Ultrahigh-sensitive detection of molecules produced in catalytic reactions by uni-atomic-composition bi-element clusters supported on solid substrate

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Abstract. An apparatus has been developed for measuring catalytic activities of uni-atomic-composition bi-element clusters supported on a solid substrate. The cluster sample is prepared by irradiating a cluster-ion beam having the uni-atomic composition onto the substrate on a soft-landing condition in an ultra-high vacuum. The catalytic activity is measured by temperature-programmed desorption (TPD) mass analysis. Molecules at a density as low as $<10^{-3}$ cm$^{-3}$ have been detected with an ultrahigh-sensitive TPD mass spectrometer consisting of a cylindrical electron gun, a quadrupole mass filter and a micro-channel-plate ion-detector. The high reproducibility has been achieved by careful calibration of the TPD mass spectrometer. As a benchmark example, thermal oxidation of CO catalysed on Pt$_{30}$ disks supported on a silicon surface was studied. The CO$_2$ products have been successfully observed at the Pt$_{30}$ density as low as $3 \times 10^{12}$ clusters in a circular area of 8 mm in diameter at the ramping rate of the sample temperature as low as 0.3 K s$^{-1}$.

1. Introduction
Clusters, which are aggregates of a few to hundred atoms, can be promoted as functional materials, considering a number of research results achieved so far [1–6]. It is sure that the mechanisms of the cluster-based functions are different from those of the corresponding bulk materials and even nanoparticles because of a number of specific properties originating from both many-body and small natures. Another advantage of the cluster materials is precise controllability of their performances in a wide dynamic range with the size and the atomic composition of the clusters. Indeed, a variety of studies on the size-dependent specific properties of the clusters have been pursued; for instance, odd-even alternation in electronic and magnetic properties, metal-insulator transition due to quantization of the electronic energy levels, magic numbers of the cluster size for stability and reactivity due to closing of electronic and atomic shells, splitting a chemical bond with a molecular wedge, etc.

Supporting the clusters on a solid substrate [5,6] is a promising way for cluster-based functional materials due to not only the practical reason in their real application but promotion of the cluster-specific properties through electronic/chemical interaction with the substrate. They are tuned further with internal species such as electric charges, spins, atomic dopants and ligands to control the internal
electric, magnetic and chemical fields as well as the corresponding external fields. Indeed, we have shown successfully in our experimental [7] and theoretical [8] studies that two-dimensional charge polarization is created at a sub-nanometer interface between a monatomic-layered platinum cluster disk [9,10] and a silicon surface. This originates from electron accumulation at the interface between the cluster disk and the substrate surface in a similar manner to the Schottky barrier junction, and the resulting positive charging in the center part of the cluster disk due to the two-dimensional metallic interaction among the Pt atoms arranged in a close-packed manner [9]. It is straightforward that the accumulated charges can be adjusted by doping another element of an electron donor or acceptor into the cluster. We have successfully produced uni-atomic-composition bi-element cluster ions of Pt and Ag with sufficient intensities [11]. Furthermore, we have found that two- to three-dimensional geometric transition occurs in tungsten clusters anchored on a graphite surface between the cluster size of 10 and 11 due to competition between the cluster-substrate and intracluster interactions [12,13].

We are aiming to deduce novel catalytic functions from clusters. It is obvious from the definitions of reduction and oxidation as capture and release of electrons, respectively, that one can obtain high catalytic activities of the reduction and the oxidation by utilizing the rich electric charges. It is highly expected that the subnano-space charge accumulation also leads to an efficient advantage of higher molecular selectivity because of the charged area as small as a molecule.

Vigorous research studies have been prosecuted on catalytic activities driven by supported clusters [6,14−30]. For instance, experimental and theoretical studies have been reported that a planar gold cluster supported on the MgO(100) thin film prepared on a metal surface is charged due to electron transfer from the metal support to the cluster [14−17]. Furthermore, the charging state relates closely to catalytic activities [18−20]; the electron transfer from an oxygen-vacancy defect of the MgO(100) film to a three-dimensional Au₈ induces a high catalytic activity in the CO oxidation, but that supported on a defect-free MgO(001) film has no catalytic activity because of much less electron transfer between them [18,19]. On the other hand, a planner Au₂₀ supported on a defect-free MgO(100) substrate has the catalytic activity due to efficient charging [20]. Distinct cluster-size dependence has been reported in the catalytic CO oxidation by platinum clusters on a thin MgO(100) film, indicating the way to tuning the heterogeneous catalyst with the cluster size [21]. Clusters, Pt₇, supported on a slightly reduced TiO₂(110) substrate reveal a high catalytic activity in the CO oxidation, while those on a strongly reduced one quenches the CO oxidation [22].

The size- and composition-selected cluster catalyst samples can be prepared by soft-landing of the uni-size cluster ions onto the substrate [4−6]. Considering a typical intensity (~100 pA) of the most intense bi-element cluster-ion sources [11], the number of the clusters on a substrate is limited as low as ~10¹² in a realistic time required for the sample preparation. Therefore, the critical procedure in this kind of experimental studies is high-sensitive and reproducible detection of the reaction products. In this report, we present our study to develop an apparatus for the detection of low-density molecules produced in a catalytic reaction on the supported-cluster sample. The thermal oxidation of CO by O₂ catalysed by the Pt₃₀ disks supported on a silicon substrate [7−9,31] was employed as a benchmark system of heterogeneous catalyses [32].

2. Experimental apparatus and method
The apparatus consists of a bi-element cluster ions source, a mass filter for the selection of the size and atomic composition, a cluster-cooling device, a reaction device and a detection device [30].

2.1. Preparation of cluster-catalyst sample
The samples were prepared by the soft-landing of the uni-atomic-composition cluster ions onto the substrate. The details have been described in elsewhere [11,30], and several modifications were made thereafter. The bi-element cluster ions were produced by means of dual magnetron-sputtering devices having different-material targets equipped in a gas-aggregation chamber and the cluster cations were selected out of the neutral and anionic species in a quadrupole ion-deflector. A desired atomic composition was selected out according to the mass difference by passing through the quadrupole
mass filter (Extrel MAX-16000 operated at 440 kHz, rod diameter is 9.5 mm, maximum mass is 16,000 dalton), and both their kinetic energies and beam diameter were reduced in collision with cold He gas at 100 K in the cooling device. The cluster ions were always guided with octopole ion guides. The low-temperature cluster ions with a uni-atomic composition were allowed to collide onto the (111)–7×7 reconstructed surface of a silicon substrate placed in the reaction chamber (see figure 1) at 300 K at a collision energy of 1 eV per atom so as to fix the uni-atomic-composition clusters on it. The ambient pressure of the reaction chamber was maintained less than 5×10⁻⁸ Pa during the cluster deposition due to two differential-pumping chambers, where the most of the residual gas in the reaction chamber was helium leaked from the upstream cooling device. The number density of the clusters was set at 4×10¹² cm⁻² in order to avoid undesired direct interaction between the clusters on the substrate; the density is obtained by time-integration of the cluster-ion current (500 nC) and the known diameter (8 mm) of the cluster-ion beam [30]. Then, the surface was terminated with hydrogen by irradiating an atomic hydrogen beam from a thermal hydrogen cracker (Tectra H-flux) in order to prevent the silicon surface from oxidation during the TPD measurements; the hydrogen-terminated silicon surface is stable below 750 K [33], while the H atoms desorb from the Pt clusters at ~300 K by analogy with the H desorption from the Pt(111) surface [34]. It has been confirmed by STM observation that the Pt₃₀ disks on the silicon substrate are stable below 673 K [31].

The (111)–7×7 reconstructed surface of the silicon substrate was prepared from a Si wafer (Nilaco n-type, specific resistance less than 0.01 Ωcm, 10×20×0.5 mm³) by repeating a series of Ar⁺ sputtering (10 µA for one hours at 5×10⁻⁴ Pa of Ar), heating resistively at 1200 K for 50 s and successive annealing down to 850 K at a rate of ~0.5 K s⁻¹ at an ambient pressure less than 1×10⁻⁷ Pa, where the temperature of the silicon surface was measured with a pyrometer (Chino IR-AH1S). Each end of stacked two silicon wafers was placed on a copper electrode through a tantalum thin plate (0.2-mm thick), and fixed with a molybdenum plate (1-mm thick) and two molybdenum bolts; the wafer stacking is employed for the accurate measurement of the substrate temperature as described in the next subsection. The reaction chamber was evacuated with a turbo-molecular pump (Mitsubishi PT-500).

2.2. Observation of catalytic reaction

The temperature-programmed desorption (TPD) mass-spectroscopy was carried out repeatedly for a given cluster catalyst sample in a series of sample cleaning, reactant adsorption and the TPD measurement. Figure 1 shows a sectional top view of the sample stage and the TPD mass spectrometer installed in the reaction and detection chambers, respectively [30]. The sample was cooled with liquid nitrogen through the copper electrodes and a copper block attached at the end of a liquid-nitrogen tank (310-mm long, 45 mm in diameter), where the liquid-nitrogen tank was placed on an x-y-z-θ manipulating stage. On the other hand, the sample was heated resistively with dc current though the silicon substrates programed for the linear temperature ramping, where the electric cables were thermally anchored on the copper block. The product molecules desorbed from the cluster catalyst were introduced into a cylindrical electron gun (Extrel axial ionizer) to be ionized through a home-made skimmer having a 6-mm hole placed at less than 1 mm far from the sample substrate. Thoriated iridium filaments, which emit electrons at lower temperature than tungsten one, were employed in order to suppress emission of contaminating species from the filaments, where they were, if produced, evacuated readily through mesh surrounding the electron gun. The ions were focused onto the entrance lens of a high-transmission quadrupole mass filter (Extrel MAX-300 operated at 1.2 MHz, rod diameter is 19 mm) with the cylindrical ion lenses and detected with a micro-channel plate (Hamamatsu MCP F4655) placed in a shielding metal box in the counting method at a time constant of 0.3–3 s. The MCP faced to 90 degrees with respective to the mass-filter axis and was placed at an off-axis position in order to suppress the back ground level by reducing the frequency of electronically-excited neutral species in metastable and Rydberg states hitting the detector. The sample surface was faced to the skimmer only during the TPD measurement in order for minimizing undesired sample heating and contamination by the electron gun.
The isotope-labelled reactants, $^{18}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}$, were employed in order to rule out contributions of the major residual $^{12}\text{C}^{16}\text{O}$ in the reaction chamber. The dose amounts of the reactants were regulated by their partial pressures measured with a calibrated cold-cathode pressure gauge (Pfeiffer IKR270) and the exposure time. The cluster catalyst was exposed to the reactant gases one by one by leaking one of the gasses through the corresponding variable leaking valve into the reaction chamber at $6\times10^{-7}$ Pa for 200 s (exposure at 0.45 L) and at the substrate temperature of 105 K. The cold-cathode gauge was calibrated independently for $^{18}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}$ in the pressure range of $3-15\times10^{-7}$ Pa everyday before and after all the series of the TPD measurements with a calibrated commercial residual-gas analyzer (SRS RGA-100) installed in the reaction chamber. However, the residual gas analyser was turned off during the TPD measurements in order to avoid sample contamination due to species produced by its electron gun. The cluster catalyst was cleaned within 20 minutes before every set of the reactant dose by burning the impurity adsorbates at 650 K after exposure to $\text{O}_2$ at more than 1 L at 105 K.

The intensity of the reaction product, $^{13}\text{C}^{16}\text{O}^{18}\text{O}$, was measured as a function of the temperature of the cluster catalyst whilst heating it from 110 K to 550 K. The temperature of the substrate was measured as that of the cluster catalyst with a chromel-alumel thermocouple (0.05 mm in diameter for each) referred to liquid nitrogen out of the vacuum chamber. Good thermal contact between the substrate and the thermocouple was achieved by tight insertion of the contact end of the thermocouple wrapped with tantalum foil (0.075-mm thick) between the stacked silicon wafers. The temperature uniformity was measured with the pyrometer (spatial resolution of 3 mm at the substrate) to be as good as $\leq10$ K in a circular area of 10 mm in diameter at the center of the substrate at the substrate.
temperature of 850 K. The ramping rate as low as 0.3 K s\(^{-1}\) was employed in the TPD measurements also for the uniform heating of the rather large substrate.

The pressure of the reaction chamber was less than 1×10\(^{-8}\) Pa during the TPD measurement by filling the tank with liquid nitrogen, while that of the detection chamber was 3×10\(^{-8}\) Pa by differential pumping with a turbo-molecular pump (Mitsubishi PT-500).

3. Results and discussion

3.1. Production of intense platinum cluster cations

Figure 2 shows mass spectra optimized for the production of Pt\(_{30}^+\) (5,853 dalton) and Pt\(_{82}^+\) (15,997 dalton); the discharging voltage and current and the flow rates for He and Ar for the Pt magnetron were (238 V, 83 mA, 53 and 21.6 sccm, standard cc per minute) and (278 V, 216 mA, 46 and 15.6 sccm) for panels (a) and (b), respectively. The series of mass peaks are assignable to Pt\(_N^+\) (N=1–82) and Ar\(^+\). In the entire size range, Pt\(_N^+\) are successfully produced as intense as or more intense than ~100 pA, which is high enough to prepare the cluster catalysis sample at the desired number density within 2 hours.

3.2. Detection efficiency of product molecules

The detection efficiency of the TPD products was calibrated also everyday before and after all the series of the TPD measurements with the residual-gas analyzer. Leaking a trace amount of argon into the reaction chamber, the intensity of Ar\(^+\) and the partial pressure of Ar were measured simultaneously with the TPD mass spectrometer and the residual gas analyser, respectively. Figure 3 shows mass spectra measured with the TPD mass spectrometer at the time constant of 0.3 s and the residual gas analyser at the Ar partial pressure of 4×10\(^{-10}\) Pa as shown in panel (c) of this figure. It is apparent that the TPD mass spectrometer has much higher sensitivity than the residual gas analyser. The mass resolution of the TPD mass spectrometer was intentionally lowered at 1 dalton in order to obtain the high-ion transmittance through the mass filter, leading to the high sensitivity. All the back ground (~300 cps) at 47 dalton (\(^{13}\)C\(^{16}\)O\(^{18}\)O) is due to the excited neutral species passing through the quadrupole mass filter to hit the detector, which cannot be distinguished from the ion signals with the discriminator because their pulse heights from the MCP detector are similar. These mass spectra show that the vacuum of the reaction and the detection chambers are sufficiently clean as the partial pressures of the hydrocarbons are smaller than 10\(^{-11}\) Pa, plausibly supposing almost the same detection efficiencies for Ar and the hydrocarbons. All the mass peaks are accompanied with a small shoulder at their higher-mass ends due to nonstandard tuning of the TPD mass spectrometer for the high detection efficiency. This is located sufficiently far from the adjacent peak, so that no influence is given to the TPD measurements.
Figure 3. Mass spectra of residual gases and Ar leaked intentionally into the reaction chamber measured with the TPD mass spectrometer (a and b) and the residual gas analyser (c), where panel (b) shows the spectrum shown in panel (a) in the expanded scale.

Figure 4 compares the Ar\(^+\) intensity, \(I_{Ar^+}\), measured at the time constant of 0.3 s and the Ar partial pressure, \(P_{Ar}\), as a function of time with reducing the leaking rate of Ar. As shown in panel (b), they are correlated in the following equation.

\[
P_{Ar} / Pa = 5.2 \times 10^{-14} (I_{Ar^+}/cps - 1550).
\] (1)

The conversion coefficients before and after the TPD measurements in a day were within the experimental errors, but changed by <20% day by day. As shown in the expanded plots in panel (b) of figure 4, the detection limit of the TPD mass spectrometer is lower than 4×10\(^{-12}\) Pa (number density at 10\(^3\) cm\(^{-3}\)) for Ar in the reaction chamber. This high sensitivity has been achieved by the high ion-transmittance through the quadrupole mass filter and the optimization of the electron-gun filament at 4.3 A and 5 V so as to obtain the electron emission current as high as 7 mA. The electron gun operated at a higher current resulted in lower sensitivity probably due to charging up in the electron gun. The off-axis arrangement of the MCP detector was also effective for the high sensitivity by suppressing the back ground noise level originating from the excited neutral species.

Figure 4. Time propagations of (a) Ar\(^+\) intensity measured with the TPD mass spectrometer and (b) Ar partial pressure simultaneously measured with the residual gas analyser (solid circles) with reducing the Ar leaking rate into the reaction chamber. In panel (b), the Ar partial pressure calculated from the Ar\(^+\) intensity according to equation (1) (see text) is also plotted as the solid curve. The insert shows the plots in the expanded scale.

3.3. TPD measurements of CO oxidation

Figure 5 shows the TPD spectra of the \(^{13}\)C\(^{16}\)O\(^{18}\)O production catalysed on the Pt\(_{30}\) disk supported on the silicon substrate at the exposure of 0.45 L for both the reactants of \(^{16}\)O\(_2\) and \(^{13}\)C\(^{16}\)O exposed in this order, where \(T\) is the temperature of the Pt\(_{30}\) disk catalyst measured with the thermocouple. Displayed are the spectra of the single TPD run measured at the time constant of 3 s and averaged for the five
sets of the TPD data measured for the same catalyst in different days, where the averaging was made by factoring in the detection efficiency measured in a manner described in the previous subsection. The single-run signal intensities are not integer, because an analogue voltage from the counting-rate meter, which is proportional to the counting number, was measured as a signal. The back-ground level (280 cps for the spectrum shown in panel (a) of figure 5) was obtained by referring the mass spectra observed 5 minutes before each single TPD run, and this was subtracted from the single-run TPD data before averaging. In the averaging, \( T \) was smoothed in the following manner; all \( T \) measured in a range of \( T_{\text{int}} \pm 0.5 \) K were smoothed into \( T_{\text{int}} \), where \( T_{\text{int}} \) is an integer. The TPD spectrum has been successfully measured with high sensitivity and good reproducibility. Even the single-run spectrum reveals a sufficient quality at the temperature ramping rate as low as 0.3 K s\(^{-1}\), where the lower the ramping rate, the lower the counting number in a unit time.

![Figure 5. TPD spectra of the \(^{13}\text{C}^{16}\text{O}^{18}\text{O} \) production from \(^{18}\text{O}_2\) and \(^{13}\text{C}^{16}\text{O} \) catalysed on the Pt\(_{30}\) disk supported on the silicon substrate. (a) Single-run TPD spectrum and (b) averaged one. \( T \) and \( T_{\text{int}} \) are the measured and smoothed temperatures of the catalyst, respectively](image)

A sharp peak and a broad one appear at 130 K and 300 K, respectively. Considering the close-packed atomic arrangement of the Pt\(_{30}\) disk [9], it is a good starting point to compare the present results with the same reaction on the bulk Pt(111) surface having the close-packed Pt arrangement [32]. Therefore, the sharp TPD peak is assigned to the CO oxidation by the molecular O\(_2\), which is activated by electron capture in its anti-bonding molecular orbitals from the catalyst, so that the internuclear distance of O\(_2\) is elongated. On the other hand, the broader one is assigned to the catalytic action by the dissociatively adsorbed O.

4. References
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