

# First-principles Thermodynamics and Statistical Mechanics Simulations of Catalytic Reactions at Solid Surfaces

T. N. PHAM, S. A. Wella, S. E. M. PUTRA, F. MUTTAQIEN, K. INAGAKI,  
Y. HAMAMOTO, I. HAMADA, and Y. MORIKAWA

*Department of Precision Science and Technology, Graduate School of Engineering,  
Osaka University, 2-1 Yamada-oka Suita, Osaka 565-0871*

In this project, we have studied atomic geometries, electronic properties and chemical reactions at surfaces and interfaces, especially, we focused on etching processes of SiC in water using Pt catalysts [1], dopants in semiconductors [2], NO dissociation by hydrogen bonding on Cu(110) [3], metal-insulator transition at LaNiO<sub>3</sub> thin-films on SrTiO<sub>3</sub> substrate [4], bonding states of single-atom Pt at graphene edges [5], the origin of the change in the absorption spectra upon oxidation and reduction in Ru-complexes [6], and formic acid adsorption on Cu(111) [7]. In the present report, we discuss the enhancement of the NO dissociation by hydrogen bonding[3].

Nitric oxide (NO) emission from the exhaustive gas of combustion process has caused negative impacts on the environment, e.g, acid rain, photochemical smog, and ozone depletion. Therefore, NO reduction to harmless substances is an important task to mitigate the environmental pollution. The catalysts of expensive precious metals such as Pt, Rh, and Pd are often employed to remove NO as well as CO and unburned hydrocarbon gases simultaneously from the exhaust gas. However, the practice requires that the catalysts must be abundant, low cost, and high catalytic activity. Among various alternative materials, copper-based catalysts are very promising owing to their excellent performances for the NO reduction.

As essential steps for the NO reduction, the NO adsorption and dissociation to N and O on the copper surfaces have been intensively studied by both experiment and theory. On low-index Cu surfaces, i.e., Cu(100), Cu(110), and Cu(111), NO is molecularly adsorbed at rather low temperature followed by formations of dimeric (NO)<sub>2</sub> and N<sub>2</sub>O species with further gas exposure. Recently, Shiotari and co-workers experimentally studied the NO adsorption and dissociation on the Cu(110) surface at low-coverage region using scanning tunneling microscopy (STM), reflection absorption infrared spectroscopy, and electron energy loss spectroscopy [8].

Herein we present a DFT calculation to clarify the role of water molecules and the mechanism of the hydrogen bonding induced NO dissociation on the Cu(110) surface.

The calculations were carried out by using the simulation tool for atom technology (STATE) package [9, 10]. The Vanderbilt's ultrasoft pseudopotentials were used to describe the electron-ion interactions. Wave functions and augmented charge density were expanded by a plane wave basis-set with cut-off energies of 36 and 400 Ry, respectively. In this study, we compared results obtained by the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) exchange-correlation functional to those obtained by van der Waals density functionals (vdW-DFs),

which take into account the dispersion interaction. We used vdW-DF1, optB86b-vdW, and rev-vdW-DF2[11] functionals as implemented in the STATE code[10].

After optimizing possible initial NO/Cu(110) configurations, we obtained two types of favorable adsorption configurations: (1) an upright NO in which N binds to the surface ( $N^*O$ ) and (2) a side-on NO connecting two short-bridge sites ( $N^*O^*$ ) along [001] direction. The van der Waals corrected functionals such as rev-vdW-DF2 and optB86b-vdW successfully reproduce the side-on configuration of adsorbed NO, which is an important precursor for the NO dissociation. The NO dissociation without water requires an activation energy of 0.76 eV. We find that hydrogen bonds efficiently reduce the activation energy of NO dissociation down to 0.34 eV and 0.27 eV with a water dimer and two water dimers near  $N^*O^*$ , respectively. Our study reveals the promotion effect of the water molecules is only dominant when one of the water molecules in a water dimer donates a hydrogen bond to O of side-on NO (see Fig. reffig:fig1. The N-O bond is weakened as the results of the enhanced back donation by the hydrogen bond between the water dimer and side-on NO. Our present results provide a physical insight of the role of hydrogen bonds from water, which may be helpful to practical applications of copper surface in NO reduction as well as the design of novel catalysts for this purpose.

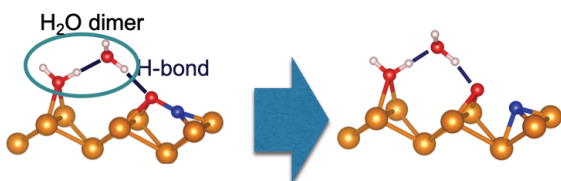


Figure 1: Hydrogen-bond enhanced N-O dissociation on Cu(110).

## References

- [1] P. V. Bui, D. Toh, A. Isohashi, S. Matsuyama, K. Inagaki, Y. Sano, K. Yamauchi, and Y. Morikawa: *Jpn. J. Appl. Phys.* **57** (2018) 055703.
- [2] Y. Takano, N. Kobayashi, and Y. Morikawa: *J. Phys. Soc. Jpn.* **87** (2018) 061013.
- [3] T. N. Pham, M. Sugiyama, F. Muttaqien, S. E. M. Putra, K. Inagaki, D. N. Son, Y. Hamamoto, I. Hamada, and Y. Morikawa: *J. Phys. Chem. C* **122** (2018) 11814.
- [4] H. D. Nguyen, B. T. Cong, and Y. Morikawa: *J. Phys. Soc. Jpn.* **87** (2018) 114704.
- [5] S. A. Wella, Y. Hamamoto, Suprijadi, Y. Morikawa, and I. Hamada: *Nanoscale Adv.* **1** (2019) 1165.
- [6] S. S. Tan, S. Yanagisawa, K. Inagaki, M. B. Kassim and Y. Morikawa: *Phys. Chem. Chem. Phys.* **21** (2019) 7973.
- [7] S. E. M. Putra, F. Muttaqien, Y. Hamamoto, K. Inagaki, I. Hamada, and Y. Morikawa: *J. Chem. Phys.* **150** (2019) 154707.
- [8] A. Shiotari, T. Mitsui, H. Okuyama, S. Hatta, T. Aruga, T. Koitaya, and J. Yoshinobu: *J. Chem. Phys.* **140** (2014) 214706.
- [9] Y. Morikawa: *Phys. Rev. B* **51** (1995) 14802.
- [10] Y. Hamamoto, I. Hamada, K. Inagaki, Y. Morikawa: *Phys. Rev. B* **93** (2016) 245440.
- [11] I. Hamada: *Phys. Rev. B* **89** (2014) 121103.