

[共同研究成果]

Self-consistent van der Waals density functional study of NO-H₂O coadsorption on Cu(111)

Thanh Ngoc Pham,* and Yoshitada Morikawa

Department of Precision Engineering, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka Suita, Osaka 565-0871

Email: thanh@cp.prec.eng.osaka-u.ac.jp

In this project, we have studied the reaction mechanisms in NO_x purification catalysts using first-principle calculations. We have studied (i) atomistic insights into the co-adsorption behavior of NO with H₂O on Cu(111) [1] and (ii) metal-support interaction of supported Pd catalysts revealed by machine-learning enhanced global optimization [2]. In this report, we discuss the importance of intermolecular interaction in co-adsorption of NO and H₂O by means of self-consistent van der Waals density functional.

NO_x purification catalysts are essential in three-way catalyst converters to reduce automotive exhaust NO_x gas to non-toxic N₂ gas [1]. Recently, Cu catalyst has been received much attention to replace scarce and expensive platinum group metal (Pt, Pd, and Rh) catalysts due to its excellent performances in NO reduction. Elucidating reaction mechanism of NO reduction on Cu catalyst is important to improve the catalytic activity and selectivity of this catalyst.

As the model for the Cu catalyst, NO adsorption and reaction on well-defined Cu surfaces have been studied. The interaction between NO and Cu surfaces are well studied but the interaction of NO with other common gases in TWC likes H₂O, NH₃, and H₂ remains ambiguously, which hinders our design of selective NO reduction systems [3]. In particular, elucidating the interaction between adsorbed nitric oxide (NO) and water (H₂O) on metal surfaces is of paramount importance to uncover mechanistic details of their competitive coadsorption behavior and to guide the design of new NO_x purification catalysts under wet condition.

Recently, Koshida *et. al* observed that the H₂O exposure to (NO)₃-preadsorbed Cu(111) results in the formation of mixed NO-H₂O complexes by scanning tunneling microscopy techniques [3]. We herein focus on elucidating the NO-H₂O interaction strength and compared that to NO-NO and H₂O-H₂O binding strengths to prove that the mixed NO-H₂O complexes is formed rather than separated NO and H₂O clusters on Cu(111). To this end, we constructed several mixed NO-H₂O complexes and compared their binding strengths to binding strengths of NO trimer and water hexamer. The adsorption energy of mixed $n\text{NO}-m\text{H}_2\text{O}$ complex is defined as

$$E_{\text{ads}} = E(n\text{NO} - m\text{H}_2\text{O}) - [E(\text{Cu}) + nE(\text{NO}) + mE(\text{H}_2\text{O})], \quad (1)$$

where $E(n\text{NO} - m\text{H}_2\text{O})$, $E(\text{Cu})$, $E(\text{NO})$, and $E(\text{H}_2\text{O})$ are total density functional theory (DFT) energies of adsorbed $n\text{NO}-m\text{H}_2\text{O}$, clean Cu(111), isolated NO, and H₂O, respectively.

The DFT calculations were carried out by using the simulation tool for atom technology (STATE) package [4]. We employed ultrasoft pseudopotentials to describe the electron-ion interactions with Cu 3d 4s, N 2s 2p, O 2s 2p, and H 1s valance states. Valance states were expanded by using plane wave basis-set with cutoff energies of 36 and 400 Ry for wave functions and augmented charge density, respectively. We used self-consistent van der Waals density functional (vdW-DF) method and the optB86b-vdW functional is adopted [5]. This approach is proved to provide a reasonable accuracy for adsorption and reaction of NO on three low-indexed Cu surfaces, namely Cu(100), Cu(110), and Cu(111) as indicated in our previous works [6,7].

First, we study the adsorption of small NO and H₂O clusters on Cu(111). We obtain the most stable sites for NO monomer and H₂O monomer are fcc-hollow and atop site with E_{ads} of -1.325 and -0.261 eV, respectively. We find that NO tend to form NO trimer ((NO)₃) on Cu(111) and (NO)₃ is more stable than separated three NO monomer by -0.123 eV. The adsorbed H₂O also tends to aggregate to form small clusters on Cu(111). The binding strength of water hexamer ((H₂O)₆) is -1.369 eV w.r.t. separated six H₂O monomer. Atomic structures of (NO)₃ and (H₂O)₆ are shown in Figure 1.

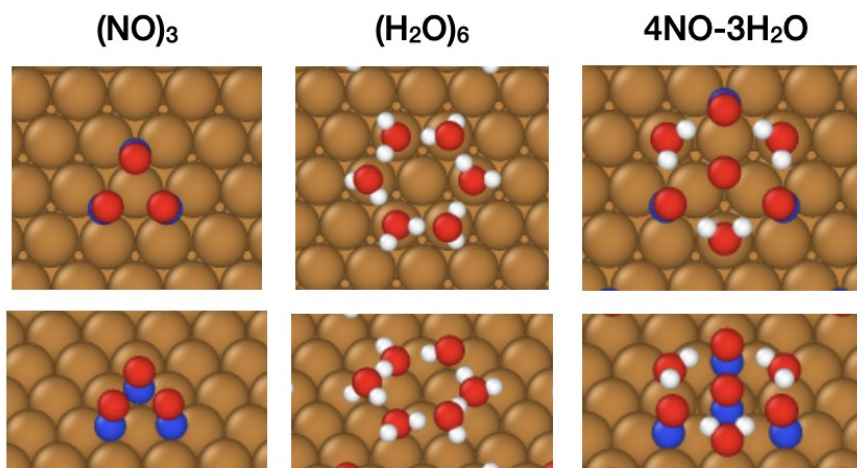


Figure 1. Atomic structures of NO trimer (NO)₃, water hexamer (H₂O)₆, and mixed 4NO-3H₂O complex. Color: Cu, orange; N, blue; O, red, and H, white.

Then, we investigate several mixed n NO- m H₂O complexes ($n = 1-4$ and $m = 1-3$) and the largest mixed complex, i.e. 4NO-3H₂O is shown in Figure 1. The calculated E_{ads} of 4NO-3H₂O is -7.424 eV, being more stable than separated $4/3(\text{NO})_3 + 1/2(\text{H}_2\text{O})_6$ state (-6.933 eV) by -0.491 eV. We find that adsorbed NO tends to receive two hydrogen bonds from two water molecules and those adsorbates aggregate to form large mixed n NO- m H₂O clusters on Cu(111). Our results imply that the mixed n NO- m H₂O complex is more stable than NO trimer and H₂O hexamer. Intermolecular interactions in n NO- m H₂O surpass the NO-NO and H₂O - H₂O interactions, leading to the formation of mixed n NO- m H₂O complex adsorbed on Cu(111). Our finding is consistent with experimental STM observation [3] and well explains their results. Intermolecular interactions in n NO- m H₂O consists of NO-H₂O and NO - NO interactions. The former is hydrogen bond where negatively-charged NO driven by back donation process from Cu(111) interacts attractively with H₂O via H-bond. The latter is the covalent interactions where $2\pi^*$ orbitals hybridized at near Fermi level.

In summary, we employed Supercomputer AOBA installed at the Cyberscience Center, Tohoku University to study atomistic insights into the co-adsorption behavior of NO with H₂O on Cu(111). Detailed results are published in reference [1].

- [1] T. N. Pham, Y. Hamamoto, K. Inagaki, I. Hamada, and Y. Morikawa, *Phys Rev Mater.* **6**, 075801 (2022).
- [2] T. N. Pham, B. A. C. Tan, Y. Hamamoto, K. Inagaki, I. Hamada, and Y. Morikawa, submitted for publication.
- [3] H. Koshida, S. Hatta, H. Okuyama, A. Shiotari, Y. Sugimoto, and T. Aruga, *J. Phys. Chem. C* **122**, 8894 (2018).
- [4] Y. Morikawa, *Phys. Rev. B* **51**, 14802 (1995).
- [5] Y. Hamamoto, I. Hamada, K. Inagaki, and Y. Morikawa, *Phys. Rev. B* **93**, 245440 (2016).
- [6] K. Kuroishi, M. R. Al Fauzan, T. N. Pham, Y. Wang, Y. Hamamoto, K. Inagaki, A. Shiotari, H. Okuyama, S. Hatta, T. Aruga et al. *Phys. Chem. Chem. Phys.* **23**, 16880 (2021).
- [7] T. N. Pham, Y. Hamamoto, K. Inagaki, D. N. Son, I. Hamada, and Y. Morikawa, *J. Phys. Chem. C* **124**, 2968 (2020).