

Isotope effects on thermal dehydrogenation of cyclohexane on Rh(111)

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1 Introduction

Activation of C-H bonds of saturated hydrocarbons by metals is a key step in conversion to more valuable functionalized molecules as well as in dehydrogenation to produce hydrogen [1]. In the case of cyclohexane adsorbed on metal surfaces, softened C-H stretching modes have been observed between 2400 and 2800 cm^{-1} [2-4]. The significant red-shift is a consequence of the electronic interaction between unoccupied C-H orbitals and occupied metal states (C-H \cdots M interaction) [5, 6]. The C-H \cdots M interaction is similar to the typical hydrogen bond. It has been revealed that the hydrogen bond shows an isotope effect; the A-D \cdots B bond is weaker than the A-H \cdots B bond due to the quantum nature of hydrogen [7]. Hence, we expect that adsorbed cyclohexane on the Rh(111) surface exhibits a similar isotope effect, which affects reactivity of cyclohexane. In this study, the isotope effect on thermal dehydrogenation of cyclohexane on the Rh(111) surface was investigated by high-resolution X-ray photoelectron spectroscopy (HR-XPS).

2 Experiment

The HR-XPS measurements were carried out at the soft X-ray undulator beam line 13A. The base pressure of the chamber was $<1 \times 10^{-8}$ Pa. HR-XPS spectra were obtained using a hemispherical electron analyzer (SPECS, phoibos 100) with photon energy of 410 eV at a normal emission angle. After cleaning of the Rh(111) surface by several sputtering-annealing cycles, the cyclohexane monolayer was prepared by exposure of an excess amount of cyclohexane molecules on the surface at 150 K, followed by the measurement at 90 K. Then, the sample was heated to 240 K at which all adsorbed molecules were desorbed or dehydrogenated.

3 Results and Discussion

Figure 1 shows C 1s spectra of monolayer cyclohexane, and residual species after heating to 240 K. The desorption and the dehydrogenation are competing processes. The main path was intact desorption. There is an isotopic difference in the reactivity of cyclohexane; a 10.6% of monolayer C_6H_{12} molecules are dehydrogenated by heating, whereas only 5.9% of C_6D_{12} go on the dehydrogenation path. In addition, stability of reaction products is also different between C_6H_{12} and C_6D_{12} . The spectra of the thermal reaction products are clearly different between two isotopes; the C 1s spectrum of the reaction products of C_6H_{12} consists of at least two components between 284 – 283.2 eV, whereas that of C_6D_{12} has a single peak at 283.9 eV. The observed peak of C_6D_{12} can be assigned to benzene. Thus, all reacted

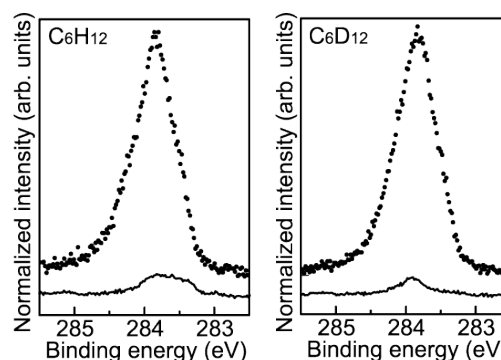


Fig. 1. C 1s photoelectron spectra ($h\nu = 410$ eV) of adsorbed cyclohexane at monolayer coverage (dots), and reaction products after heating to 240 K (solid lines).

C_6D_{12} molecules are dehydrogenated to C_6D_6 at 240 K. In the case of C_6H_{12} , the other components at lower binding energy (Fig. 1; left) are tentatively attributed to the π -allyl C_6H_9 based on results of vibrational spectroscopy [8]. Hence, the C_6H_6 and π -allyl species can coexist at 240 K.

The isotope effect in the reactivity of cyclohexane on the Rh(111) surface is caused by the weaker C-D \cdots M interaction compared to the C-H \cdots M interaction. The weaker C-D \cdots M interaction leads to faster desorption and slower dehydrogenation of C_6D_{12} . This affects the branching ratio between desorption and dehydrogenation processes. Based on the similarity to the typical hydrogen bond, we attribute the origin of the isotope effects to the quantum nature of hydrogen in the C-H \cdots M interaction [8].

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