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Trapping of V(benzene)$_2$ sandwich clusters in a n-alkanethiol self-assembled monolayer matrix

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Abstract. V(benzene)$_2$ sandwich cluster cations produced in the gas phase were size-selectively deposited onto a self-assembled monolayer of *n*-hexadecanethiols (HDT-SAM) chemisorbed on a Au(111) surface as well as onto a bare Au(111) surface. The thermal chemistry of the neutralized clusters on each substrate was studied with temperature programmed desorption (TPD). From the analyses of the threshold in the TPD, the desorption activation energies of the clusters deposited were determined to be 64.4 ± 12.8 kJ/mol for the Au(111) and 130 ± 10 kJ/mol for the HDT-SAM. The remarkably large desorption activation energy from the SAM suggests that the deposited clusters are incorporated into the SAM matrix and firmly trapped inside the alkyl chains of the SAM.

PACS. 36.40.Qv Stability and fragmentation of clusters

1 Introduction

Soft-landing of nanometer-scale ionic compounds such as nanoclusters, nanoparticles and proteins, onto modified solid surfaces is one of the most effective ways to fine-tune the production of unique nanoscale functional materials, e.g., nanocatalysts [1–5], nanomagnetics [6,7], and biological microarrays [8]. In particular, one-dimensional (1D), multi-decker organometallic sandwich clusters are regarded as attractive candidates for use as building blocks for nanoscale functional materials, because these 1D clusters exhibit unique electronic and magnetic properties in the gas phase [9].

Examples of experiments studying the adsorption of sandwich complexes on surfaces include the thermal deposition of organometallic 1D complexes, such as metal-cyclopentadienyl complex [10] and the chromium-benzene complex, Cr(benzene)$_2$ [11], on bare metal surfaces, which have been studied with temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS). These studies have revealed that surface-adsorbate interactions accompany the decomposition of these stable complexes on the metal surface. Hence, it is necessary to deposit some chemically inert spacers and/or buffer matrices on these metal surfaces to reduce the interaction between the adsorbates and the metal surface, and to trap the adsorbates without any decomposition.

The discovery of self-assembled monolayers (SAMs) formed by organosulfur compounds on metal surfaces, such as a gold surface, has opened up the possibility of using these to construct an organic monolayer spacer on the surfaces. Indeed, the effective trapping of atoms, molecular ions and molecules in the SAM matrix has been reported for species in the gas phase [12–14] and in solutions [15–17]. Thus, an intriguing opportunity exists to soft-land the organometallic complexes onto the SAM matrix and to evaluate their thermal stabilities. In this paper, we report on a TPD study of the thermal chemistry of V(benzene)$_2$ sandwich clusters soft-landed onto an *n*-hexadecanethiol SAM (HDT-SAM) and onto a Au(111) surface. Recently, Judai et al. have non-dissociatively deposited V(benzene)$_2$ sandwich cluster cations produced in the gas phase into a low-temperature Ar-matrix, and have confirmed by infrared spectroscopy that the neutralized clusters retains the sandwich structure [18].

2 Experimental section

The details of the soft-landing apparatus have been described elsewhere [18]. Briefly, it consists of a cluster source, a mass selection stage, and a deposition chamber where the TPD and infrared reflection absorption

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spectroscopy (IRAS) experiments are performed. Vanadium (V)-benzene sandwich clusters were produced in the expansion from a piezo-driven pulsed valve under the He stagnation pressure of 2−5 atm by the reaction between laser-vaporized vanadium and benzene vapors. The clusters thus produced were guided by a series of ion optics i.e. octapole ion guides, a quadrupole deflector, and electrostatic lens. The cluster cations were separated from the neutrals and anions by the quadrupole deflector, and size-selected by a quadrupole spectrometer (4−4000 amu, Extrel); subsequently the clusters were deposited onto substrates with 20 ± 10 eV collision energy under ultra-high vacuum (UHV) conditions ($\sim 2 \times 10^{-10}$ Torr). The substrates were cooled down to 180 K by a liquid nitrogen cryostat, and the total amount of the deposited cluster ions was obtained by integrating the ion current at the substrate during the deposition time.

The TPD experiments were carried out by placing a sample substrate at ∼1 mm in front of another quadrupole mass spectrometer (4−4000 amu, Extrel) equipped with an electron impact ionizer and an entrance restricted by a skimmer (with entrance and exit diameters of 6 mm and 20 mm). By heating the sample substrate linearly with a rate of ∼1 K/s, the desorbed species were detected by the mass spectrometer.

A commercially available gold substrate, Au(111)/Ti/Silica (Auro Sheet, Tanaka Precious Metal), was used for the Au(111) surfaces (100 nm thickness) where the typical dimension of a terrace was about 50×50 nm^2. To remove organic contaminants from the Au(111) substrate, the substrate was immersed into a piranha solution (H_2SO_4:H_2O_2 = 3:1) [19]. The substrate, covered with an *n*-hexadecanethiol ($CH_3(CH_2)_{15}SH$) SAM (HDT-SAM), was prepared by immersing the gold substrates into ethanol solutions of 2 mM HDT at room temperature for 1−2 days. The prepared HDT-SAM substrate was immediately transferred into the deposition chamber and annealed up to ∼60 °C under the UHV condition. The formation of HDT-SAMs was confirmed by IRAS [20] and by cyclic voltammetry (CV).

3 Results and discussion

Figure 1 shows typical TPD spectra for the V(benzene)$_2$ clusters on Au(111) and HDT-SAM substrates that were prepared by the size-selective deposition of 4.0×10^{13} cations of the V(benzene)$_2$ clusters onto Au(111) and HDT-SAM substrates at a collision energy of ∼20 eV. In this study, the total amounts of the deposited clusters were set to provide a relatively low coverage (θ), $\theta \approx 0.2$, to make the level of collisions and interactions between deposited clusters themselves on the substrate negligible. The desorbed species were detected to be mainly three kinds of ions: V(benzene)$_2^+$ ($m/z = 207$), V(benzene)$^+$ ($m/z = 129$), and benzene$^+$ ($m/z = 78$). The TPD spectra for all three ions exhibit an identical appearance and peak shape. Thus, the V(benzene)$^+$ and benzene$^+$ ions are due not to fragments produced on adsorption, but to fragmentation of the parent V(benzene)$_2$ clusters in the mass spectrometer ionizer. Indeed, it has been reported that the electron impact ionization of a similar compound, Cr(benzene)$_2$, produces almost identical fragmentations in the gas phase [21]. From the results of the TPD experiments, it is evident, especially for the HDT-SAM, that a large of number of the V(benzene)$_2$ clusters are adsorbed on the substrates without decomposition. When the deposition efficiencies of Au(111) and HDT-SAM are compared with respect to the amount of V(benzene)$_2$ clusters that desorb, the SAM matrix, like an Ar matrix [17], behaves as a several times more efficient buffer to reduce the decomposition of incoming clusters. In the case of Au(111), therefore, the actual coverage of the deposited clusters might be much less than 0.2.

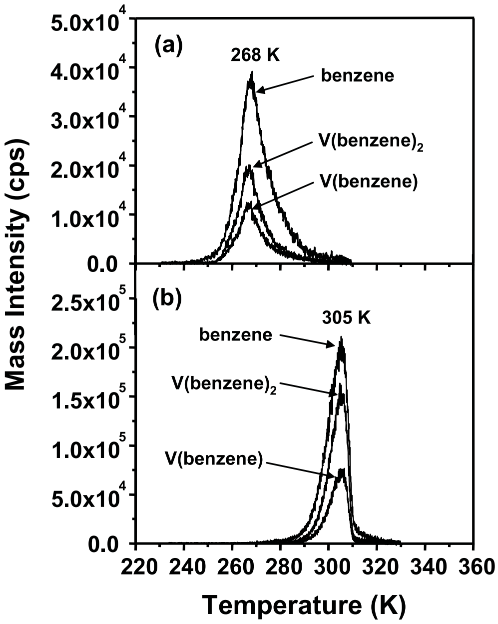

Fig. 1. TPD spectra from (a) Au(111) and (b) HDT-SAM after the deposition of 4×10^{13} V(benzene)$_2$ ions at 180 K.

As shown in Figure 1a, the desorption of the V(benzene)$_2$ clusters from the Au(111) substrate starts at ∼250 K (i.e. a threshold desorption temperature) and the desorption rate reaches a maximum at 268 K. The TPD curves of Figure 1a display a nearly symmetric shape, in which the ion intensity slowly decreases after the peak maximum. The reaction order of the desorption can be evaluated by the TPD profile [22], and the symmetric profile suggests that the desorption of the deposited clusters from Au(111) is a second-order process. In the case of the HDT-SAM, on the other hand, the threshold desorption temperature, the peak maximum temperature and the shape of the TPD curves are much different from those of Au(111), as shown in Figure 1b. The threshold desorption temperature on the HDT-SAM substrate is ∼30 K higher than that on Au(111), a difference suggesting that the deposited clusters are more strongly trapped on the HDT-SAM substrate than on the Au(111). Furthermore, in contrast to the case of the Au(111), the TPD curve shape for the HDT-SAM exhibits a rapid decrease after the peak maximum at 305 K. This shape is typically

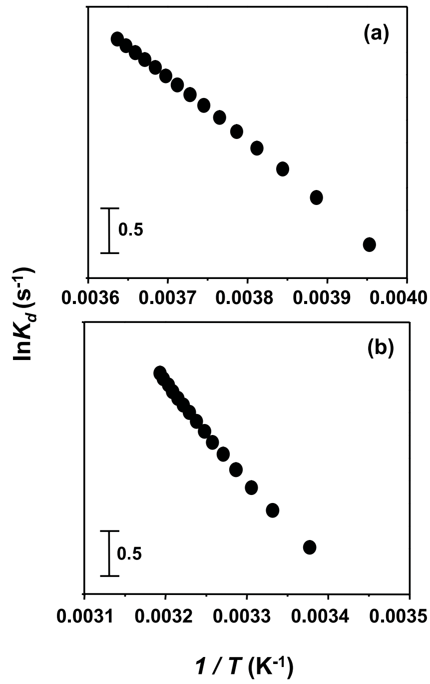

Fig. 2. Arrhenius plots for TTPD of V(benzene)$_2$ from (a) Au(111) and (b) HDT-SAM. The calculation was performed for decreases from 1% to 15% of the initial coverage.

characteristic of a first-order (or direct) desorption reaction [22]. The difference in the desorption reaction order further suggests that the adsorption states of V(benzene)$_2$ clusters deposited on the HDT-SAM matrix are very different from those on Au(111).

To examine the stronger trapping of the clusters by the SAM, the activation energies for the desorption of the clusters from the HDT-SAM and Au(111) substrates were evaluated through analyses of the TPD spectra. On solid surfaces, the desorption rate equation (Polanyi-Wigner equation) of adsorbates is given by

$$-\frac{d\theta}{dt} = \nu_d \theta^n \exp\left(-E_d/RT\right) = k_d \theta^n, \qquad (1)$$

where ν_d is the pre-exponential factor, θ is the coverage, n is the reaction order, and E_d is the activation energy for the desorption [23]. In this study, a threshold TPD (TTPD) analysis [24] was employed to determine the activation energy of the deposited clusters at low coverage ($\theta \approx 0.2$). Typical Arrhenius plots of the TTPD analyses are presented in Figure 2.

The activation energy of the clusters on Au(111), 64.4 ± 12.8 kJ/mol, was obtained from the linear Arrhenius plot in the TTPD analysis of equation (1) with $n = 2$. This activation energy is comparable to the adsorption energy of benzene molecules on Au(111), a value which has been reported to be 57.9 kJ/mol [25]. Since the benzene molecules themselves are adsorbed on Au(111) at a submonolayer coverage via a "flat-lying" geometry [26], where the benzene ring is parallel to the surface plane, the deposited V(benzene)$_2$ clusters ($\theta < 0.2$) might also favor a "flat-lying" geometry on Au(111).

Table 1. Desorption temperatures and activation energies of V(benzene)$_2$ adsorbed on bare and SAM-terminated Au(111) substrates.

Substrates	Desorption temperature (K)		Activation energy
	Threshold	Peak maximum	(kJ/mol)
Au(111)	248	268	64.4 ± 12.8
HDT-SAM	278	305	130 ± 10

From the linear Arrhenius plots using equation (1) with $n = 1$, the desorption activation energy of the clusters from the HDT-SAM matrix was determined to be 130 ± 10 kJ/mol, a value which, we note, is comparable to the typical adsorption heat of chemisorptions (i.e. ~1 eV). The activation energies determined are summarized in Table 1, together with the temperatures for threshold desorptions and the peak maximum.

In general, adsorbates on solid metal surfaces behave like two-dimensional gases, except at extremely low temperatures, because the potential barriers to translational migrations on metal surfaces are usually small enough to permit diffusion of adsorbates [27]. Thus, the V(benzene)$_2$ clusters most likely diffuse on the Au(111) with increasing surface temperature, and the encounter collisions of the clusters lead to the second order desorption of the clusters from the surface. In the case of the HDT-SAM, both the threshold desorption temperature and the activation energy for desorption rise remarkably in comparison with those of the Au(111). Furthermore, the shape of the TPD curve strongly indicates that the V(benzene)$_2$ clusters were desorbed directly from the SAM without encounter collisions (i.e. in a first order desorption reaction). The most plausible explanation is that the V(benzene)$_2$ clusters (whose size is ~5 Å [28]) are incorporated into the thick HDT-SAM matrix, where the C$_{16}$-SAM thickness has been estimated to be ~20 Å, assuming that the molecular chains are tilted 30° against the normal direction [19]. There, they are firmly trapped among the spaces between the alkyl chains of the hexadecanethiols. Such a penetration seems plausible, because the projectile cluster cations are deposited onto the surface with a collision energy of ~20 eV. The penetration would probably inhibit the free two-dimensional diffusion of the clusters in the SAM matrix, resulting in their direct desorption from the matrix without encounter collisions. Indeed, similar penetrative trappings of atoms, ions and molecules in a SAM matrix have been reported for species in the gas phase [12–14] and in solutions [15–17].

For the HDT-SAM, the desorption process of the clusters could be represented by a cluster diffusion inside the SAM matrix toward the very top of the SAM surface. Assuming that the clusters penetrate into the SAM matrix homogeneously, the diffusion flux J of the clusters is given by Fick's first law:

$$J = \frac{d\theta}{dt} = -D\frac{dC}{dx} \qquad (2)$$

where D is the diffusion coefficient and $\partial C/\partial x$ is the concentration gradient in the direction of the surface normal.

Here, the concentration gradient is assumed to be proportional to the coverage of clusters, $\partial C/\partial x = A\theta$. In addition, the diffusion coefficient is given by an Arrhenius equation as follows,

$$-\frac{d\theta}{dt} = \nu_D \theta \exp\left(-E_D/RT\right) = k_D \theta, \qquad (3)$$

where ν_D comprises the pre-exponential factor of the Arrhenius equation and the proportionality constant of coverage A, and E_D is the activation energy of diffusion. Equation (3) is identical to the first-order desorption rate equation given by equation (1) with $n = 1$. Consequently, the desorption activation energy E_d of the clusters trapped in the SAM matrix corresponds to the diffusion activation energy E_D in the matrix.

Nuzzo and co-workers have suggested that the dense packing of the headgroups (i.e. the methyl groups) of the HDT-SAM [20] could provide steric screening effects; only a portion of the functional group is accessible to molecules in a contacting phase [29]. If the V(benzene)$_2$ clusters were assumed to contact the "methyl surface" of the HDT-SAM, however, the activation energy should be rather small (less than 100 kJ/mol [29]) because of weak van der Waals interactions between the methyl surface and the clusters, Specifically, the large activation energy in this study indicates that the V(benzene)$_2$ clusters are strongly trapped by the SAM matrix. As mentioned above, the projectile cluster ions are deposited onto the surface with a collision energy of $\sim$20 eV. Thus, the projectiles could deeply penetrate into the SAM matrix, presumably accompanied by the structural disordering of the SAM chains. Indeed, a strong trapping of molecular ions that have penetrated into the fluorinated SAMs has been achieved using 5−20 eV collision energies [12,13]. Using IRAS, furthermore, we have found that the vibrational spectra of the V(benzene)$_2$ clusters in the HDT-SAM matrix show a characteristic orientational preference [30], in which the molecular axis of V(benzene)$_2$ is tilted to 70−80°. away from the normal direction. The orientational preference indicates that the V(benzene)$_2$ is inserted between the alkyl chains of the SAM. Thus, it is evident that the V(benzene)$_2$ clusters are strongly trapped in the SAM matrix by their penetration into the SAM. We expect that the thickness of a SAM (i.e. the chain length of n-alkanethiols) is an important determinant to increase the desorption activation energy and the number of trapped clusters. Experiments are currently underway to reveal the chain length effect on the desorption activation energy of the deposited clusters [31].

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