au and NiO are joined, it becomes easier for charges to flow from the orbitals of the junction interface, making it easier to oxidize NiO. As shown in Fig. 10, the source of the charge is the antibonding orbital of gold and oxygen. Thus, the origin of the facile oxidation of the NiO shell of Au@NiO can be traced to the ability of Au to bond directly to O and the complete filling of its d shell.

ACKNOWLEDGMENTS

This study is supported by a Grant-in-Aid for Scientific Research (c) (No. 17K05752), ALCA, and Elements Strategy Initiative for Catalysts and Batteries (ESICB) of Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT).
[1] S. Yamamatsu, T. Yamaguchi, K. Yokota, O. Nagano, M. Chono, and A. Aoshima, Catal. Surv. Asia 14, 124 (2010).
[2] K. Ekoue-Kovi and C. Wolf, Chem. Eur. J. 14, 6302 (2008).
[3] L. Chao, W. Jing, M. Lingkui, D. Yi, L. Yao, and L. Aiwen, Angew. Chem. 123, 5250 (2011).
[4] Y. Diao, R. Yan, S. Zhang, P. Yang, Z. Li, L. Wang, and H. Dong, J. Mol. Cat. A 303, 35 (2009).
[5] K. Suzuki, T. Yamaguchi, K. Matsushita, C. Iitsuka, J. Miura, T. Akaogi, and H. Ishida, ACS Catal. 3, 1845 (2013).
[6] H.-J. Freund and G. Pacchioni, Chem. Soc. Rev. 37, 2224 (2008).
[7] H.-J. Freund, Chem. Eur. J. 16, 9384 (2010).
[8] N. Nilius, T. Risse, Schauerman, S. Shaikhutdinov, M. Sterrer, and H.-J. Freund, Top. Catal. 54, 4 (2011).
[9] A. Visikovskiy, K. Mitsuhara, M. Hazama, M. Kohyama, and Y. Kido, J. Chem. Phys. 139, 144705 (2013).
[10] L. Yu, M. Lewandowski, Y.-N. Sun, Y. Fujimori, M. Yuljia, M. N. G. Irene, M. J. Randall, L. Giordano, G. Pacchioni, J. Goniakowski, C. Noguera, S. Shaikhutdinov, and H.-J. Freund, ChemCatChem 3, 671 (2011).
[11] Y. N. Sun, Z. H. Qin, M. Lewandowski, E. Carrasco, M. Sterrer, S. Shaikhutdinov, and H.-J. Freund, J. Catal. 266, 359 (2009).
[12] Y. N. Sun, L. Giordano, J. Goniakowski, M. Lewandowski, Z.-H. Qin, C. Noguera, S. Shaikhutdinov, G. Pacchioni, and H.-J. Freund, Angew. Chem. Int. Ed. 49, 4418 (2010).
[13] H. Koga, K. Tada, A. Hayashi, Y. Ato, and M. Okumura, Catal. Lett. 147, 1827 (2017).
[14] A. Hellman, S. Klacar, and H. Grönbeck, J. Am. Chem. Soc. 131, 16636 (2009).
[15] H.-J. Shin, J. Jung, K. Motobayashi, S. Yanagisawa, Y. Morikawa, Y. Kim, and M. Kawai, Nat. Mater. 9, 442 (2010).
[16] D. Shin, S. Sintihka, M. Choi, R. Thapa, and N. Park, ACS Catal. 4, 4074 (2014).
[17] A. Gonchar, T. Risse, H.-J. Freund, L. Giordano, C. Di Valentin, and G. Pacchioni, Angew. Chem. Int. Ed. 50, 2635 (2011).
[18] G. Kresse and J. Hafner, Phys. Rev. B 47, 558(R) (1993); G. Kresse and J. Hafner, Phys. Rev. B 49, 14251 (1994).
[19] G. Kresse and J. Furthmüller, Comput. Mat. Sci. 6, 15 (1996).
[20] G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
[21] http://www.advancesoft.jp/product/advance_phase/
[22] J. P. Perdew, K. Burke, and M. Erzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[23] P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
[24] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[25] S. L. Dudarev, G. A. Savrasov, C. H. Hamphreys, and A. P. Sutton, Phys. Rev. B 57, 1505 (1998).
[26] A. M. Ferrari, C. Pisani, F. Cinquini, L. Giordano, and G. Pacchioni, J. Chem. Phys. 127, 174711 (2007).