2 Chemistry

2-1 Water Formation Reaction on Pt(111) Studied by Time-resolved NEXAFS and Kinetic Monte Carlo Simulation

Water formation from oxygen and hydrogen on a platinum surface is one of the oldest known catalytic reactions, but the reaction mechanism has not been fully understood yet. Recently, Sachs *et al.* studied water formation below 170 K by means of scanning tunneling microscopy (STM) [1]. They observed that OH domains propagate on the O-covered Pt(111) surface by producing H_2O in backward areas, and proposed the reaction mechanism that a cycle of two elementary reaction processes, $OH + H \rightarrow H_2O$ and $O + 2\ H_2O \rightarrow 2\ OH + H_2O$, is repeated by the diffusion of H_2O. However, the STM observations provide information only in a limited area, while the OH domains rapidly propagate on a mesoscopic scale over the whole surface. It is necessary to measure the kinetics for the whole surface and to examine whether the observed kinetics can be explained by the proposed microscopic mechanism. To this end we have measured the kinetics of the reaction species (O, OH, and H_2O) by using the newly developed energy-dispersive near-edge X-ray-absorption fine structure (NEXAFS) method, and investigated the reaction mechanism using a kinetic Monte Carlo simulation [2].

The experiments were performed at BL-7A under ultrahigh vacuum conditions. The water formation reaction was conducted by exposing (2×2) O-covered Pt(111) to

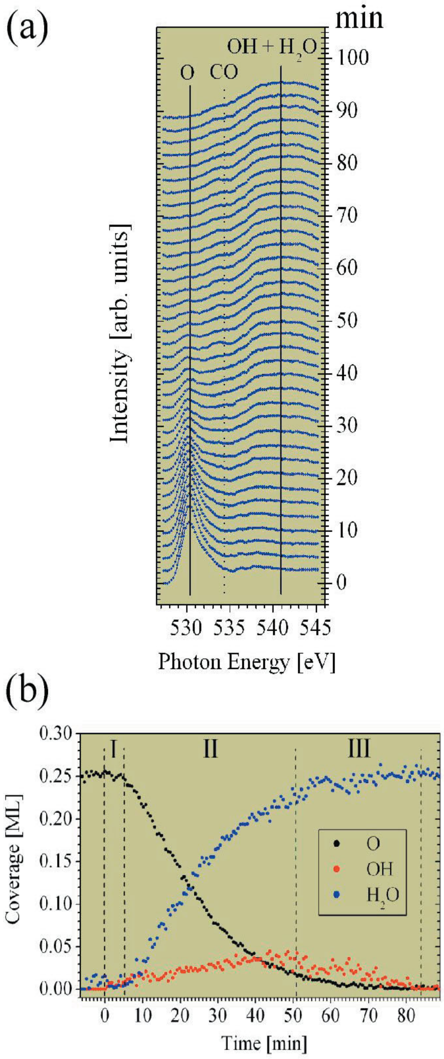

Figure 1
(a) O K-edge NEXAFS spectra at normal incidence as a function of time, recorded during the exposure of gaseous H_2 (5.0×10^{-9} Torr) at 130 K. Each spectrum was recorded over 35 sec and some selected spectra are shown. (b) Coverages of O, OH, and H_2O as a function of time obtained from analysis of the NEXAFS spectra.

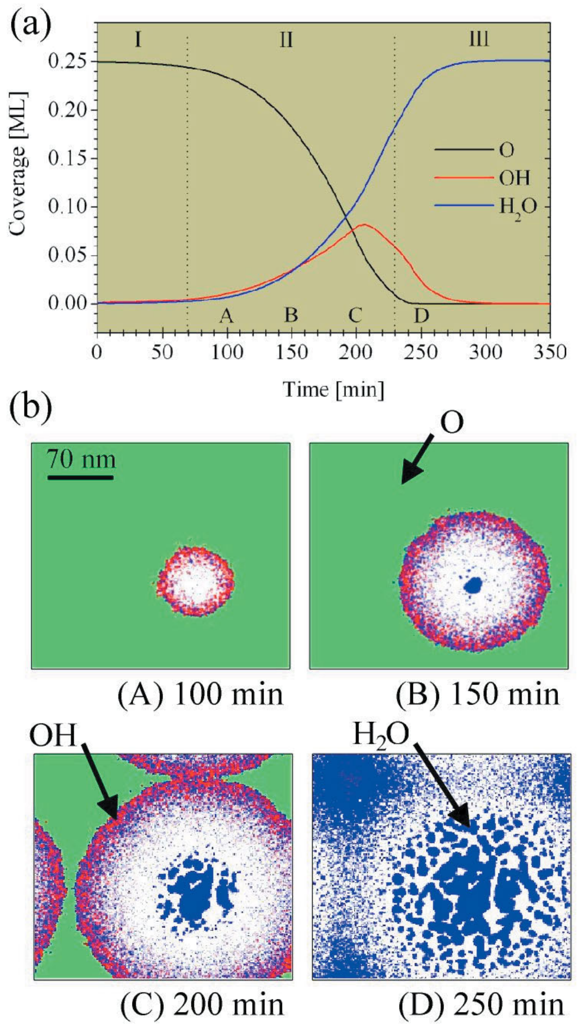

Figure 2
(a) Coverages of O, OH, and H_2O as a function of time calculated using a kinetic Monte Carlo simulation. (b) Series of the surface configurations at the times labeled A, B, C, and D in Fig. 2 (a). The size of these images is 280 nm × 280 nm. O, OH and H_2O species are represented by green, red and blue spots, respectively.

gaseous H_2 (5.0×10^{-9} Torr) at 130 K. Each O-K NEXAFS spectrum was recorded over 35 sec during the reaction. Fig. 1(a) shows the time evolution of the NEXAFS spectra, where the peak due to O disappears and the broad structure associated with OH and H_2O increases as the reaction progresses. The spectra were fitted using a superposition of the standard spectra from O, OH, and H_2O. As a result, the changes of O, OH, and H_2O coverages are obtained as shown in Fig. 1(b). It is clearly recognized that the reaction has three steps; an induction period (I), fast increase of OH and H_2O by consuming O (II), and slow conversion from OH to H_2O (III).

To understand the reaction mechanism, a kinetic Monte Carlo (KMC) simulation was performed on a scale of 280 nm × 280 nm. Fig. 2(a) shows the changes of O, OH, and H_2O coverages obtained in the KMC simulation, which well-reproduce the observed three periods. As shown in Fig. 2(b), the surface configurations also clearly reproduced the STM results, which show that the OH reaction fronts proceed on the O-covered Pt(111) surface by producing H_2O [1]. Moreover, the KMC simulation revealed that proton transfer between H_2O and OH plays a significant role for the propagation of the reaction fronts. As a result, the KMC simulation reproduced both the macroscopic and microscopic behaviors, suggesting that not only the diffusion of H_2O but also proton transfer between H_2O and OH combines the above two elementary reaction processes.

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2-2 A Time-resolved DXAFS Study of CO-induced Disintegration of Surface Rh-Clusters

Knowledge of the dynamic structural changes at the active site is important for the complete understanding of catalytic reactions. In the study of catalysis, the relationship between structure and reactivity is the key to understanding how a given catalyst works and, therefore, how one may design or modify a catalyst for a specific purpose. While the reaction kinetics and dynamics of molecules adsorbed on catalyst surfaces have been extensively studied, little is known about the dynamic structural change of active metal sites in supported metal cluster/nanoparticle catalysts, such as the time scale of integration and disintegration of the active structure induced by reaction gases and the sequence of bond rearrangements involved in the dynamic event on the surfaces.

Although structural changes have previously been characterized by many different physicochemical methods, only X-ray-absorption fine structure (XAFS) can directly provide the electronic and structural information. XAFS can be a suitable technique for the structural analysis of active sites under reaction conditions, however it takes ten minutes or more to record an extended XAFS (EXAFS) spectrum for dispersed species using conventional techniques even if synchrotron radiation is used. Therefore, an *in-situ* method of time-resolved structural characterization using the energy-dispersive XAFS (DXAFS) technique is essential for investigating dynamic properties on an atomic basis, which has been a long-term challenge [1-3]. We have succeeded in observing the CO-induced disintegration process of Rh clusters on an Al_2O_3 surface using DXAFS at BL-9C [1,3].

X-ray-absorption near-edge structure (XANES) spectra and k^3-weighted EXAFS oscillations at the Rh K-edge, recorded during the carbonylation process are shown in Figs. 3 and 4. The DXAFS spectra were recorded every 100 ms. The amplitude of EXAFS oscillations did not change significantly between 0 and 600 ms, but a remarkable decrease of amplitude in the higher k range was observed between 600 and 3000 ms. Before CO exposure (at t=0) Rh atoms in the cluster interact with the surface oxygen atoms of Al_2O_3 at a distance (R) of 0.213 nm. The coordination number (CN) and R of Rh–Rh were 5.0 and 0.265 nm. These structural parameters suggest that the Rh cluster consists of 7 atoms (first layer) and 3 atoms (second layer) as shown in Fig. 5A. During the first step of the dynamic processes (0-600 ms) Rh-clusters rapidly adsorb CO, showing a CN of 0.7 for Rh–CO, and indicating that one CO molecule adsorbs on each Rh atom of the top layer. At this stage no Rh-Rh bond breaking occurs. During the second step of the processes after 600 ms the Rh-Rh bonds become weaker due to further

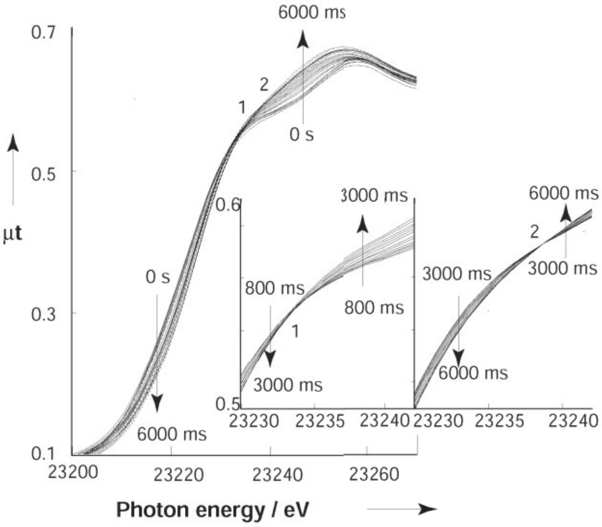

Figure 3
A series of XANES spectra at the Rh K-edge during the carbonylation of Rh/Al_2O_3 under CO (26.7 kPa) at 298 K. The acquisition time for each spectrum was 100 ms, and the Cat.weight (wafer) was 80 mg.

CO adsorption and the Rh cluster is completely disintegrated at 3000 ms, where the ratio of adsorbed CO to Rh reaches one. The existence of an isosbestic point (1) in Fig. 3 indicates that the second step consists of a one-to-one direct conversion, from [$Rh_{10}(CO)_3$] (Fig. 5B) to [Rh-CO]$_{10}$ (Fig. 5C). The [Rh–CO] can migrate across the Al_2O_3 surface to react with OH groups. Fragmentation of the Rh cluster permits the adsorption of further CO molecules on the Rh atoms during the third step (3000-6000 ms) to form [$Rh(CO)_2$] (Fig. 5D) which interacts with three surface O atoms (yellow circles in Fig. 5D). This process is also a direct transformation process as evidenced by the second isosbestic point (2) in Fig. 3, where the Rh atoms interact more strongly with the surface due to a decrease in the Rh–O distance from 0.213 to 0.200 nm.

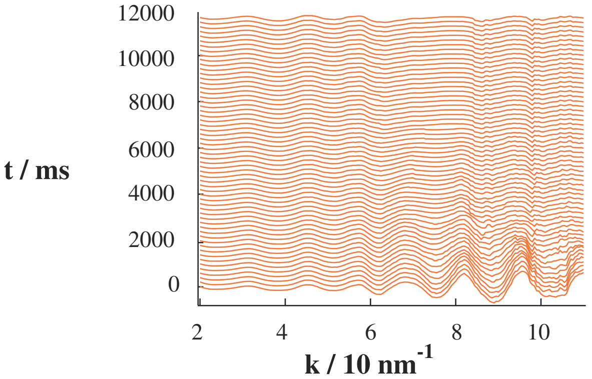

Figure 4
k^3-weighted EXAFS oscillations for Rh/Al_2O_3 at the Rh K-edge during the carbonylation process at 298 K measured by DXAFS every 100 ms.

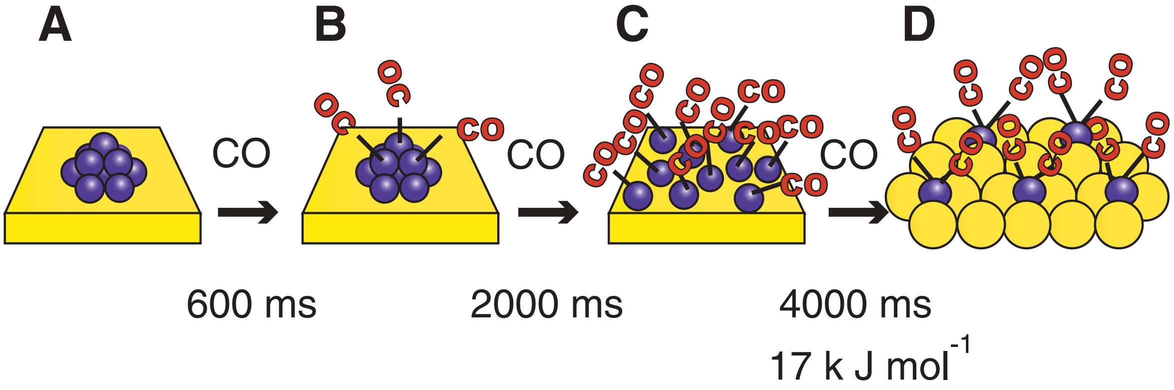

Figure 5
An illustrative mechanism showing time scales of the three elementary steps for the disintegration of Rh clusters on Al_2O_3 during CO adsorption by at 298 K as inferred from time-resolved DXAFS.

The time-resolved structural analysis described here provides crucial information for understanding the mechanism of dynamic surface processes and contributes to a new area of research into the structural dynamics of metal clusters/nanoparticles dispersed on surfaces.

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2-3 High-temperature XAFS Measurements of Molten Salt Systems

Pyrochemical reprocessing of spent nuclear fuels is expected as a new technology in the nuclear fuel cycle. Polyvalent metals such as actinide, lanthanide and the noble metals are recovered by electrorefining in the process. Thus, knowledge of the physical properties of high-temperature molten polyvalent halides in alkali chloride solvents (such as LiCl-KCl eutectic melt) is important for developing an effective reprocessing system of nuclear fuels. We have developed a high-temperature apparatus for X-ray absorption fine structure analysis (XAFS) and performed XAFS measurements of various molten salts including uranium mixture.

The XAFS measurements of molten salts were performed at BL-27B. An electric furnace and sandglass-type quartz cell specialized for hygroscopic molten metal halides were used [1]. Fig. 6 shows the Y K-edge (E_0 = 17.038 keV) XAFS Fourier transform $|FT(k^3\chi(k))|$ of molten YCl_3 and its mixtures with LiCl-KCl eutectic [2]. The intensity of the 1st peak, which corresponds to the nearest Y^{3+}-Cl^- correlation increases by mixing with the alkali chlorides. The correlation between Y^{3+} ions suggesting edge-shared connection was observed in the pure melt. On the other hand, no peaks were found at the same position in the mixture melts. These results suggest breaking of the connections and stabilization of $(YCl_6)^{2-}$ complex ion.

At BL-27B, radioactive materials containing Tc, Th, U, Np, Am and Cm can be used for XAFS experiments. We studied a high-temperature molten chloride mixture melt containing UCl_3. The local structure around uranium was clarified from XAFS analysis. Fig. 7 shows U L_3-edge XANES spectra of some uranium compounds [3]. In molten 15%UCl_3-(LiCl-KCl eutectic), it is concluded that the

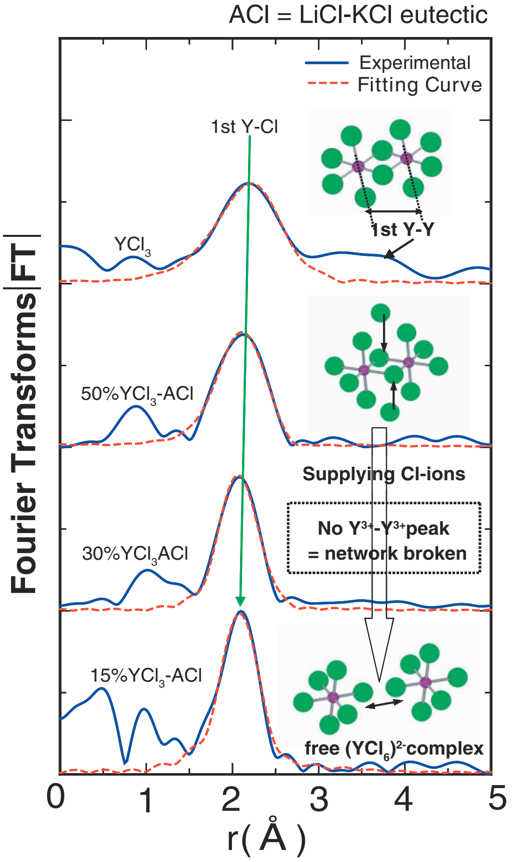

Figure 6
Fourier transform magnitude functions |FT(k$^3\chi$(k))| of molten YCl$_3$ and its mixtures in LiCl-KCl eutectic melt. Increasing of the 1st Y^{3+}-Cl$^-$ peak and disappearance of the Y^{3+}-Y^{3+} correlation show that stability of the octahedral complex (YCl$_6$)$^{3-}$ increases by mixing with the alkali chlorides.

uranium is behaving as a trivalent ion. We are planning an *in-situ* XAFS/XANES measurement of uranium in the electrorefining process of nuclear fuels.

XAFS data analysis of high-temperature liquids has some problems such as anharmonic vibration effect, multielectron excitation effect and validity of the Fourier filtering operation. Especially it has been pointed out that the wrong result may be obtained from the normal curve fitting analysis. We have proposed a new XAFS data simulation method for high-temperature liquids. It is a combinational use of molecular dynamics (MD) technique and XAFS simulation program FEFF8. The FEFF8 itself is not optimized for liquid XAFS data analysis. However, we assumed that averaging FEFF8 computations for all MD output data is expected to result in simulated XAFS function including the fluctuation factors like Debye-Waller factor. Fig. 8 shows Sr K-edge (E_0 = 16.105 keV) XAFS function k$^3\chi$(k) of SrCl$_2$ simulated by averaging 25600 FEFF8 computations using MD output clusters [4,5]. From solid at room temperature to molten state, the experimental XAFS functions were nicely reproduced by the simulation.

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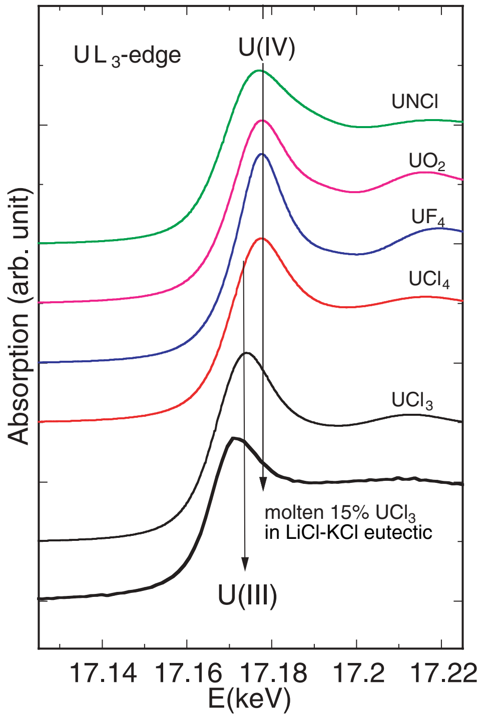

Figure 7
Uranium L$_3$-edge XANES spectra of some uranium halides.

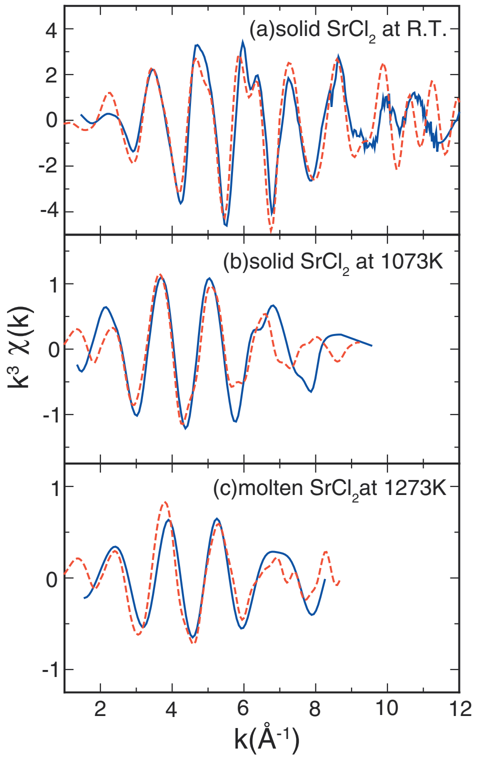

Figure 8
XAFS function k$^3\chi$(k) of solid and molten SrCl$_2$. (Solid line: experimental, Dashed line: average of 25600 MD+FEFF8 computations)

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