

論文内容の要旨
Dissertation Abstract

論文題目 **Microscopic view of intermolecular interaction
for CO chemisorbed on Pt(111)**
Dissertation Title

(吸着分子間相互作用に関する微視的考察：
Pt(111)上に化学吸着した CO)

氏 名 梁 賢眞

Considering a molecular adsorption at solid surfaces, the adsorption energy (E_{ads}) is the ensemble average of each molecules and the interaction in between. Compared to the low coverage regime, development of geometrical structure of over-layer molecules is not simple as surface coverage increases. This is a reflection of complex growth of the intermolecular interaction among the adsorbates. This interaction determines the relative energetics of adsorption system, governing the surface dynamic process as well as overlayer structures. In this doctoral dissertation, carbon monoxide (CO) chemisorbed on Pt(111) surface has been adopted as a model system to study a microscopic structure and energetics of coverage-dependent intermolecular interactions through coverage-dependent real-space observation, by means of scanning tunneling microscopy (STM) and related spectroscopic methods.

CO chemisorbed on Pt(111) is one of the most extensively studied adsorption system, due to the fundamental importance to understand the surface dynamics, as well as practical importance as a model catalyst to understand the catalytic process. Moreover, CO poisoning, the reduction of catalytic activity due to densely-packed overlayer of CO on catalyst surface [1], also lead comprehensive studies with plenty of information for the electronic structure [2–4], vibrational frequency and overlayer structures [5,6], diffusion properties [7], so on. In spite of richness of the obtained information, there still exist ambiguities in the interpretation of experimental results, as well as lack of information at the intermediate coverage region other than extensively-studied surface coverage.

This doctoral dissertation aims to achieve microscopic investigation of CO adsorbed on Pt(111) surface by means of STM and STM-related spectroscopies, from isolated molecules at a low coverage limit, to high coverage overlayer structures. In the viewpoint of "interaction", the microscopic information obtained in this STM investigation is combined with preceding results, and discussed to draw new information beyond the bulk spectroscopic information. The topics covered in this dissertation are like below: the adsorbate-substrate interaction at a very low surface coverage — adsorption site and the electronic structure (Chapter 3), coverage-dependent overlayer structures and the intermolecular interaction beyond the structures (Chapter 4), and local dynamics of bridge CO in the form of bridge-to-ontop switching (B-T* switching) within the overlayer structures by means of STM-action spectroscopy, and the potential energy surface (Chapter 5).

Adsorbate-substrate interaction of an isolated CO molecule

Isolated CO molecules appear as protrusion in STM images as shown in Figure 1a. As expected in previous studies which resolved the coverage-

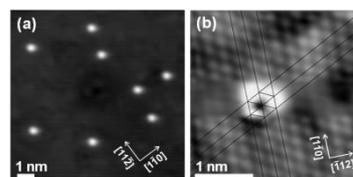


Figure 1 (a) typical STM image of CO on Pt(111) (b) atomic-resolution determination of adsorption site

dependent adsorption site, the ontop-adsorption at low coverage was confirmed in atomic resolution (Figure 1b). At this surface coverage most of the adsorbates show identical protrusion with ontop adsorption, consequently the probability to find isolated bridge-adsorbed CO is very low as $\sim 2.0 \times 10^{-4}$. This result is consistent with previous studies which estimated the energy difference of ontop and bridge adsorption (ΔE) to be 60 meV [8], leading to the order of population ratio (CO_B/CO_T) to be less than 10^{-6} .

In terms of electronic structure, two distinguishable features were observed, according to the energy level in unoccupied region. In the intermediate energy level (< 3.5 V), radial distribution of density of state (DOS) differs according to the sample bias, as shown in the spatially resolved STS (Figure 2). This results in the change of topography according to the sample bias, from simple protrusion near Fermi level to donut shape in elevated sample bias (~ 2 V). The off-center features in 1 ~ 3 V energy level exhibit donut shape, which may show the lateral distribution of broad tail from adsorbate-induced unoccupied state, contributed from $2\pi^*$ state.

Further increase in sample bias induces the lateral hopping of the adsorbate, and the resultant action spectrum and wide-range STS measured with larger tip-sample distance are given in Figure 3. The spectra show a threshold of STS signal increase near 4 V and the rapid increase of hopping yield at the 4.5 eV. Therefore we insist that the main portion of the $2\pi^*$ state of CO on Pt(111) exist near 4.5 eV, consistent with previous results of 2PPE [3] and IPES [4] experiments.

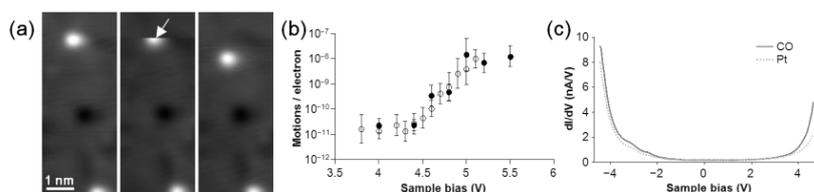


Figure 3 (a) Lateral hopping of ontop CO before/during/after bias pulse (b) Corresponding action spectrum, and (c) wide-range STS

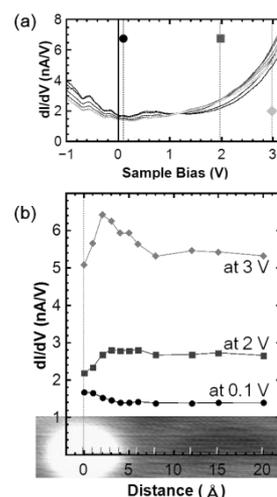


Figure 2 (a) Spatially resolved STS and (b) cross-section at the designated sample bias

Adsorption structure: Coverage-dependency of overlayer structures

In addition to the substrate-adsorbate interaction, the adsorbate-adsorbate interaction plays a dominant role in higher coverage, effects to the formed overlayer structures. In the CO on Pt(111) case, there are two available adsorption states, namely ontop CO and bridge CO, so there are three interactions to consider in overlayer structure: intermolecular interaction between identical species (ontop-ontop and bridge-bridge) and intermolecular interaction between different adsorption states (ontop-bridge).

With increase of the surface coverage, appearance of $(\sqrt{3} \times \sqrt{3})R30^\circ$ near 0.3 monolayer (ML, 1.58×10^{15} molecules / cm^2) and $c(4 \times 2)$ arrangement near 0.5 ML was one of the well known feature from CO adsorbed on Pt(111), in LEED studies. [5] Still the detail of the overlayer structure do not coincide to the population analysis which clearly insisted that the existence of bridge CO at the coverage of $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure. In this study molecularly resolved STM observation (Figure 4) clarified that the (i) the existence of island structure with local geometry $(\sqrt{3} \times \sqrt{3})R30^\circ$, (ii) appearance of bridge CO at the boundary of $(\sqrt{3} \times \sqrt{3})R30^\circ$ islands, and (iii) existence of bridge-vacant $c(4 \times 2)$ domain. [5,6] Bridge-adsorbed CO mainly appeared at the center of local geometry $c(\sqrt{3} \times 2)rect$, which is the unit cell of $c(4 \times 2)$ domain.

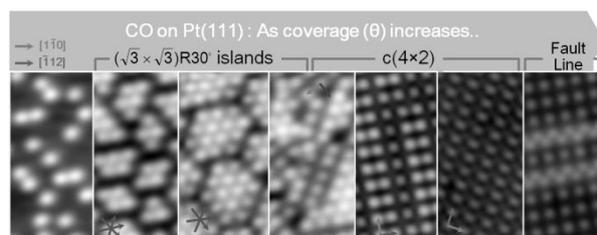


Figure 4 Structural evolution according to the surface coverage increase.

The existence of bridge-vacant $c(4\times 2)$ domain and the bridge COs at the boundary of $(\sqrt{3}\times\sqrt{3})R30^\circ$ islands suggest previously unknown intermolecular interaction between ontop CO and bridge CO. In Figure 5b, the height of ontop CO in bridge-vacant $c(4\times 2)$ domain obviously decreases according to the number of neighboring bridge CO (N_{bCO}). This indicates the change in charge density of ontop CO by neighboring bridge site occupation. The opposite direction of charge transfer between ontop CO and bridge CO suggested from coverage-dependent workfunction measurement [9] can explain the change in charge density of ontop CO with neighboring bridge CO in the STM images, i.e. the locally charged Pt atom by ontop occupation is depolarized with neighboring bridge occupation in $c(4\times 2)$ geometry by metal-to-molecule back-donation.

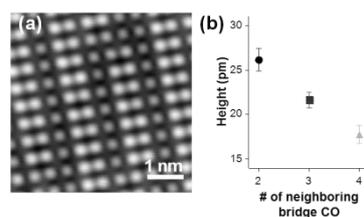


Figure 5 (a) STM image of bridge-vacant $c(4\times 2)$ domain, and (b) N_{bCO} dependence of ontop CO height

Bridge site-adsorbed CO and dynamics of the overlayer structure

Considering the coverage-dependent population of adsorption sites, bridge site occupation CO should involve the modification of potential energy surface to stabilize the bridge site by intermolecular interaction among increased population of adsorbates (Figure 6a). Regarding the precise potential energy surface near the occupied bridge site in $c(4\times 2)$ geometry, it has been suggested that the adjacent ontop site at energetically-elevated state (T^* state, Figure 6a) should appear. [8] However, there has been no experimental evidence to characterize the T^* state. In this study, I successfully confirmed the existence of the T^* state by means of inelastic electron-induced hopping of bridge-adsorbed CO.

Once the bridge site is occupied to form local geometry of $c(\sqrt{3}\times 2)\text{rect}$, the bridge CO hops to nearby ontop site by injecting tunneling electrons with a bias voltage of ~ 250 mV, in contrast to the ontop CO which is not mobile up to ~ 4 V. If the whole unit including four ontop COs at the $c(\sqrt{3}\times 2)\text{rect}$ frame and one bridge CO at the center is confined by adjacent CO adsorbates outside the frame, the lateral CO hopping reversibly occurs in a manner of “bridge-to-ontop* switching (B- T^* switching)”. The switching events was quantitatively measured by the STM-AS as shown in Figure 6b. The action spectra and the current dependence of switching rate in Figure 6c indicate a threshold at 230 mV with single-electron process. The threshold energy observed at 230 mV corresponds to the vibrational energy of internal stretch mode of the bridge CO, implying energy transfer via anharmonic coupling between the C-O internal stretch mode and a reaction coordinate mode (e.g., hindered translational mode) for CO hopping.

Interestingly, the B- T^* switching can also occur even if the electrons are injected to the ontop CO at the frame of $c(\sqrt{3}\times 2)\text{rect}$ (Figure 6b), which suggests that the enough degree of orbital hybridization between ontop and bridge CO to trigger the switching. Also the residence time of B and T^* state shows clear dependence on the

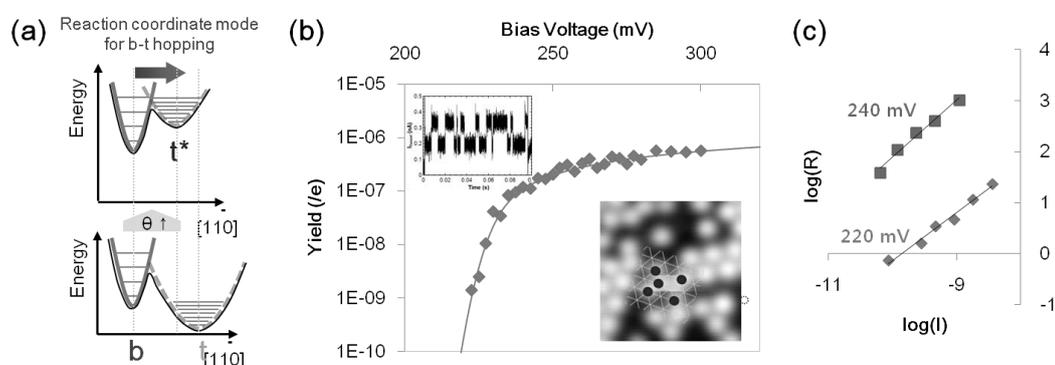


Figure 6 (a) Change in potential energy surface near bridge site, (b) action spectrum measured on bridge CO (diamond) and ontop CO (square). inset : STM image when B- T^* switching occurs. (c) Current-dependence of switching rate, log-log plot. Both curves show single-electron process.

coverage and relevant arrangement outside the $c(\sqrt{3}\times 2)$ rect frame. These dynamic behaviors can contribute to construction of a potential energy surface to understand the energetic feature for the switching in the overlayer structure depending on the surface coverage.

In summary, microscopic investigation of CO adsorbed on Pt(111) using STM has been done over various range of surface coverage, and the result interpreted in terms of substrate-adsorbate and adsorbate-adsorbate interaction. Adsorbate-substrate interaction at very low coverage, adsorbate-adsorbate interaction with increasing surface coverage, and the dynamics of bridge CO inside the overlayer structures were not only clarifying the ambiguities in preceding experimental results, but also providing new insight which can be only available with real-space, microscopic investigation.

References

- [1] G. Ertl, *Angew. Chem. Int. Edit.* **47**, 3524 (2008).
- [2] M. Trenary, S. L. Tang, R. J. Simonson, and F. R. McFeely, *Surf. Sci.* **124**, 555 (1983).
- [3] T. Anazawa, I. Kinoshita, and Y. Matsumoto, *J. Electron Spectrosc. Relat. Phenom.* **88-91**, 585 (1998).
- [4] V. Dose, J. Rogozik, A. M. Bradshaw, and K. C. Prince, *Surf. Sci.* **179**, 90 (1987).
- [5] H. Steininger, S. Lehwald, and H. Ibach, *Surf. Sci.* **123**, 264 (1982).
- [6] M. Tüshaus, E. Schweizer, P. Hollins, and A. M. Bradshaw, *J. Electron Spectrosc. Relat. Phenom.* **44**, 305 (1987).
- [7] J. E. Reutt-Robey, D. J. Doren, Y. J. Chabal, and S. B. Christman, *Phys. Rev. Lett.* **61**, 2778 (1988).
- [8] E. Schweizer, B. N. J. Persson, M. Tüshaus, D. Hoge, and A. M. Bradshaw, *Surf. Sci.* **213**, 49 (1989).
- [9] G. Ertl, M. Neumann, and K. M. Streit, *Surf. Sci.* **64**, 393 (1977).
- [10] H. Ueba, T. Mii, N. Lorente, and B. N. J. Persson, *J. Chem. Phys.* **123**, 084707 (2005).

Publication

- [1] Yang, H. J., Minato, T., Kawai, M. & Kim, Y. STM Investigation of CO Ordering on Pt(111): From an Isolated Molecule to High-Coverage Superstructures. *J. Phys. Chem. C* **117**, 16429–16437 (2013).
- [2] Hyun Jin Yang et al. Dynamics of bridge-site adsorbed CO on Pt(111): Intermolecular interaction-driven switching. *In Preparation* (2013).
- [3] Hyun Jin Yang et al. Electronic structure of isolated CO molecules on Pt(111) in microscopic scale. *In Preparation* (2013).