In-Situ Observation of π-Allyl *c*-C$_6$H$_9$ Intermediate during High-Pressure Cyclohexene Catalytic Reactions on Pt(111) Using Sum Frequency Generation Vibrational Spectroscopy

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Surface vibrational sum frequency generation (SFG) has been used to identify surface species in situ during catalytic reactions of 1.5 Torr cyclohexene (C$_6$H$_{10}$) in the presence and absence of 15 Torr H$_2$ on Pt(111) crystal surfaces. Various surface species were observed during the reactions in the range 303−483 K. Upon adsorption at 303 K in the absence of H$_2$, cyclohexene is dehydrogenated to form 1,4-cyclohexadiene (C$_6$H$_8$). At 323 K, this species converts to π-allyl *c*-C$_6$H$_9$ intermediate. At temperature higher than 423 K, benzene coexists with C$_6$H$_9$ on the surface. Similar results were obtained in the presence of 15 Torr H$_2$ except that in this circumstance 1,3-cyclohexadiene coexists with 1,4- cyclohexadiene at 303 K, and with C$_6$H$_9$ at temperature higher than 403 K. This study reports, for the first time, the existence of π-allyl *c*-C$_6$H$_9$ as a major surface species in the presence of high-pressure cyclohexene and H$_2$ on Pt(111). In addition, adsorbed 1,3-cyclohexadiene has been observed as a reactive intermediate in the process of dehydrogenation to benzene. Finally, it has been found that excess hydrogen increases the disordering and decreases the surface coverage of the C$_6$H$_9$ on the surface.

1. Introduction

Identifying reactive surface intermediates is a central issue for understanding mechanisms of hydrocarbon catalytic reforming on metal surfaces. Despite its importance, monitoring surface species during the reactions, which are usually performed under ambient pressure, has been a difficult task to perform. This is mainly due to lack of experimental techniques that have sufficient surface sensitivity to overcome contributions from gas-phase species to the experimental observations.

Surface analytical vibrational techniques, such as high-resolution electron energy loss spectroscopy (HREELS) and reflection−absorption infrared spectroscopy (RAIRS), require ultrahigh vacuum (UHV) or low-pressure ($<10^{-6}$ Torr) environments to operate. Under UHV, only strongly bound species can exist on a surface while weakly bound ones, which may be key reaction intermediates under ambient conditions, desorb quickly. Therefore, the surface species observed under UHV or low-pressure environments are not necessarily the same as those present during the reactions under ambient conditions. Sum frequency generation (SFG), a nonlinear optical spectroscopy, has sufficient surface sensitivity to monitor surface species during the catalytic reactions in high-pressure environments.[1−4] In SFG experiments, a visible and a tunable infrared beam are spatially and temporally overlapped on a surface. As the infrared beam is scanned over the frequency range of interest, vibrational spectra of molecules present on the surface are obtained via a second-order nonlinear optical process.[5,6]

Catalytic reactions of cyclohexene (C$_6$H$_{10}$) on Pt(111) have been considered prototypical for cyclic hydrocarbon conversion, which is important in naphtha reforming processes.[7] Cyclohexene (C$_6$H$_{10}$) on Pt(111) is not only one of the possible intermediates in the multiple steps of cyclohexane (C$_6$H$_{12}$)

dehydrogenation to benzene (C$_6$H$_6$), but also a reactant molecule to be hydrogenated to cyclohexane in the presence of excess hydrogen. Despite the large amount of research on the hydrogenation/dehydrogenation reactions of cyclohexene on Pt(111), there are still unsolved questions concerning the definite identification of the surface intermediates and their surface chemistry in the reactions.

Cyclohexene adsorption on Pt(111) at low pressures ($<10^{-6}$ Torr) has been studied using various surface analytical techniques, such as thermal desorption spectroscopy (TDS),[8] bismuth postdosing TDS (BPTDS),[8,9] laser-induced thermal desorption (LITD),[10] HREELS,[10,11] and RAIRS.[12] Briefly, cyclohexene exists in a di-σ form on Pt(111) at 100 K. It converts to π-allyl *c*-C$_6$H$_9$ at about 200 K.[9,12] At about 300 K, π-allyl *c*-C$_6$H$_9$ converts to benzene. Further heating induces desorption and decomposition of benzene.[9,10,12] These surface species that are present at low pressures, however, may not be directly related to those present at high pressures/temperatures and in the presence of excess hydrogen, which are the conditions in most chemical and petrochemical processes.

In this study, we utilized the SFG technique to identify the surface intermediates during high-pressure (1.5 Torr) cyclohexene catalytic reactions on Pt(111). The SFG process is only allowed in a medium without centrosymmetry under the electric dipole approximation.[5,13] Platinum bulk is centrosymmetric, and its contribution to SFG is usually negligible. Isotropic gases in the reaction cell do not generate SFG. Only the metal surface and the adsorbates on the surface can generate SFG under the electric dipole approximation. We monitored the surface species in real-time during the reactions at various temperatures in the range 303−483 K. We also investigated the effects of excess hydrogen on the surface species by performing the reactions with and without high-pressure H$_2$ (15 Torr). The importance of studying the effects of hydrogen on the reactions arises from the fact that most of the cyclohexene conversion processes are

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carried out in the presence of high-pressure H$_2$. Extensive studies have shown that hydrogen pressure is an important parameter to determine the conversion rate and selectivity in many catalytic reactions.[7,14] Nevertheless, it is not well-known at the molecular level how excess hydrogen affects the adsorption structure and chemical activity of surface intermediates. This is mainly due to lack of techniques to monitor surface species during the reactions at high pressures of hydrocarbons and hydrogen.

We report, for the first time, the existence of π-allyl c-C$_6$H$_9$ as a main surface species in the presence of high-pressure cyclohexene and H$_2$ on the Pt(111) crystal surface. In addition, 1,3-cyclohexadiene, which was not found under low-pressure conditions, has been observed as a reactive intermediate in the process of dehydrogenation to benzene. The determination of adsorbed 1,3-cyclohexadiene over 403 K exemplifies the differences in the types of surface species that are present under low-pressure (<10^{-6} Torr) and high-pressure conditions. Finally, our SFG results will show that excess hydrogen increases the disordering and desorption rate of π-allyl c-C$_6$H$_9$. Excess hydrogen also induces the temperature-dependent orientational change of the surface species.

2. Experimental Section

All experiments were carried out on a Pt(111) single-crystal surface in a high-pressure/ultrahigh-vacuum (HP/UHV) system. The HP/UHV system is composed of a UHV chamber with a base pressure of 4×10^{-10} Torr and a high-pressure (HP) cell. The HP cell, where high-pressure catalysis studies were carried out, was connected to the UHV chamber through a gate valve. Two CaF$_2$ windows on the HP cell allowed input and output of both infrared and visible beams for SFG experiments. The Pt-(111) crystal was cleaned by sputtering with Ar$^+$ ions (1 keV), heating it at 1100 K in the presence of 5×10^{-7} Torr O$_2$ for 2 min, and then annealing it at 1100 K in UHV for 2 min. After a few cycles of cleaning, the Pt(111) crystal was transferred to the HP cell for SFG measurements. The Pt(111) surface was routinely checked by Auger electron spectroscopy (AES) for contamination.

For SFG experiments, a mode-locked 20 ps, 20 Hz Nd:YAG laser with a 25 mJ/pulse energy output at 1064 nm was used to generate a tunable infrared (1300−3150 cm^{-1}) and a visible beam at 532 nm. The visible (200 μJ/pulse) and the infrared (100 μJ/pulse) beams were spatially and temporally overlapped on the Pt(111) surface with incident angles of 55° and 60°, respectively, with respect to surface normal. Both the infrared and visible beams were p-polarized. As the infrared beam is scanned over the frequency range of interest, the sum frequency output from the Pt(111) crystal was collected by a photomultiplier and a gated integrator. The sum frequency output was then normalized by the intensity of the incident infrared beam on the surface. This is necessary because gas molecules in the HP cell absorb some portion of the incident infrared beam, to which sum frequency output is linearly proportional. Detailed descriptions on the HP/UHV system and SFG measurement can be found elsewhere.[15]

Cyclohexene (C$_6$H$_{10}$, 99.5%, Aldrich) was purified by freeze−pump−thaw treatment before being introduced in the HP cell. The reactant pressure was 1.5 Torr cyclohexene, or 1.5 Torr cyclohexene and 15 Torr hydrogen. In the latter case, hydrogen was always introduced first, followed by cyclohexene. Note that mixing the two gases before introduction produced the same results in our SFG experiments.
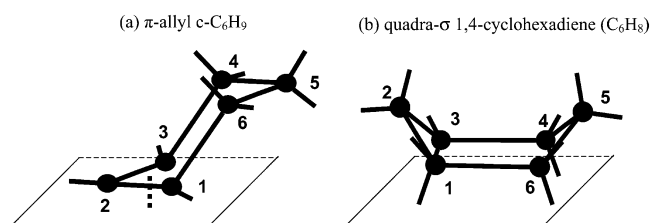

Figure 1. Schematic diagram of (a) π-allyl c-C$_6$H$_9$ and (b) quadra-σ 1,4-cyclohexadiene (C$_6$H$_8$) intermediates.

3. Results

For our SFG spectral analysis, it is important to review the results of studies of cyclohexene in the gas phase and also of cyclohexene adsorbed on Pt(111) under low-pressure (<10^{-6} Torr) conditions.

The equilibrium structure and the vibrational spectra of cyclohexene (C$_6$H$_{10}$) vapor molecules have been studied by electron diffraction,[16] Raman,[17] IR,[17] and theoretical calculations.[18] Cyclohexene vapor molecules adopt a half-chair conformation with C_2 symmetry at the energy minimum. The IR spectrum of gaseous cyclohexene contains features at 3040 (vinylic =CH stretch), 2942 (asymmetric =CCH$_2$−CH$_2$ stretch), 2890 (asymmetric =C−CH$_2$ stretch), 2878 (symmetric =CCH$_2$−CH$_2$ stretch), and 2858 (symmetric =CCH$_2$ stretch) cm^{-1} in the CH stretching region.[17]

When cyclohexene adsorbs on Pt(111) at low pressures below 200 K, it binds molecularly to the surface in a di-σ fashion.[8,9,11] IR bands for the di-σ-type cyclohexene on the surface are shown at 2938, 2902, and 2864 cm^{-1}.[11,12] The bands at 2938 and 2864 cm^{-1} are assigned to asymmetric and symmetric stretch of the unperturbed CH$_2$ group, respectively, and the band at 2902 cm^{-1} is assigned to CH stretch interacting with the metal surface. The di-σ cyclohexene undergoes a conformational change at about 200 K,[9] probably from a half-chair to a half-boat form, as suggested by Lamont et al.[11] The half-boat form shows almost the same IR spectrum as the half-chair form in the CH stretching region.[11] As an alternative possibility, Sheppard et al.[19] suggested a conformational change from cis-di-σ (near-parallel to the surface) to $trans$-di-σ (near-perpendicular to the surface) species, based on HREELS results[9] in the lower wavenumber ranges. At higher than 200 K, it is dehydrogenated to form a cyclohexenyl, C$_6$H$_9$.[9,10,12,20] It is believed that the cyclohexenyl, C$_6$H$_9$, has an allylic structure on the C$_1$, C$_2$, and C$_3$ positions with C_s symmetry (see Figure 1a), or π-allyl c-C$_6$H$_9$. The π-allyl c-C$_6$H$_9$ is characterized by two IR bands at 2846 and 2930 cm^{-1}.[12] At about 300 K, π-allyl c-C$_6$H$_9$ converts to benzene. Benzene on the surface desorbs or decomposes at higher temperature.[9,10,12] Note that, at low pressures, none of the intermediates with stoichiometries between C$_6$H$_9$ and benzene, such as C$_6$H$_8$ and C$_6$H$_7$, have been observed in the process of dehydrogenation of cyclohexene to benzene. The observed surface species at low pressures are summarized in Scheme 1.

In this study, we first perform high-pressure cyclohexene catalytic reactions in the absence of high-pressure H$_2$ in the temperature range 303−453 K. These results will be utilized to analyze SFG spectra in the presence of high-pressure H$_2$. Our experimental setup set the lowest temperature limit to room temperature.

3.1. Temperature Dependence of SFG Spectra Obtained upon Cyclohexene Adsorption at 1.5 Torr in the Absence of High-Pressure H$_2$. Temperature-dependent SFG spectra of surface species on Pt(111) under 1.5 Torr cyclohexene are shown in Figure 2. At 303 K, the C−H stretching region features a dominant band at 2760 cm^{-1}. The band at 2760 cm^{-1} is assigned
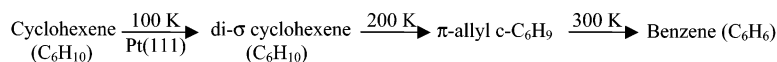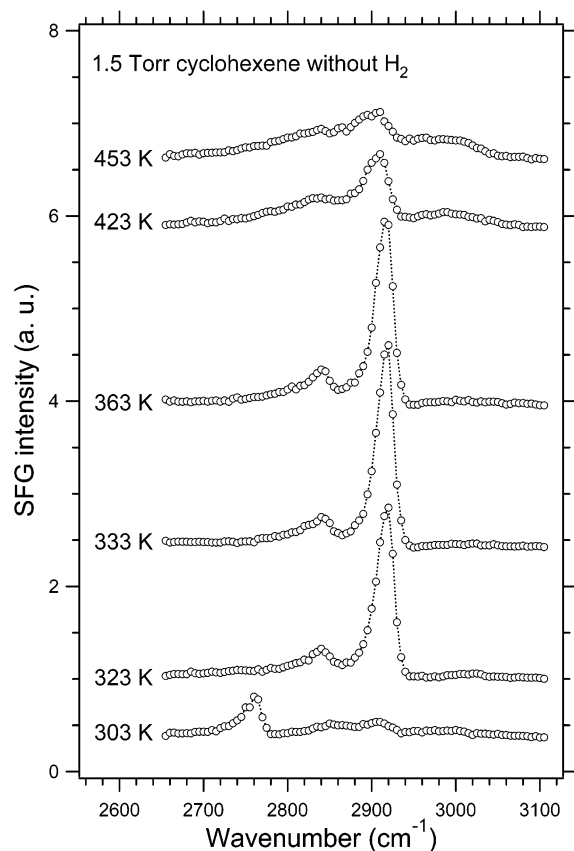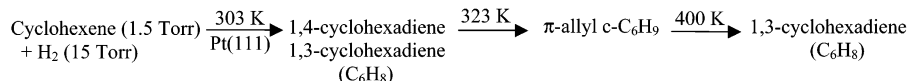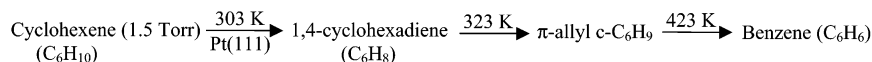
SCHEME 1:   Schematic Diagram of Observed Surface Species (a) at Low Pressure (from Ref 9) and (b) at 1.5 Torr Cyclohexene with/without 15 Torr H$_2$

(a) At low pressure (<10^{-6} Torr, in UHV environments)

Cyclohexene $\xrightarrow[\text{Pt(111)}]{\text{100 K}}$ di-σ cyclohexene $\xrightarrow{\text{200 K}}$ π-allyl c-C$_6$H$_9$ $\xrightarrow{\text{300 K}}$ Benzene (C$_6$H$_6$)
(C$_6$H$_{10}$)   (C$_6$H$_{10}$)

(b) At high pressure (with and without 15 Torr H$_2$)

Cyclohexene (1.5 Torr) $\xrightarrow[\text{Pt(111)}]{\text{303 K}}$ 1,4-cyclohexadiene $\xrightarrow{\text{323 K}}$ π-allyl c-C$_6$H$_9$ $\xrightarrow{\text{423 K}}$ Benzene (C$_6$H$_6$)
(C$_6$H$_{10}$)   (C$_6$H$_8$)

Cyclohexene (1.5 Torr) $\xrightarrow[\text{Pt(111)}]{\text{303 K}}$ 1,4-cyclohexadiene $\xrightarrow{\text{323 K}}$ π-allyl c-C$_6$H$_9$ $\xrightarrow{\text{400 K}}$ 1,3-cyclohexadiene
+ H$_2$ (15 Torr)   1,3-cyclohexadiene   (C$_6$H$_8$)
                                         (C$_6$H$_8$)

Figure 2. Temperature-dependent SFG spectra of surface species on Pt(111) under 1.5 Torr cyclohexene in the range 303−453 K. Dotted lines were drawn for visual aides.

to the axial C−H stretch from 1,4-cyclohexadiene.[12,21] SFG,[21,22] RAIRS,[12] and density functional studies[23] have shown that 1,4-cyclohexadiene adsorbs on Pt(111) in a boat conformation. The surface bonding is believed to be a quadra-σ-type with four covalent Pt−C bonds (see Figure 1b).[23,24] The axial C−H bonds on the C$_2$ and C$_5$ positions are vertical, but the equatorial C−H bonds are nearly parallel to the metal surface. As a result, the axial C−H stretch is IR- and SFG-active but the equatorial C−H stretch is not, according to IR and SFG surface selection rules. Therefore, we have assigned the band at 2760 cm^{-1} as that arising from the axial C−H stretch. This band is red-shifted about 100 cm^{-1} from typical methylene C−H stretching frequencies in the gas phase. Saeys et al.[23] proposed from density functional studies that the origin of the red shift is the axial C−H bond weakening by electron density withdrawal from the C−H bond, as a result of π-electron donation to the surface upon adsorption.

At 323 K, the band at 2760 cm^{-1} completely disappears while two new bands appear at 2840 and 2920 cm^{-1}. The band at 2920 cm^{-1} becomes more intense at higher temperature. The bands at 2840 and 2920 cm^{-1} are typical of symmetric and antisymmetric C−H stretches of a methylene group, respectively. In terms of their positions and relative intensity for the two bands, the SFG spectrum at 313 K is consistent with that for π-allyl c-C$_6$H$_9$, referring to the RAIR and SFG results for cyclohexene adsorption on Pt(111) in UHV environments.[12,21] It should be noted that the SFG spectrum at 313 K is clearly different from the RAIR and SFG spectra of di-σ-type cyclohexene (C$_6$H$_{10}$) and cyclohexadienes (C$_6$H$_8$) on Pt(111). The RAIR[12] (SFG[21]) spectrum of di-σ-type cyclohexene on Pt(111) is characterized by three bands at 2938 (2958), 2902 (2918), and 2864 (2875) cm^{-1}, and the relative intensities of the three bands are comparable. The RAIR[12] (SFG[21]) spectrum of 1,3-cyclochexadiene (C$_6$H$_8$) shows bands at 2816, 2825 (2830), 2859 (2875), and 2881 (2900) cm^{-1}.

Upon heating to 423 K, the peak intensities at 2840 and 2920 cm^{-1} decrease while a broad peak appears around 2990 cm^{-1}. The broad band at 2990 cm^{-1} can be assigned to the aromatic C−H stretch from adsorbed benzene.[25] At 453 K, multiple bands are shown at 2840, 2865, 2895, and 2910 along with a broad band around 2990 cm^{-1}. These small bands were reproducible, and the peak positions were consistent. The multiple peaks at 2840, 2865, 2895, and 2910 cm^{-1} are assigned to the C−H stretch of methylene groups from coexisting π-allyl c-C$_6$H$_9$ and 1,3-cyclohexadiene. The absence of a band at 2760 cm^{-1} indicates that 1,4-cyclohexadiene does not exist on the surface at 453 K. The observed surface species with various temperatures are summarized in Scheme 1.

3.2. Temperature Dependence of SFG Spectra Obtained upon Cyclohexene Adsorption at 1.5 Torr in the Presence of 15 Torr H$_2$. Temperature-dependent SFG spectra of surface species on Pt(111) under 1.5 Torr cyclohexene and 15 Torr H$_2$ are shown in Figure 3. At 303 K, a dominant band at 2760 cm^{-1} is assigned to the C−H stretch from 1,4-cyclohexadiene. Three discernible bands at 2855, 2880, and 2900 cm^{-1} are characteristic of 1,3-cyclohexadiene adsorbates on a Pt(111) surface.[12,21,22] At 323 K, the band at 2760 cm^{-1} completely disappears while two new bands appear at 2840 and 2920 cm^{-1}, remaining up to 483 K. The band positions (2840 and 2920 cm^{-1}) and their relative intensities are consistent with those of π-allyl c-C$_6$H$_9$. It should be noted that the SFG spectrum at 323 K is clearly different from the RAIR and SFG spectra of di-σ-type cyclohexene (C$_6$H$_{10}$) and cyclohexadienes (C$_6$H$_8$) on Pt(111), as described in a previous section. Above 403 K, two additional bands grow at 2870 and 2900 cm^{-1}, becoming more discernible at 483 K. In fact, the SFG spectrum in the range
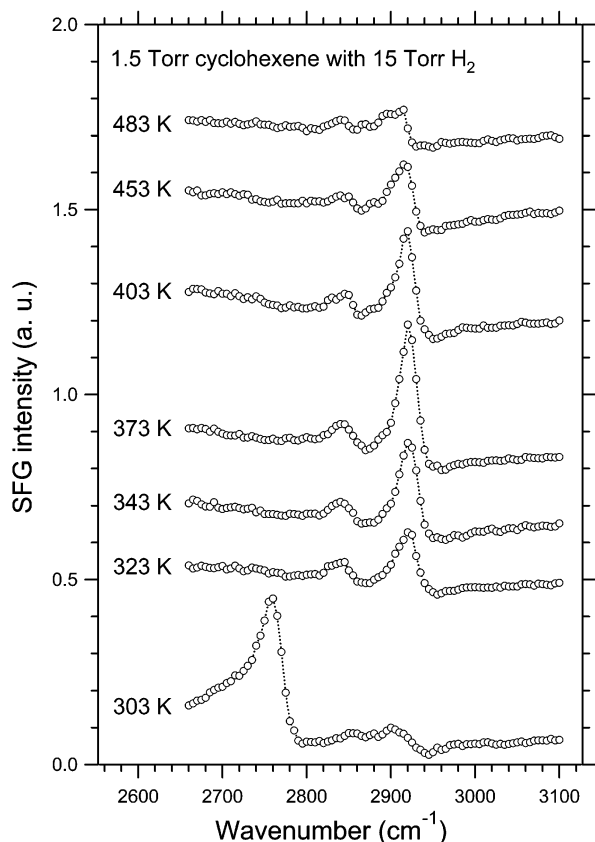
Figure 3. Temperature-dependent SFG spectra of surface species on Pt(111) under 1.5 Torr cyclohexene and 15 Torr H_2 in the range 303–483 K. Dotted lines were drawn for visual aides.
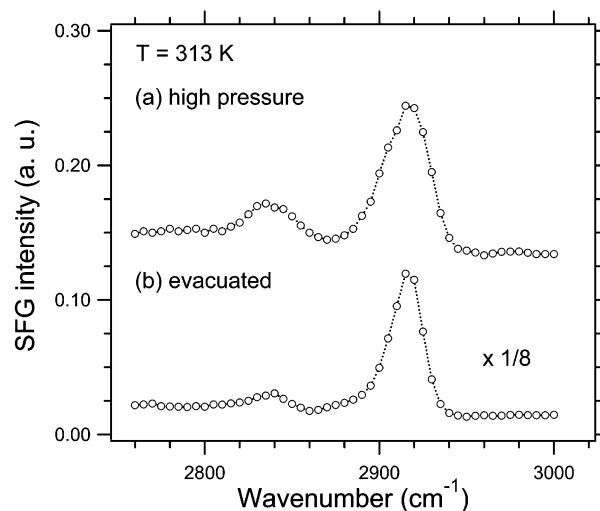

Figure 4. SFG spectra at 313 K taken (a) under 1.5 Torr cyclohexene and 15 Torr H_2 and (b) after evacuation. Dotted lines were drawn for visual aides.

2800–3000 cm^{-1} at 483 K is similar to that at 303 K, indicating that 1,3-cyclohexadiene exists on the surface at 483 K. The observed surface species at various temperatures are summarized in Scheme 1.

One might think that the presence of excess hydrogen may enhance the hydrogenation of π-allyl c-C_6H_9 to form cyclohexyl (C_6H_{11}) or cyclohexane (C_6H_{12}) on the surface. However, we exclude the possibility of coexisting cyclohexyl (C_6H_{11}) or cyclohexane (C_6H_{12}) with π-allyl c-C_6H_9 on the surface in the range 323–483 K. Cyclohexane adsorbs on Pt(111) in a chair configuration (C_{3v}) where three axial CH bonds are directly over three surface metal atoms.[26] A hydrogen-bonding-type interaction of these axial CH bonds with the metal atoms causes a very broad C–H stretching band in the range 2400–2820 cm^{-1}.[27] We observed that, when a SFG spectrum was taken in the range 2400–2800 cm^{-1}, it showed no peak at all. This implies that cyclohexane does not exist on the surface during the reactions at high-pressure cyclohexene and H_2. For cyclohexyl (C_6H_{11}) on Pt(111), there is no reported vibrational spectra in the C–H stretching region (2800–3000 cm^{-1}). Thus, our discussion will rely on the relative thermodynamic stability of these intermediates. According to semiempirical thermodynamic calculations by Koel et al.,[28] π-allyl c-C_6H_9 on Pt(111) is much more stable than cyclohexyl (C_6H_{11}) by 20 kcal/mol. Assuming the surface intermediates are at equilibrium in the range 323–483 K, a dominant species on the surface must be π-allyl c-C_6H_9. Considering the thermodynamic stability, we can also explain the absence of cyclohexyl (C_6H_{10}) or cyclohexane (C_6H_{12}) on the surface because they are less stable than π-allyl c-C_6H_9 by 32 and 27 kcal/mol, respectively.[28]

It is interesting to find that the relative intensity of symmetric (2840 cm^{-1}) and antisymmetric (2920 cm^{-1}) bands in Figure 3

changes with temperature in the presence of excess hydrogen. It was also found that the SFG spectra are changed reversibly in the range 323–373 K. Another interesting observation is that the SFG band intensities of π-allyl c-C_6H_9 in the presence of high-pressure H_2 are about an order lower than those in the absence of high-pressure H_2.

The effect of excess hydrogen on SFG spectra was further investigated by collecting SFG spectra taken under 1.5 Torr cyclohexene with 15 Torr H_2 and collecting SFG spectra after the HP cell was evacuated. Given that the associative desorption energy of H_2 on Pt(111) is 9.4 kcal/mol,[29] the surface coverage of hydrogen atom at 313 K and at 1×10^{-8} Torr is estimated to be below 10^{-3}. The dominant intermediate on this hydrogen-free surface is expected to be π-allyl c-C_6H_9. Figure 4a shows the SFG spectrum at 313 K under 1.5 Torr cyclohexene and 15 Torr H_2, and Figure 4b shows the SFG spectrum taken after the HP cell is quickly evacuated below 5×10^{-9} Torr. The SFG spectrum in Figure 4a is consistent with that in Figure 4b in terms of the peak positions and their relative intensity, indicating that both of them are π-allyl c-C_6H_9. Note that the SFG bands of the C_6H_9 in Figure 4a are broader than those in Figure 4b, and their intensities are about an order of magnitude lower than those in Figure 4b. The effects of excess hydrogen on the adsorption of π-allyl c-C_6H_9 will be discussed in the next section.

4. Discussion

4.1. Comparison of the Observed Surface Species at High Pressure (1.5 Torr Cyclohexene with/without 15 Torr H_2) to Those at Low Pressure ($<10^{-6}$ Torr). Our SFG results have revealed the presence of various surface species during the adsorption and reaction of high-pressure cyclohexene catalytic reactions on Pt(111) with and without excess hydrogen. Most of all, we report, for the first time, the existence of π-allyl c-C_6H_9 as a main surface species under the high-pressure conditions. In addition, 1,4- and 1,3-cyclohexadienes have been observed during the reactions. These species have not been found from the cyclohexene adsorption on Pt(111) in low-pressure ($<10^{-6}$ Torr) conditions. The observed surface species at low and high pressures are summarized in Scheme 1. The conversion temperature of cyclohexene to π-allyl c-C_6H_9 at high pressure is higher than that at low pressure by about 100 K. This is probably due to a site-blocking effect of high-coverage

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surface species at high-pressure cyclohexene. It is known that dehydrogenation processes require free active sites for a C−H bond cleavage. High-coverage surface species block active sites for C−H bond cleavage, inhibiting dehydrogenation. The site-blocking effect has been observed for the dehydrogenation of cyclic hydrocarbons.[30,31]

It is important to examine correlations between the surface species observed in this study and the reaction rates from gas chromatograph experiments by Su et al.[21] Their results have shown that the hydrogenation of cyclohexene to cyclohexane becomes noticeable around 300 K. The hydrogenation rate increases with increasing temperature in the range 300−400 K and then decreases slowly after 400 K. The dehydrogenation of cyclohexene to benzene is not observed until 400 K, after which its rate increases, reaching a peak at 480 K. As seen in Figure 3, our SFG results showed that π-allyl c-C_6H_9 and 1,3-cyclohexadiene appear above 323 K (upper limit) and 400 K, respectively. These temperatures are consistent with the onsets of cyclohexane and benzene formations, respectively, from the GC experiments.[21] This implies that π-allyl c-C_6H_9 and 1,3-cyclohexadiene are reactive surface intermediates in the hydrogenation and dehydrogenation processes of cyclohexene at high pressures on Pt(111).

Observation of 1,3-cyclohexadiene over 400 K exemplifies the difference in chemical environments on the surface under low-pressure ($<10^{-6}$ Torr) and high-pressure (>1 Torr) conditions. At low pressure, none of the intermediates with stoichiometries between C_6H_9 and benzene, such as C_6H_8 and C_6H_7, have been observed in the process of dehydrogenation of cyclohexane (or cyclohexene) to benzene.[9−12] This can be understood by considering the thermochemistry of these intermediates on Pt(111). According to semiempirical thermodynamic calculations by Koel et al.,[28] a C−H cleavage from π-allyl c-C_6H_9 is the rate-determining step with an activation energy of 22 kcal/mol for benzene formation on the surface. Once 1,3-cyclohexadiene (C_6H_8) is formed from π-allyl c-C_6H_9, only 7 kcal/mol is necessary for further dehydrogenation to benzene on the surface. Therefore, the surface coverage of C_6H_8 and C_6H_7 should be much lower than those of π-allyl c-C_6H_9 and benzene. High-pressure conditions allow one to observe such a metastable reactive intermediate as 1,3-cyclohexadiene. This unique capability of SFG in observing low-coverage reactive intermediates has been previously demonstrated by Cremer et al.[1] Their SFG results showed that π-bonded ethylene with coverage of 0.04 ML (ML = monolayer) exists on Pt(111) during hydrogenation of 35 Torr ethylene at 295 K.[1] In UHV environments, by contrast, π-bonded ethylene exists only below 52 K.[32] Moreover, the π-bonded ethylene has proven to be the primary intermediate in the high-pressure ethylene hydrogenation on Pt(111).[1]

It is interesting to find that 1,4-cyclohexadiene (C_6H_8) is hydrogenated to form π-allyl c-C_6H_9 at 323 K even in the absence of high-pressure H_2. Adsorption isotherms for hydrogen on Pt(111) obtained from work function measurements[29] showed that surface coverage of hydrogen atoms on Pt(111) is very low at 6×10^{-7} Torr H_2 and at 318 K. This means that, for the hydrogenation of 1,4-cyclohexadiene (C_6H_8) to π-allyl c-C_6H_9, a substantial amount of hydrogen adatoms should be provided from cyclohexene. One of the possible mechanisms is a disproportionation reaction between adsorbing cyclohexene and existing 1,4-cyclohexadiene on the surface. Adsorbed cyclohexene on the surface at 323 K is quickly dehydrogenated to form a π-allyl c-C_6H_9 by losing one hydrogen atom. The hydrogen adatom immediately hydrogenates an adjacent 1,4-

cyclohexadiene to form a π-allyl c-C_6H_9 intermediate, as described by

$$C_6H_{10}(gas) + C_6H_8(ads) \rightarrow 2C_6H_9(ads)$$
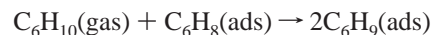
A different disproportionation reaction may also be possible, in which an adsorbing cyclohexene on the surface at 323 K forms a 1,4-cyclohexadiene instead of π-allyl c-C_6H_9 by losing two hydrogen atoms. Then the two hydrogen adatoms immediately hydrogenate two adjacent 1,4-cyclohexadienes to form π-allyl c-C_6H_9 intermediates, as described by

$$C_6H_{10}(gas) + 2C_6H_8(ads) \rightarrow C_6H_8(ads) + 2C_6H_9(ads)$$
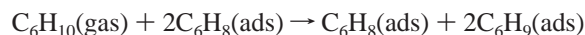
Another interesting observation is that the hydrogenation of 1,4-cyclohexadiene to π-allyl c-C_6H_9 occurs upon heating, although it is an exothermic reaction by 22 kcal/mol.[28] This implies that the conversion is a kinetically controlled process.

4.2. Effects of Excess Hydrogen on the SFG Spectra of π-Allyl c-C_6H_9. Most hydrocarbon reforming reactions are carried out in the presence of excess hydrogen. Extensive studies of hydrogen effects on the reactions have shown that hydrogen pressure is an important parameter to determine the conversion rate and selectivity in many catalytic reactions.[7,14] Nevertheless, it is not well-known at the molecular level how excess hydrogen affects the adsorption structure and chemical activity of surface intermediates.

Our SFG results showed that excess hydrogen affects the SFG spectra of π-allyl c-C_6H_9. The SFG band intensities of π-allyl c-C_6H_9 in the presence of high-pressure H_2 are about an order of magnitude lower than those in the absence of high-pressure H_2. The band broadening as well as intensity decrease by excess hydrogen is also observed in Figure 4, where the SFG spectrum of high-pressure cyclohexene and H_2 was compared with that obtained after evacuating the HP cell.

The band broadening in the SFG vibrational spectrum is a result of increase in the degree of disordering of π-allyl c-C_6H_9 on the surface. When the surface species is more disordered on the surface, there exist multiple chemisorption sites and intermolecular interactions, giving rise to inhomogeneous broadening of the SFG spectra. The increased disordering of π-allyl c-C_6H_9 could be one of the reasons for the intensity decrease of the SFG bands in the presence of excess H_2 as well. This is because SFG is a coherent process.[13] Another possible reason for the intensity change is the reduction of the surface coverage of π-allyl c-C_6H_9. Excess hydrogen on the surface may increase the conversion rate of π-allyl c-C_6H_9 to cyclohexene (C_6H_{10}) or cyclohexane (C_6H_{12}) that will quickly desorb from the surface. In summary, excess hydrogen increases the disordering and/or decreases the surface coverage of π-allyl c-C_6H_9 on Pt(111). This is probably due to the C_6H_9−Pt bond weakening by excess hydrogen on the surface. Pansoy-Hjelvik et al.[33] recently studied the effects of coadsorbed hydrogen on the dehydrogenation of cyclohexane on Pt(111) using TPD and LITD. Their results showed that coadsorbed hydrogen causes a lower temperature shift of the onset of both cyclohexane dehydrogenation and molecular desorption. It was suggested that coadsorbed hydrogen weakens the cyclohexane−Pt bonding, resulting in enhanced cyclohexane desorption and dehydrogenation rates. Our spectroscopic evidence supports their observations.

The relative intensities between the symmetric (2840 cm^{-1}) and antisymmetric (2920 cm^{-1}) bands for π-allyl c-C_6H_9 change with temperatures in the presence of high-pressure H_2, as seen in Figure 3. We found that the SFG spectra are changed

reversibly at 323−373 K. In this temperature region, dehydrogenation of the C_6H_9 is negligible.[21] This leads us to conclude that the molecular orientation of π-allyl c-C_6H_9 on the surface changes with temperature in the range 323−373 K. It is known that the relative SFG intensity of the symmetric and antisymmetric C−H stretching is sensitive to geometrical orientation of CH_2 and CH_3 groups.[34−36] Since this occurs only in the presence of excess hydrogen, the temperature-dependent molecular orientational change could be originated from the C_6H_9−Pt bond weakening induced by excess hydrogen.

5. Summary

Using SFG surface vibrational spectroscopy, we have identified surface species at various temperatures during high-pressure catalytic reactions of cyclohexene (1.5 Torr) on Pt(111) with and without excess hydrogen (15 Torr). When cyclohexene adsorbs on Pt(111) at the high pressure at 303 K, it forms 1,4-cyclohexadiene (C_6H_8) as a major species on the surface. As the temperature increases up to 323 K, 1.4-cyclohexadiene converts to π-allyl c-C_6H_9. Above 400 K, the C_6H_9 coexists with 1,3-cyclohexadiene. The observed π-allyl c-C_6H_9 and 1,3-cyclohexadiene are likely to be reactive intermediates for the hydrogenation/dehydrogenation of high-pressure cyclohexene with excess hydrogen. Our experiments show that excess hydrogen causes the broadening and intensity decrease of the SFG bands corresponding to π-allyl c-C_6H_9 on the surface. This can be explained by an increase in the disordering and decrease in the surface coverage of π-allyl c-C_6H_9 due to the hydrocarbon−Pt bond weakening in the presence of excess hydrogen. The hydrocarbon−Pt bond weakening by excess hydrogen may also be the reason for the temperature-dependent orientational change of π-allyl c-C_6H_9 in the range 323−373 K as well.

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