

IX-I Spectroscopy and Chemistry of Metal Nanoclusters on Surfaces

The structure and reactivity of metal nanoclusters are important issues because of their relevance to heterogeneous catalysis. In particular, Au nanoclusters on titanium oxide surfaces has attracted a lot of interest since the discovery of its catalytic activity on CO oxidation. We apply various surface science techniques to clarify correlations between structures and reactivity of metal nanoclusters deposited on surfaces. In this year, we use alkanethiolate-coated gold nanoclusters as a primary target in collaboration with Tsukuda (IMS) and Al-Shamery (U. Oldenburg) groups.

IX-I-1 STM Observation and Fabrication of Films of Gold Nanoclusters with and without Alkanethiolate Ligands on TiO₂(110)

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Films of Au nanoclusters protected with alkanethiolate ligands fabricated before and after etching on the TiO₂(110) surface were investigated by scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS). The Au nanoclusters were produced by reducing HAuCl₄ in micelles and fractionalized by

size with gel permeation chromatography. Au nanoclusters with hexanethiolate formed single layers and were coated on TiO₂(110). Replacing the ligands with *n*-octadecanethiolate resulted in forming three layers. Au nanoclusters with ligands are mobile on TiO₂ at room temperature and it is possible to manipulate their positions by a STM tip. XPS spectra showed that O-atom etching removes ligands effectively and produces gold oxide on nanocluster surfaces. The oxide was reduced effectively by H atom etching. These etching procedures causes aggregation of Au nanoclusters, increasing apparent height from ~1.5 nm to 3–6 nm. Adding hexanethiol and decane to the films of Au nanocluster with hexanethiolate did not show significant changes before and after etching. No diffusion was induced by STM tips after O atom etching.

IX-J Photochemistry on Well-Defined Surfaces

Upon the irradiation of light in the wavelength range from visible to ultraviolet, a number of adsorbed molecules on metal surfaces reveal variety of photochemical processes, including photo-stimulated desorption, rearrangement of adsorbed states, photodissociation, and photo-initiated reactions with coadsorbates. A central and fundamental question in the surface photochemistry is to clarify how adsorbate-substrate systems are excited by photon irradiation. In addition, since photo-initiated reactions can be induced without any thermal activation of reactants, they may provide good opportunities for studying a new class of surface reactions that may not be induced thermally. We have studied photochemistry of various adsorption systems on well-defined metal and semiconductor surfaces mainly by temperature-programmed desorption (TPD), infrared reflection absorption spectroscopy (IRAS), x-ray photoelectron spectroscopy (XPS), work function measurements, and angular-resolved time-of-flight (TOF) mass spectrometry of photodesorbed species associated with pulsed laser irradiation. In this year, the photochemistry of cyclic alkane on Pt(111) and Cu(111) surfaces was studied mainly by TPD, XPS, and IRAS.

IX-J-1 Photochemistry of Cyclohexane on Cu(111)

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[*Phys. Chem. Chem. Phys.* **8**, 179–185 (2006)]

The photochemistry of cyclohexane on Cu(111) and its excitation mechanism have been studied by temperature-programmed desorption, ultraviolet and X-ray photoelectron spectroscopy. Cyclohexane weakly adsorbed on Cu(111) has been known to show a broadened

and redshifted CH stretching band, *i.e.*, CH vibrational mode softening. Although no dehydrogenation takes place thermally on this surface and by the irradiation of photons at 5.0 eV, adsorbed cyclohexane is dissociated to cyclohexyl and hydrogen by the irradiation of photons at 6.4 eV. This is a marked contrast to cyclohexane in the gas phase where the onset of absorption is located at 7 eV. When the surface irradiated by 6.4-eV photons is further annealed, cyclohexyl is dehydrogenated to form cyclohexene that desorbs at 230 K. The systematic measurements of photochemical cross sections at 6.4 eV with linearly polarized light as a function of incident angle indicate that the electronic transition from the highest occupied band of cyclohexane to a partially occupied hybridized band near the Fermi level is respon-

sible for the photochemistry. The hybridized band is formed by the interactions between the electronic states of cyclohexane and the metal substrate. The role of the hybridized band in the photochemistry and the CH vibrational mode softening is discussed.

IX-J-2 Photochemistry and Post-Irradiation Chemistry of Cyclohexane on Pt(111)

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Photochemistry and post-irradiation thermal chemistry of cyclohexane on Pt(111) were investigated by TPD, XPS and IRAS. From TPD results, photo-dehydrogenation of cyclohexane was confirmed on Pt(111). IRAS spectra after photo-irradiation indicate that the primary photoproduct is cyclohexyl. The photoreaction cross sections of cyclohexane on Pt(111) at 6.4 and 5.0 eV are $(3.1 \pm 0.2) \times 10^{-21}$ and $(1.1 \pm 0.6) \times 10^{-21}$ cm², respectively. The appreciable cross section at 5.0 eV suggests the larger adsorbate interactions on Pt(111)

compared with those on Cu(111). The excitation mechanism was investigated by the same procedure for Cu(111). The cross sections with p-polarized light again deviate from the absorbance of the substrate. This indicates clearly that the excitation mechanism is the same on Cu(111). On Pt(111), it has been known that cyclohexane is thermally dehydrogenated to benzene *via* C₆H₉. Benzene converted from the monolayer of cyclohexane does not desorb molecularly because benzene is further dehydrogenated to atomic C. In contrast, after photo-irradiation at 6.4 eV, the desorption of benzene in post-irradiation TPD was clearly observed. Then, the thermal reactions of the primary photoproduct, cyclohexyl, were investigated by IRAS. Absorption bands attributable to cyclohexene appeared at 200 K. This species has not been identified in the studies on thermal reactions of cyclohexane on Pt(111). UV photons can produce a larger amount of cyclohexyl than that induced thermally. In this case, the adsorption sites are largely occupied by produced cyclohexyl and hydrogen, which may increase the activation barriers for dehydrogenation of cyclohexene and benzene in the post-irradiation thermal chemistry.

IX-K Ultrafast Dynamics at Well-Defined Surfaces

To understand the mechanism of surface photochemistry, it is vital to know how photoinduced electronic excitation induces adsorbate nuclear motions that ultimately lead to chemical reactions. We demonstrate the real-time observations of surface phonons and adsorbate-substrate vibrational modes by fs time-resolved second harmonics generation (TRSHG). If an excitation light pulse has a duration sufficiently shorter than a period of a vibrational mode or a phonon mode, it can excite the mode with a high degree of temporal and spatial coherence. This coherent nuclear motion modulates the second-order susceptibility $\chi^{(2)}$. Thus, by monitoring the intensity modulation of the second harmonics (SH) generation of a probe pulse, we can observe the evolution of the coherent nuclear motion subsequent to the electronic excitation at the surfaces. This year, in particular, we have focused on K on Pt(111) and Na on Cu(111) adsorption systems.

IX-K-1 Coherent Surface Phonon Dynamics at K-Covered Pt(111) Surfaces Investigated by Time-Resolved Second Harmonic Generation

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[Phys. Rev. B submitted]

We have investigated coherently excited surface phonons at K-covered Pt(111) surfaces by using femto-second time-resolved second harmonic generation spectroscopy. The frequency of the K–Pt stretching phonon mode depends on the superstructure of K: 5.0–5.3 and 4.5–4.8 THz for (2×2) and $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructures, respectively. In addition to the stretching mode, a couple of Pt surface phonon modes are simultaneously observed when the $(\sqrt{3} \times \sqrt{3})R30^\circ$ superstructure is formed. The dephasing time of the K–Pt stretching mode becomes shorter and its frequency redshifts as the absorbed fluence of a pump pulse increases. This is

in stark contrast to the Pt surface phonon modes whose frequencies are independent of fluence. The fluence dependence of the K–Pt stretching mode is interpreted to be due to anharmonic coupling between the K–Pt stretching and lateral modes.

IX-K-2 Excitation Mechanism of Coherent Surface Phonons on Na-Covered Cu(111)

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We observed time-resolved second harmonic signals from the Cu(111) surface with a full monolayer of Na in ultra-high vacuum and investigated the excitation-wavelength dependence of the wave packet dynamics of the coherently excited Na–Cu stretching mode. Changing the photon energy of the pump pulse (25 fs) from 2.0 to 2.5 eV, the oscillation amplitude derived from the Na–Cu stretching motion is enhanced. The careful measurements of photon-energy dependence indicates that the

excitation efficiency mimics the absorbance of bulk Cu. Holes created in the d-bands by the optical transitions could be filled by electrons in the adsorbate-induced occupied state of the metallic quantum well by an Auger-type transition. Hence, holes can be created in the adsorbate-induced occupied state. Moreover, since this Auger decay can occur significantly faster than the oscillation period of the Na–Cu stretching mode, the substrate excitation may be a possible excitation mechanism for the coherent oscillation.

IX-K-3 Electron Transfer Dynamics from Organic Adsorbate to a Semiconductor Surface: Zinc-Phthalocyanine on TiO₂(110)

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[*J. Phys. Chem. B* **109**, 18018–18024 (2005)]

The femtosecond time-evolutions of excited states in zinc-phthalocyanine (ZnPC) films and at the interface with TiO₂(110) have been studied by using time-resolved two-photon photoelectron spectroscopy (TR-2PPE). The excited states are prepared in the first singlet

excited state (S₁) with excess vibrational energy. Two different films are examined: ultrathin (monolayer) and thick films of ~30 Å in thickness. The decay behavior depends on the thickness of the film. In the case of the thick film, TR-2PPE spectra are dominated by the signals from ZnPC in the film. The excited states decay with $\tau = 118$ fs mainly by intramolecular vibrational relaxation. After the excited states cascaded down to near the bottom of the S₁ manifold, they decay slowly ($\tau = 56$ ps) although the states are located at above the conduction band minimum of the bulk TiO₂. The exciton migration in the thick film is the rate determining step for the electron transfer from the film to the bulk TiO₂. In the case of the ultrathin film, the contribution of electron transfer is more evident. The excited states decay faster than those in the thick film, because the electron transfer competes with the intramolecular relaxation processes. The electronic coupling with empty bands in the conduction band of TiO₂ plays an important role in the electron transfer. The lower limit of the electron transfer rate was estimated to be 1/296 fs⁻¹. After the excited states relax to the states whose energy is below the conduction band minimum of TiO₂, they decay much slowly because the electron transfer channel is not available for these states.

IX-L Vibrational Dynamics at Surfaces and Interfaces Studied by Time-Resolved Sum Frequency Spectroscopy

In addition to time-resolved second harmonic generation and two-photon photoemission spectroscopy, we have developed fs time-resolved sum frequency generation (SFG) spectroscopy to study ultrafast surface dynamics. Time-resolved SFG is a versatile tool for investigating vibrational dynamics at surfaces and interfaces. In this year, we applied this technique to probe vibrational energy transfer at the interface between Pt(111) and ice layers where CO monolayer is inserted.

IX-L-1 Vibrational Energy Relaxation at the Interface of Ice/CO/Pt(111) Studied by fs Time-Resolved Sum Frequency Generation

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We studied the vibrational excitation and relaxation dynamics of surface adsorbate for D₂O/CO/Pt(111) by the femtosecond time resolved vibrational SFG spectroscopy (VIS: 800 nm, 3 ps; IR: 3–5 μm, 130 fs; pump: 400 nm, 130 fs) under ultra vacuum condition. D₂O/CO/Pt(111) was prepared by dosing D₂O molecules on the CO covered Pt(111) surface at 140 K. Two peaks were observed in CO stretching region at 2068 and 2095 cm⁻¹ when 10 ML D₂O layer was formed on the surface, because D₂O crystals exhibit island growth on this surface. The former peak (ν*(CO)) is assigned to the adsorbed CO intact with D₂O and the latter (ν(CO)) is assigned to the CO free from D₂O. Both peaks were

redshifted and broadened by the irradiation of a pump pulse, because the frustrated translation and rotation modes of CO coupled to Pt hot electrons generated by the excitation pulse. We found the following features in the transient SFG spectra. The maximum peak shift of ν*(CO) was larger than that of ν(CO) and the peak shift of ν*(CO) shows much faster recovery than that of ν(CO) within 3 ps after the excitation. We analyze the spectra by the numerical simulation of SFG polarization based on the Bloch equations, which describe the time-dependent evolution of the density matrix for the CO stretching mode. The transient response of time-resolved SFG spectra can be characterized by the time dependent adsorbate temperature, where the key parameter is the time scale on which energy flows between substrate electrons and the CO frustrated mode, τ_e. To reproduce the experimental data, coupling times of τ_e = 0.8 ps and τ_e = 1.6 ps for ν*(CO) and ν(CO), respectively, are required, indicating that the ν*(CO) mode couples to the substrate hot electrons more effectively than ν(CO).

IX-M Chemistry of One-Dimensional Nano-Surface Compounds Studied by Scanning Tunneling Microscopy

The fluctuating configurations of low-dimensional structures can be thermodynamically favorable at finite temperatures, because the energy gain overcomes the energy cost that accompanies local structural fluctuation. In particular, one-dimensional (1D) systems have a propensity to be sensitive to these fluctuations as described by one of the maxims of condensed matter physics, *i.e.*, one chain does not make a crystal. Thus, the dynamical formation of active species and sites by these fluctuations is a key factor in establishing a microscopic model for chemical reactions at surfaces and nano-structured compounds.

IX-M-1 Direct Observation of a Propagating Chemical Wave in Disproportionation Reactions of Water on Oxidized Ag(110) Surface by Scanning Tunneling Microscopy

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[*J. Phys. Chem. B* submitted]

It is well known that the adsorption of O on Ag(110) results in the formation of quasi-1D structures, AgO chains, accompanied by the mass transfer of substrate atoms. AgO chains arrange periodically to form ($n \times 1$) ($n = 2 \sim 7$) depending on the fractional O coverage due to repulsive inter-chain interactions. On the added-row reconstructed Ag(110)($n \times 1$)-O surfaces, one-dimensional -Ag-O-Ag-O- chains arrange periodically. Scanning tunneling microscopy was used for studying spatio-temporal evolution of the disproportionation reaction of H₂O with O adatoms on oxidized Ag(110) surfaces where quasi-one dimensional AgO chains form ordered structures. Initially the reaction takes place slowly on Ag(110)-(5 \times 1)O at the end of AgO chain, whereas the reaction accelerates explosively upon the appearance of a chemical wave that propagates along the direction perpendicular to the chain. The surface morphology of the region swept over by the chemical wave completely changes from (5 \times 1)-O to that with many rectangular islands, indicating the formation of H₂O(OH)₂. The induction time and explosive acceleration with the propagating chemical wave imply that the reaction is autocatalytic. Water clusters hydrating OH produced likely play a central role in serving as a reservoir of H₂O to feed to the reaction and enhancing the reactivity of H₂O with O adatoms in AgO chains.