

SOLID STATE PHYSICAL CHEMISTRY

Annual Research Highlights

(1) “Reaction mechanism of the CO oxidation reaction on Pt(111)”

CO oxidation reaction on the oxygen-precovered Pt(111) surface has been studied with many kinds of experimental and theoretical methods. Recent STM study has revealed that the reaction initiates at the fringe of O islands after CO adsorption on all the vacant sites. We applied the time-resolved NEXAFS method to this system to confirm the reaction mechanism.

All the experiments were performed at the soft x-ray beamline BL-7A of the Photon Factory. O K-NEXAFS spectra were measured as a function of elapsed time after CO exposure under several conditions of the CO pressure and the substrate temperature. Peak intensities of atomic O and CO were converted to corresponding coverages. Decay of the O coverage is the measure how the reaction ($\text{CO} + \text{O}_{\text{ad}} \rightarrow \text{CO}_2 \uparrow$) proceeds.

As shown in Fig. 1, there are two kinds of reaction process: the early stage reaction which is newly found in the present experiment and that after an induction period. The former is revealed to be a reaction of isolated oxygen atoms with adsorbed CO, and the latter is a reaction of island-periphery oxygen atoms. Between these reaction paths, there is an induction period, in which CO molecules saturate the vacant sites.

It is found that CO coadsorption plays a role to induce the dynamic change in spatial distribution of O atoms, which switches over the two reaction paths.

These mechanisms were confirmed by kinetic Monte Carlo simulations.

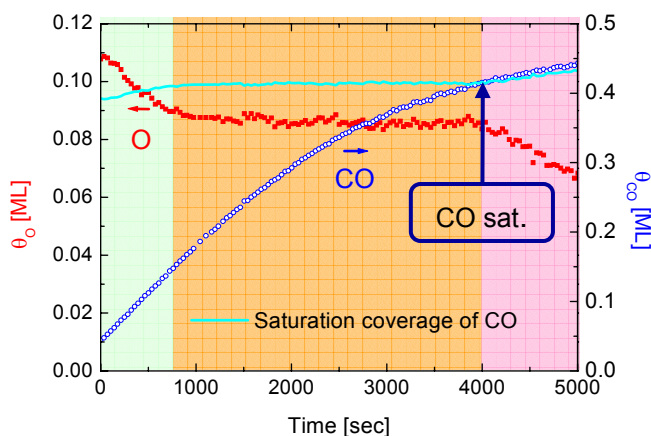


Fig. 1 Time evolution of O coverage (θ_{O}) and CO coverage (θ_{CO}) during the CO exposure on O-precovered Pt(111). Green line indicates the available sites for CO adsorption, expressed by the coverage. It clearly shows that the second reaction starts just after CO saturation. Substrate temperature was 252 K and CO pressure was 5×10^{-10} Torr.

1.(1)-11) *J. Chem. Phys.* **122**, 134709(10 pages) (2005)

(2) “Development of a photoelectron yield soft X-ray standing wave method ”

To know molecular positions as well as molecular alignment in a film of a functional organic molecular device is essential to understand the electronic structure of the film and the dynamic response to external stimuli.

The x-ray standing-wave (SW) technique provides a unique measure of the location of specific atoms relative to the extended substrate-scatter-plane locations. Since the size of organic molecules that are actually used for molecular devices is typically several tens angstroms, it is needed to generate SWs with a fairly long periodicity. For this purpose, we used a multilayer ($\text{W}(12.0 \text{ \AA})/\text{C}(18.9 \text{ \AA})_{80}$ ($d = 30.9 \text{ \AA}$) and soft x-rays with energies lower than 1 keV ($\lambda \sim 12 \text{ \AA}$). Photoelectron-yield SW-profile measurements with soft x-rays offer high sensitivity to light elements like C, N, O and S that constitute organic molecules.

We applied this method to an organic monolayer of an amphiphilic azobenzene derivative $\text{CH}_3(\text{CH}_2)_7\text{AzO}(\text{CH}_2)_5\text{COOH}$ ($\text{Az}:\text{C}_6\text{H}_5\text{N}=\text{NC}_6\text{H}_5$) prepared on the multilayer by the Langmuir-Blodgett method. Cd cations were used as a stabilizer. Standing wave profiles of W4f, N1s and Cd3d photoelectron peaks were analyzed to reveal the relative height of N and Cd ion from the (W/C) multilayer. Combining with the polarization dependent NEXAFS spectra, we can obtain the structure model of the monolayer on a (W/C)₆₀ monolayer.

This technique is a powerful tool for determining element specific *atomic positions in height* in organic monolayers

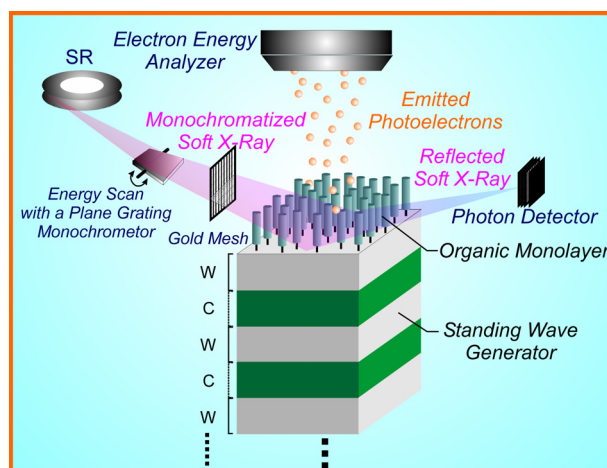


Fig. 2 Schematic illustration of the scanned energy photoelectron yield soft x-ray standing wave measurement for an organic monolayer film formed on a W/C multi-layer which works as a standing wave generator.

1.(1)-1) *Appl. Phys. Lett.* **87**, 031911(3 pages) (2005)

物性化学研究室

研究レビュー

(1) Pt(111)面上のCO酸化反応の機構解明

Pt(111)表面上において CO 分子と原子状酸素から CO₂ を生成する反応は触媒反応の単純なモデル系であり、その機構に関する研究がこれまでも盛んになされてきた。原子状酸素は凝集し、アイランド構造をつくるが、ここに CO ガスを導入したとき、アイランドが反応にどのように関与するかについて、興味もたれる。最近の STM による研究では、CO が空きサイトを全部埋め尽くすまで反応が起こらず、その誘導期を経た後にアイランドの縁から反応が起こることが報告されている。我々はこの報告を検証するために、エネルギー分散型 NEXAFS を適用し、基板温度、CO ガス圧を変えてこの機構を定量的に調べた。

実験は KEK-PF BL-7A において行った。図 1 には O K-NEXAFS のスペクトル解析から得られた原子状酸素と CO の被覆率の時間変化を示す。反応は「誘導期」を挟んで 2 つの領域に分けられる。領域 (II) は、これまでから知られていたアイランドの縁の酸素原子が関与する反応である。この反応過程は、CO が表面を埋めつくすまで開始しない。一方、領域 (I) は今回初めて見出された反応過程で、アイランドの間で孤立拡散する酸素原子と CO 分子と反応する過程であることが分かった。更に Monte Carlo シミュレーション解析を行い、CO の吸着は孤立酸素原子を凝集させる作用があることが明らかになった。

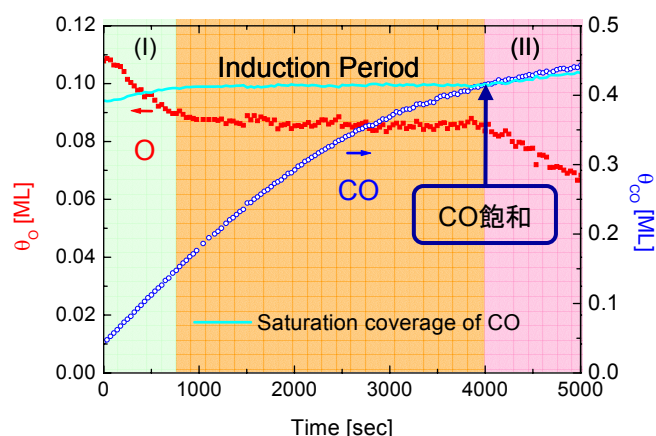


図 1 反応中の O, CO の被覆率時間変化。緑の線は O の被覆率から見積もった CO の可能な吸着サイトの割合。

(2) 光電子収量法を用いた軟 X 線定在波法の開発

機能性有機分子の薄膜において、分子の配列や構造を知ることは分子デバイスの電子構造の理解、外部刺激によるダイナミック応答の理解に欠かせない。分子配列を調べる方法は多くあるが、分子の位置情報を得る方法は殆どない。

X 線定在波法は基板結晶上の特定の原子の相対位置を調べる方法であるが、分子デバイスに用いる有機分子のサイズは数十 Å にもなるので、これを調べるためにはかなり長い周期の定在波を発生させる必要がある。そこで、W/C の多層膜 ($d=30.9$ Å) と 1 keV (波長 1.2 Å) より低い軟 X 線を光源にして定在波源とした。また、定在波プロファイルを得るために特定原子の光電子ピークの収量を用いた。適用した系は両親媒性アゾベンゼン誘導体 CH₃(CH₂)₇AzO-(CH₂)₅COOH (Az: C₆H₅N=NC₆H₅) の単分子層を W/C 多層膜上に Cd イオンを安定剤として LB 法で作成したものである。W4f, N1s, Cd3d 光電子ピークの強度変化を Bragg 条件を満足する角度で求めて定在波プロファイルとし、その解析から W/C 多層膜基板上的 Cd, N の相対位置を求めた。これと C K-NEXAFS の偏光依存性から求めた分子鎖の傾きから、この有機単分子膜の構造情報を得ることに成功した。さらに照射後の分子の配向の変化についても明らかにすることができた。

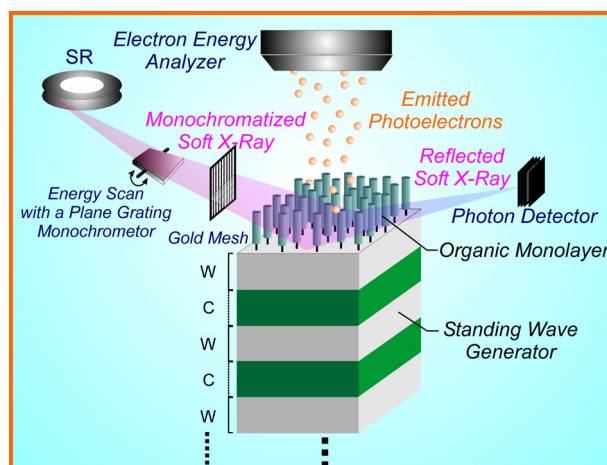


図 2 光電子収量法を用いた軟 X 線定在波法の模式図。基板には (W(12.0 Å)/C(18.9 Å))₈₀ の多層膜を用いている。

1. 原著論文

(1) Refereed Journals

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- 12) K. Tono, A. Terasakki, T. Ohta, and T. Kondow, "Weak metal-metal bonding in small manganese cluster ions, Mn_N⁺(N<7)" *J. Chem. Phys.* **123**, 174314 (6 pages) (2005).
- 13) K. Amemiya, D. Matsumura, H. Abe, S. Kitagawa, T. Yokoyama, and T. Ohta, "Direct Observation of surface and interface magnetism with the probing-depth dependent X-ray magnetic circular dichroism" *J. Electron. Spectrosc. Relat. Phenom.* **144-147**, 689-693 (2005).
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(2) その他 (Proceedings)

- 1) K. Amemiya, D. Matsumura, H. Abe, S. Kitagawa, T. Yokoyama, and T. Ohta, "Oscillations of surface magnetization in Fe/Ni/Cu(100) films observed with the depth-resolved x-ray magnetic circular dichroism technique" *Photon Factory Activity Report*, Vol. 22, Part A, p.19 (2004).
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- 4) E. Sako, A. Nojima, J. Miyawaki, H. Kondoh, and T. Ohta, "S K-edge X-ray absorption fine structure

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2. 総説・解説

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3. 著書

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