

論文の内容の要旨

論文題目 : Adsorbed cyclohexane on Rh(111): two-dimensional superstructure, energy level alignment, and kinetic and geometric isotope effects

(Rh(111)表面に吸着したシクロヘキサン : 二次元超構造、エネルギーレベルアラインメント、および速度論的、幾何学的同位体効果)

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Introduction

Activation of C-H bonds of adsorbed alkanes through interaction with metal surfaces is a key process of dehydrogenation on heterogeneous catalysts. Although alkane molecules are chemically inert in nature, there is an electronic interaction between C-H σ^* orbitals of adsorbed alkanes and metal d-states (C-H \cdots metal interaction) [1]. This interaction causes the softening of C-H bonds of adsorbed alkanes, which is evidenced by the significant red-shift of the C-H stretching vibrational mode (soft mode) [2]. I reported that the soft mode of cyclohexane adsorbed on the Rh(111) surface consists of multiple peaks that are broadened with increasing temperature (Figs. 1(a)-(d)) [3]. The observed broadening can be explained by the dephasing due to anharmonic coupling between the soft mode and thermally excited frustrated modes. On the other hand, the soft mode disappears completely on the hydrogen-saturated Rh(111) surface, indicating drastic weakening of the cyclohexane-substrate interaction by preadsorption of hydrogen (Fig. 1(e)).

In this thesis, I investigated interactions and two-dimensional (2D) superstructures of cyclohexane on the clean and hydrogen-preadsorbed Rh(111) surfaces using several experimental techniques to obtain further insight into the nature of the C-H \cdots metal interaction, and the role of preadsorbed hydrogen.

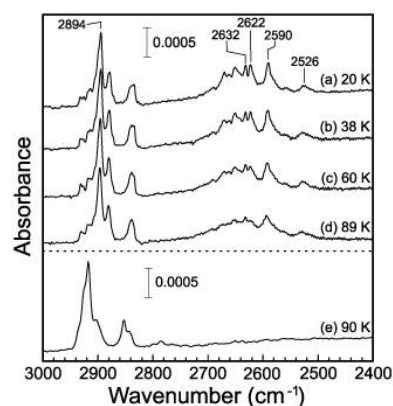


FIG. 1. (a) - (d) IRAS spectra of cyclohexane on Rh(111) as a function of temperature. (e) An IRAS spectrum of cyclohexane on H-saturated Rh(111) at 90 K.

Results and Discussion

A. 2D superstructures and energy level alignment of cyclohexane on Rh(111)

Fig. 2(a) shows an STM image of cyclohexane adsorbed on the clean Rh(111) surface at cyclohexane coverage (θ) below 0.7 ML (1 ML = 0.17 molecules/surface Rh atom). Adsorbed molecules form an ordered structure due to an attractive intermolecular interaction. In addition, molecular images show a periodic change in apparent height and shape (moiré structure). Fig. 2(b) shows a line profile of the apparent height along the line in Fig. 2(a). The corrugation amplitude (height difference between the highest and lowest molecules) is about 0.2 Å. The observed superstructure can be assigned to a higher-order commensurate (HOC) $(2\sqrt{79} \times 2\sqrt{79})R17.0^\circ$ structure. The intermolecular distance (d_m) of this superstructure is 6.83 Å. The variation in the apparent height results from the intermolecular difference in the adsorption distance. Thus, the multiple peaks of the soft mode originate from the variation in the adsorption distance. At $\theta \geq 0.7$ ML, the structural phase transition from the moiré structure to a densely packed structure (Fig. 3) was observed. The dense cyclohexane layer shown in Fig. 3(a) is an HOC $(2\sqrt{13} \times 2\sqrt{13})R139^\circ$ superstructure ($d_m = 6.47$ Å). A line profile (Fig. 3(b)) shows periodic distribution of lower protrusions (denoted by “O”) which are assigned to molecules adsorbed on the on-top site.

An STM image of adsorbed cyclohexane on the hydrogen-saturated Rh(111) surface is shown in Fig. 4(a). There is no clear difference in the apparent height and the shape of each molecular image of adsorbed cyclohexane. In a line profile shown in Fig. 4(b), the variation in apparent height is less than 0.05 Å, much smaller than those observed in the cyclohexane layers on the clean surface (Figs. 2 and 3). The cyclohexane overlayer on the hydrogen-saturated surface is incommensurate with respect to the substrate, and the value of d_m was estimated to be 6.44 Å from LEED measurements. The results indicate that the adsorption state of cyclohexane on the hydrogen-saturated surface is insensitive to the adsorption site.

A C 1s XPS spectrum of 1 ML cyclohexane [$(2\sqrt{13} \times 2\sqrt{13})R139^\circ$ structure] on the clean Rh(111) surface is shown in Fig. 5(a). On the clean Rh(111) surface, there are two C 1s components (284.04 eV and 283.69 eV). The peak at 283.69 eV is assigned to molecules on the on-top site. The intermolecular difference in the C 1s binding energy results from the site-specific energy level alignment of cyclohexane. The energy level alignment of cyclohexane on the

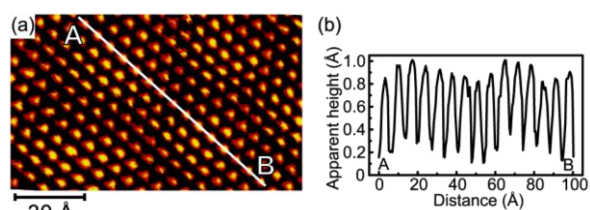


FIG 2. (a) An STM image of cyclohexane on the Rh(111) surface at $\theta \leq 0.7$ ML ($V_s = 0.31$ V, $I_t = 0.13$ nA, $T_s = 86$ K). (b) A line profile along the line in (a).

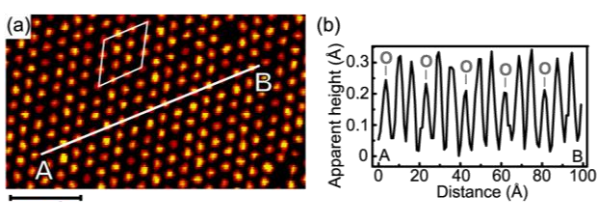


FIG 3. (a) An STM image of cyclohexane on the Rh(111) surface at $\theta \geq 0.7$ ML ($V_s = 0.53$ V, $I_t = 0.19$ nA, $T_s = 95$ K). (b) A line profile along the line in (a).

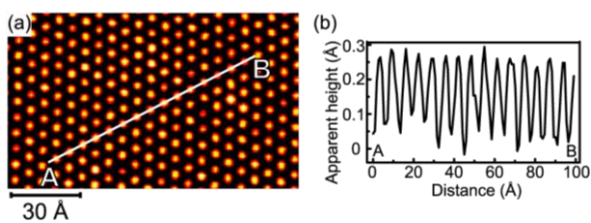


FIG 4. (a) An STM image of cyclohexane on the H-saturated Rh(111) surface ($V_s = 0.63$ V, $I_t = 0.09$ nA, $T_s = 97$ K). (b) A line profile along the line in (a).

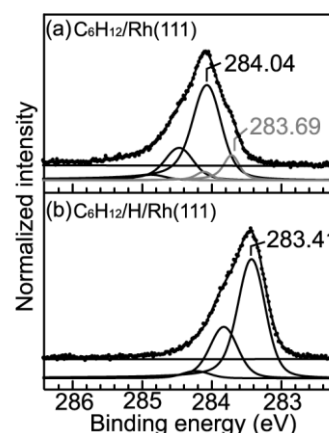


FIG 5. C 1s spectra of monolayer cyclohexane on (a) clean and (b) H-saturated Rh(111) surfaces ($h\nu = 380$ eV, $T_s = 90$ K).

Rh(111) surfaces is determined by the vacuum level (VL) shift and the final-state screening effects; both factors depend on the adsorption distance.

A C 1s spectrum of cyclohexane on the hydrogen-saturated Rh(111) surface (Fig. 5(b)) shows a significant peak shift to the lower binding energy by 0.6 eV compared to the main peak on the clean Rh(111) surface. This is a consequence of the longer cyclohexane-surface distance due to the Pauli repulsion between cyclohexane and preadsorbed hydrogen, which leads to the smaller VL shift and the insufficient screening on the hydrogen-saturated surface as schematically illustrated in Fig. 6.

B. Kinetic and geometric isotope effects in molecular adsorption of cyclohexane on Rh(111)

Fig. 7 shows the desorption energy of cyclohexane on the clean Rh(111) surface obtained from TPD measurements at $\theta < 0.7$ ML. The desorption energies of C_6D_{12} are smaller than those of C_6H_{12} , which is opposite to the normal kinetic isotope effect (inverse kinetic isotope effect).

Fig. 8 shows the work function change as a function of cyclohexane coverage on the clean Rh(111) surface measured by UPS. The work function change by adsorption of C_6D_{12} molecules is smaller than that by C_6H_{12} adsorption at any cyclohexane coverage. This indicates that the C_6D_{12} molecules are slightly more distant from the surface than the C_6H_{12} molecules because the work function change is mainly controlled by the adsorption distance [1].

Fig. 9 illustrates adsorption potential energy curves that are derived from the observed results of TPD and UPS at $\theta = 0.3$ ML. The adsorption potential is different between C_6H_{12} and C_6D_{12} . Note that no isotope effect was observed on the hydrogen-saturated Rh(111) surface where the C-H...metal interaction is drastically weakened. This indicates that the C-H...metal interaction plays a key role in the observed isotope effects. Based on the similarity between the C-H...metal interaction and the typical hydrogen bond, the origin of the isotopic difference in the adsorption potential should be attributed to the quantum nature of hydrogen in the C-H...metal bond.

The isotope effects on the cyclohexane-substrate interaction also influence the 2D superstructures. Fig. 10 shows LEED patterns of C_6H_{12} and C_6D_{12} adsorbed on the clean Rh(111) surface ($\theta = 0.3$ ML). The diffraction patterns are clearly different between two isotopes. The d_m in the C_6D_{12} superstructure (6.73 Å) is smaller than that in the C_6H_{12} superstructure (6.83 Å). This is a lateral geometric isotope effect (GIE) in

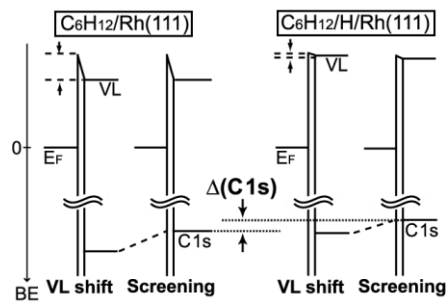


FIG. 6. Schematic illustrations of the effects of the vacuum level (VL) shift and the final-state screening on the energy level alignment of cyclohexane.

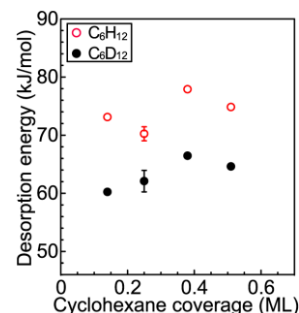


FIG. 7. Cyclohexane desorption energy as a function of coverage obtained from TPD measurements.

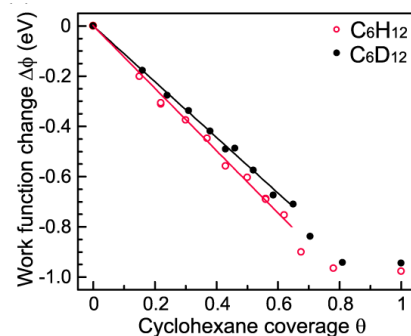


FIG. 8. Work function change by cyclohexane adsorption as a function of cyclohexane coverage measured by UPS at 90 K.

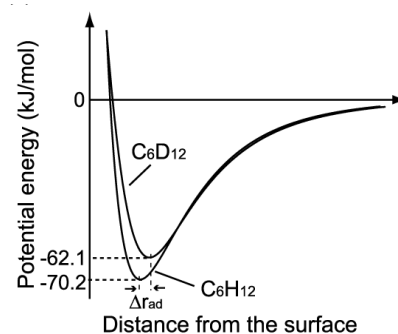


FIG. 9. Schematic adsorption potentials of C_6H_{12} and C_6D_{12} ($\theta = 0.3$ ML).

the superstructure of adsorbed cyclohexane observed at $\theta \leq 0.7$ ML.

The intermolecular distance in cyclohexane superstructure is determined by the balance between the attractive van der Waals interaction and the repulsive interaction between the interfacial dipoles. The lateral GIE in the cyclohexane superstructure can be attributed to the isotopic difference in the repulsion between the interfacial dipoles. The interfacial dipole by C_6D_{12} adsorption is smaller than that by C_6H_{12} adsorption, which is evidenced by the smaller work function change by C_6D_{12} adsorption. Thus, the repulsive interaction between interfacial dipoles is weaker for C_6D_{12} than C_6H_{12} . As a result, C_6D_{12} molecules can be more densely packed in the 2D superstructure.

Conclusions

The higher-order commensurate superstructures of adsorbed cyclohexane on the clean Rh(111) surface are controlled by the delicate balance between adsorbate-adsorbate and adsorbate-substrate interactions. There is a variation in the adsorption distance which is responsible for the multiple peaks of the soft mode, and the site-specific energy level alignment of adsorbed cyclohexane. The preadsorption of hydrogen atoms weakens the cyclohexane-substrate interaction. This affects both the superstructure and the energy level alignment of cyclohexane.

Cyclohexane adsorbed on the clean Rh(111) surface shows the “inverse kinetic” and “geometric” isotope effects in the adsorption energy and the 2D superstructure. These isotope effects originate from the quantum nature of hydrogen in the C-H...metal interaction as in the case of the typical hydrogen bond.

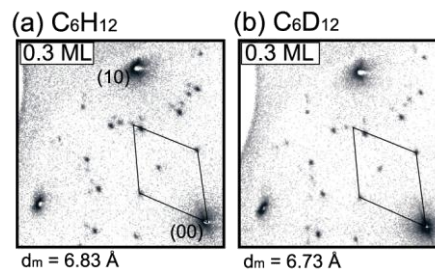


FIG. 10. LEED patterns of (a) C_6H_{12} and (b) C_6D_{12} on the clean Rh(111) surface at 90 K.

[References]

- [1] Y. Morikawa et al., Phys. Rev. B 69, 041403 (2004).
- [2] J. E. Demuth et al., Phys. Rev. Lett. 40, 1044 (1978).
- [3] T. Koitaya et al., Phys. Rev. B 80, 193409 (2009).