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Cyclohexene dehydrogenation and hydrogenation on Pt(111) monitored by SFG surface vibrational spectroscopy: different reaction mechanisms at high pressures and in vacuum

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The hydrogenation and dehydrogenation reactions of cyclohexene on Pt(111) crystal surfaces were investigated by surface vibrational spectroscopy via sum frequency generation (SFG) both under vacuum and high pressure conditions with 10 Torr cyclohexene and various hydrogen pressures from 30 up to $\sim$600 Torr. At high pressures, the gas composition and turnover rate (TOR) were measured by gas chromatography. In vacuum, cyclohexene on Pt(111) undergoes a change from π/σ-bonded, σ-bonded cyclohexene and c-C_6H_9 surface species to adsorbed benzene when the surface was heated from 130 to 330 K. A site-blocking effect was observed at saturation coverage of cyclohexene that caused dehydrogenation to shift to somewhat higher surface temperature. At high pressures, however, none of the species observed in vacuum conditions were detectable. 1,4-cyclohexadiene (1,4-CHD) was found to be the major species on the surface at 295 K, even with the presence of nearly 600 Torr of hydrogen. Hydrogenation was the only detectable reaction at the temperature range between 300 and 400 K with 1,3-cyclohexadiene (1,3-CHD) on the surface, as revealed by SFG. Further increasing the surface temperature results in a decrease in hydrogenation reaction rate and an increase in dehydrogenation reaction rate and both 1,3-CHD and 1,4-CHD were present on the surface simultaneously. The simultaneous observation of the reaction kinetic data and the chemical nature of surface species allows us to postulate a reaction mechanism at high pressures: cyclohexene hydrogenates to cyclohexane via a 1,3-CHD intermediate and dehydrogenates to benzene through both 1,4-CHD and 1,3-CHD intermediates. Isomerisation of the 1,4-CHD and 1,3-CHD surface species is negligible.

Keywords: cyclohexene, dehydrogenation, hydrogenation, SFG surface vibrational spectroscopy, reaction mechanism, surface intermediate, π/σ-bonded and σ-bonded cyclohexene, c-C_6H_9 species, cyclohexadienes

1. Introduction

The dehydrogenation of cyclic alkanes and alkenes to aromatic molecules is one of the key reactions during naphtha reforming [1]. The hydrogenation of olefins is also an important reaction in the chemical technology. The dehydrogenation and hydrogenation of cyclohexene provides us with information on both processes [2,3]. By changing the hydrogen pressure or the temperature the equilibrium shifts towards hydrogenation or dehydrogenation when the reaction is performed over a transition-metal catalyst. We explored the mechanisms of these reactions over a platinum single-crystal surface of (111) orientation in the 300–570 K temperature and 30–600 Torr pressure range using sum frequency generation (SFG) surface vibrational spectroscopy. Using SFG, we have also explored the molecular species that form upon the chemisorption of a monolayer of cyclohexene as a function of temperature and coverage. Simultaneously we monitored the reaction rate and gas composition by gas chromatography.

Previous surface science studies of cyclohexene chemisorption on Pt(111) in vacuum found that the molecule dehydrogenates to benzene readily around 300 K [4–13]. Evidence for a c-C_6H_9 intermediate was found from both high-resolution electron energy-loss spectroscopy (HREELS) and laser-induced transient desorption–Fourier transform mass spectrometer (LITD-FTMS) during the dehydrogenation of cyclohexene (C_6H_{10}) studies as well as during cyclohexane (C_6H_{12}) dehydrogenation by abstraction of three hydrogen atoms at 220 K [14,15]. Both 1,3- and 1,4-cyclohexadienes (C_6H_8) species dehydrogenate to benzene readily around room temperature [16]. Our studies in vacuum confirm the findings of others.

Our high-pressure SFG studies of cyclohexene dehydrogenation and hydrogenation, the first of its kind, shows that 1,4-cyclohexadiene is an important reaction intermediate. Its dehydrogenation produces benzene. 1,3-cyclohexadiene, which is also present on the surface, is the reaction intermediate mainly responsible for the hydrogenation reaction to produce cyclohexane.

2. Experimental

The experiments were carried out over a Pt(111) single-crystal surface in a UHV-batch reactor dual system which has been described previously [17]. The UHV chamber was pumped by a turbomolecular pump and an ion pump and had a base pressure lower than 1×10^{-10} Torr. The platinum(111) single crystal was cut, oriented and polished by the normal procedures. An ion gun that can be used to sputter-clean the crystal, a mass spectrometer, and a retarding field analyzer (RFA) for Auger and LEED were used in the chamber.

A passive–active mode-locked Nd:YAG laser and nonlinear optical setup were employed in the optical measurements. A visible beam at 532 nm generated by a frequency-doubling crystal, KDP, was used as the visible input in SFG. An infrared beam tunable between 2500 and 4000 cm^{-1} [18] was generated by a $\mathrm{LiNbO_3}$ OPG/OPA setup. The SF output from the Pt crystal was collected by a photo-multiplier and a gated integrator.

The SFG technique has been widely used in the interfacial studies due to its surface specificity [19,20]. Briefly, SFG is a second-order nonlinear optical process. This process is only allowed in the electric dipole approximation in a medium without centrosymmetry. As a result, the SFG signal in our case is dominated by contribution from the Pt(111) surface and the adsorbed layer, where inversion symmetry is necessarily broken.

Cyclohexene chemisorption studies followed by SFG monitoring of the adsorbed species as a function of temperature in the 130–330 K range were carried out by introducing cyclohexene into the ultrahigh vacuum (1×10^{-10} Torr) system at pressures of 5×10^{-8} Torr. The chemisorbed layers were monitored by SFG surface vibrational spectroscopy. The background pressure during SFG measurements in vacuum was $\sim 2 \times 10^{-10}$ Torr. High-pressure catalysis studies were carried out in a batch mode by introducing high-pressure gases into the vacuum chamber. Gas pressure was measured by a Baratron gauge that is capable of measuring pressure from 100 mTorr up to 1000 Torr. A recirculation pump was employed to circulate the gas mixture and a septum was used as a sampling port. An HP-5890 series II gas chromatograph (GC) with a column that can separate cyclohexadienes, cyclohexene, cyclohexane and benzene was used to follow the gas-phase kinetics.

All reactants from Aldrich were further purified by freeze–pump–thaw treatment and then were introduced into the reactor as a vapor. The typical reaction condition was ten Torr of cyclohexene and hundreds Torr of hydrogen. The total pressure was made up to one atmosphere by helium gas. The sample was then heated up to different temperatures via resistive heating. The SFG spectra were taken during the reaction, while the gas-phase compositions were analyzed by GC.

3. Results and discussion

3.1. Cylcohexene dehydrogenation in vacuum at low and saturation coverages

The clean Pt(111) surface was exposed to 0.2 L (L: unit of exposure, 1 L $= 10^{-6}$ Torr s) c-$\mathrm{C_6H_{10}}$ at 130 K, and all the SFG spectra were taken at 130 K after the surface was heated to different temperature, as indicated in figure 1.

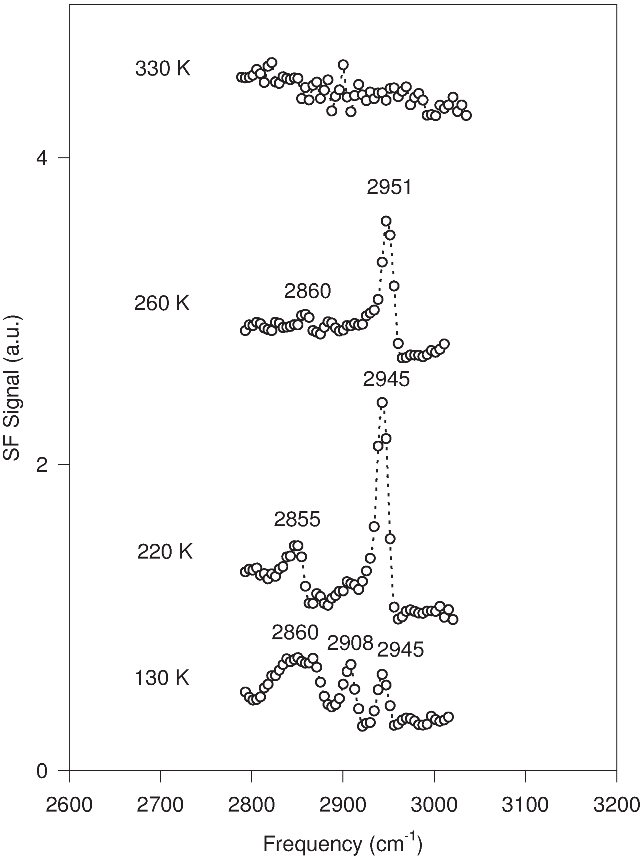

Figure 1. SFG spectrum of cyclohexene thermal dehydrogenation on Pt(111) at low coverage (0.2 L exposure) in the 130–330 K temperature range.

This exposure resulted in an low coverage of cyclohexene on Pt(111). However, we were not able to calibrate the absolute coverage by temperature-programmed desorption (TPD), because cyclohexene dehydrogenates rather than desorbs upon heating [2]. At 130 K, two sharp features at 2945 and 2908 cm^{-1} and a third peak at 2860 cm^{-1} with a broad tail extending to 2810 cm^{-1} were seen. This spectrum is similar to the Raman spectrum of cyclohexene in liquid phase [21], which has peaks at 2865, 2916 and 2940 cm^{-1} in this frequency range. Therefore, the 2860 and 2945 cm^{-1} features are assigned to C–H stretch modes in $\mathrm{CH_2}$ groups. The 2908 cm^{-1} peak is ascribed to the Fermi resonance of the bending mode of the C–H bond [22]. The broad feature in the spectrum is probably due to the C–H bond weakened by the metal surface, as found in other studies [13]. Upon heating, the surface spectrum changed dramatically at 220 K with a strong peak at 2945 cm^{-1} and a weak feature at 2855 cm^{-1}. The spectral features up-shifted to 2951 and 2860 cm^{-1} as the surface temperature was raised to 260 K. The spectral features disappeared as the flat adsorbed benzene formation occurred [2].

The SFG spectrum at saturated coverage and at low temperature shows only slightly differences (figure 2). The three peaks in the spectrum of 130 K appear to be sharper, especially the lowest frequency one, and they blue shifted

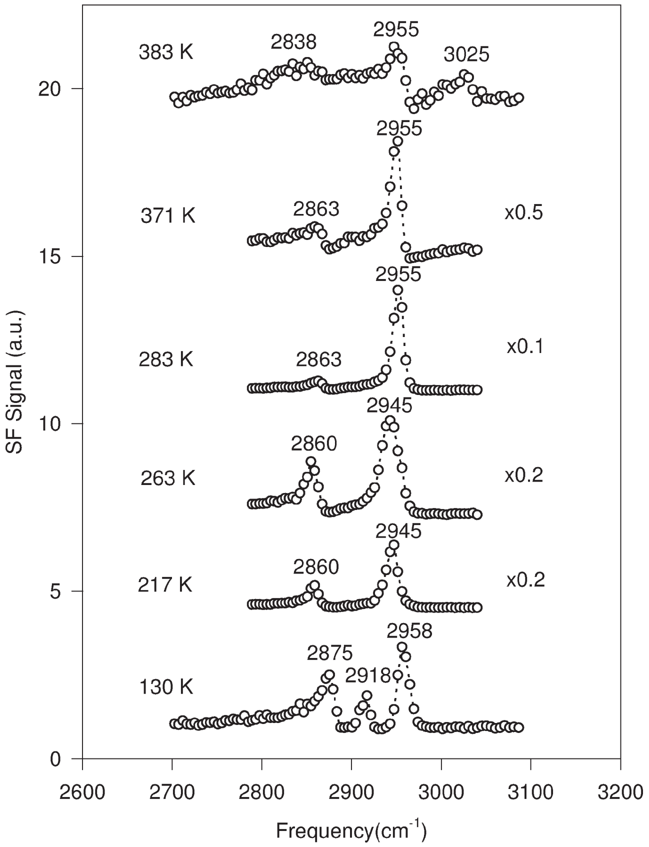

Figure 2. SFG study of cyclohexene thermal dehydrogenation at saturation coverage of cyclohexene on Pt(111) in the temperature range of 130–380 K.

by ∼10 cm^{-1}. This blue shift is probably due to the interaction of the surface species as the coverage increased. This spectrum remains the same until 130 K. The SFG spectrum changed at 217 K with two peaks at 2860 and 2945 cm^{-1}, which is identical to the spectrum at 220 K in the low-coverage case (figure 1). The spectral intensity also increased by a factor two compared to the previous spectrum at 130 K. The intensity enhancement suggests a more ordered cyclohexene layer on the surface. The temperature for further dehydrogenation of surface species shows difference. The spectrum did not change until 283 K, and the spectrum at 283 K is essentially the same as the one at 260 K in the low-coverage case with a few wavenumber blue shift in frequencies. This species survives on the surface until 371 K, and further decomposition occurs as evidenced by the greatly attenuated spectral intensity and the appearance of the 3025 cm^{-1} peak, which implies the presence of sp^2 carbon species.

The origin of the SFG spectral features of cyclohexene needs further discussion. Cyclohexene has a double bond in its molecular structure and has a half-chair conformation with C_2 symmetry as a free molecule [21,22]. A stable conformation is shown in figure 3.

Cyclohexene donates its π-electron density in the double bond to the metal as it bonds to the surface. The spectral features observed at 130 K are similar to the IR/Raman spectra of cyclohexene molecules [22]; therefore, the presence of molecular cycloyhexene is suggested. Due to the different electronic coupling with the carbon ring in the axial and equatorial position, the equatorial C–H has higher stretching frequency [23,24]. This spectrum is nearly identical to the Raman spectrum of deuterated cyclohexene 3,3,6,6-d_4 with a small shift in frequencies [22]. In the substituted molecule, the signal comes from CH_2 groups at the C_4 and C_5 positions (figure 3). Therefore, the SFG spectrum observed at 130 K can then be more specifically assigned to C–H bonds at C_4 and C_5.

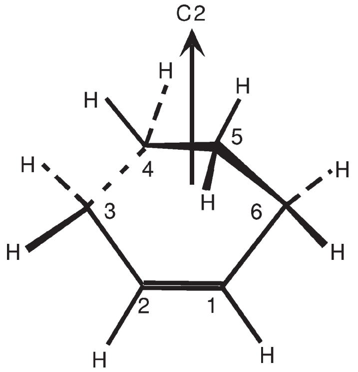

Figure 3. The half-chair conformation of cyclohexene.

The lack of seeing any features from CH_2 groups at the C_3 and C_6 positions and CH groups at C_1 and C_2 positions can be rationalized if these C–H bonds are parallel to the surface and the metal surface selection rule prohibits us from seeing any of the stretching transitions [25,26]. The molecular identity of this species implies that the double bond is barely perturbed or partially hybridized; therefore, a π/σ-hybridized cyclohexene species is proposed. This has also been found by Henn et al. [2] who proposed the formation of molecular di-σ species.

This molecular species is stable below 200 K. It converts to a new species around 220 K, as evidenced by the two new peaks at 2860 and 2945 cm^{-1}. This result fits very well to a di-σ cyclohexene species formed at this temperature, as proposed by others [2]. The shift in frequencies of the two features is probably due to changes in bonding as the π/σ species converts to the di-σ species. The π/σ-cyclohexene probably keeps the sp^2 hybridization in the double-bond carbons and interacts with the metal surface via side-on geometry. As it converts to di-σ-cyclohexene, the hybridization of the double-bond carbons changes from sp^2 to sp^3 and two σ-bonds form between platinum atoms and cyclohexene. The lack of site-blocking effect as π/σ species converts to di-σ species implies that both species occupy the same number of surface sites.

Further dehydrogenation shows coverage dependence. For low coverage, at 260 K, this new species can be assigned as a π-allyl c-C_6H_9 species on the surface according to other studies of cyclohexane and cyclohexene dehydrogenation on the same surface [2,14,15]. This assignment is consistent with our spectral results, since the stronger peak at 2951 cm^{-1} can be attributed to the equatorial C–H

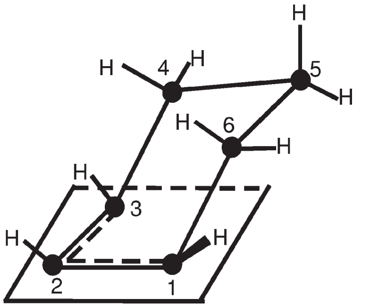

Figure 4. The possible structure of c-C_6H_9 species on the Pt(111) surface.

stretch. For this intermediate, c-C_6H_9 (shown in figure 4), the equatorial C–H on C_5 is nearly vertical, since half of the carbon ring is nearly perpendicular to the surface.

With further heating to 330 K, the disappearance of the spectral feature in the low-coverage case is due to the complete dehydrogenation of the surface species to benzene [2], which is invisible on metal surface by the SFG technique.

At saturated coverage, however, the dehydrogenation of the c-C_6H_9 species shifts to higher temperature. This upshift of the temperature is apparently due to a site-blocking effect and has been observed for other hydrocarbon dehydrogenation on Pt(111) [27]. Since these sites needed for dehydrogenation of the c-C_6H_9 species are not readily available at high coverage, this affects the chemistry in the dehydrogenation pathway. Only at higher temperature, some of the species desorb or decompose and make available the necessary dehydrogenation sites. Based on the above discussion, a reaction pathway can be proposed, as shown in figure 5.

3.2. Hydrogenation and dehydrogenation reactions of cyclohexene at high pressures

High-pressure reaction studies were carried out typically at 10 Torr pressure of cyclohexene with various hydrogen pressures up to 600 Torr in the temperature range of 300–560 K. Approximately 0.1% of 1,4-CHD and benzene were present in the gas phase after both cyclohexene and hydrogen were introduced into the chamber at 295 K, as found by gas chromatography. No further dehydrogenation was observed at this condition, and only a slow hydrogenation rate of ~5 molecules per platinum site per second was obtained, which, as we shall show below, is comparable to the hydrogenation rate of 1,4-CHD on the same surface, which was studied at similar conditions.

The prominent feature in the surface SFG spectrum is at 2765 cm^{-1} at 295 K in the presence of 10 Torr cyclohexene and various hydrogen pressures in the range of 30–590 Torr (figure 6(a)). This feature was attributed to 1,4-CHD on the surface and the weak peaks in the spectrum were from 1,3-CHD [16]. The assignment of the spectrum was made by comparison to the spectra of 1,4-CHD and 1,3-CHD in vacuum (figure 6(b)) and the spectra of cyclohexadienes at high pressures (figure 10). Interestingly, there was no evidence for the presence of C_6H_{10} and c-C_6H_9 species on the surface, which are the important species in chemisorbed cyclohexene dehydrogenation in vacuum (figures 1 and 2).

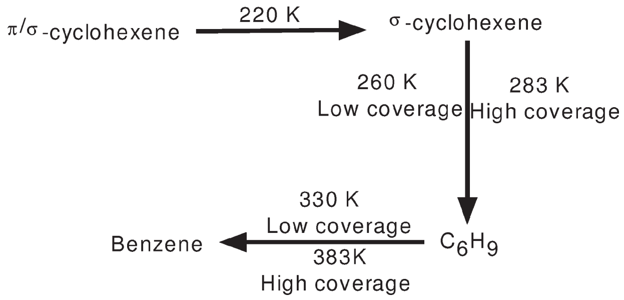

Figure 5. The reaction pathway of chemisorbed cyclohexene dehydrogenation on Pt(111) in vacuum.

Above 300 K, the 2765 cm^{-1} peak disappeared (spectrum at 403 K in figure 6(a)), and the weak features in the spectrum at 295 K representing 1,3-CHD became stronger and dominated the spectrum. The vibrational SFG spectrum remains unchanged in the temperature range of 300–400 K. Further increasing the surface temperature to 480 K, the feature representing 1,4-CHD appeared in the spectrum again in addition to the features from 1,3-CHD. This spectrum indicates that both 1,3-CHD and 1,4-CHD coexist on the surface during high-pressure reaction and there is no evidence for isomerisation of these two species.

The reaction kinetics were also measured as a function of both temperature and hydrogen pressure. The hydrogenation rate was greatly enhanced with increasing surface temperature and reached its maximum rate of 77.6 molec/site/s around 400 K at 10 Torr cyclohexene/100 Torr H_2. The temperature dependence of the reaction rate of 10 Torr cyclohexene/100 Torr H_2 was depicted in figure 7. Above 400 K, dehydrogenation became observable and the hydrogenation reaction rate decreased. The maximum dehydrogenation reaction rate of 58 molec/site/s was obtained at 480 K (figure 7).

The hydrogen pressure dependence of the reaction rates was depicted in figure 8. The reaction exhibits almost first order in hydrogen pressure below 200 Torr, and the order dependence declines as the pressure increased. This implies hydrogen saturation of the surface at high hydrogen pressure. It should be noted that, at 403 K, the dehydrogenation rate exhibits almost zero-order dependence on hydrogen pressure. This is probably due to the low probability of benzene desorption that slows down the dehydrogenation reaction at this temperature [11].

Since the dehydrogenation reaction rate may be taken as negligible, as revealed by analyzing the gas-phase composition in the temperature range between 300 and 400 K, we can make the approximation that only the hydrogenation reaction occurs in this temperature range. Thus, the Arrhenius law can be applied solely to the hydrogenation reaction. An activation energy of 8.9 kcal/mol for the hydrogenation reaction at a reaction condition of 10 Torr of cyclohexene and 100 Torr of hydrogen was obtained from the Arrhe-

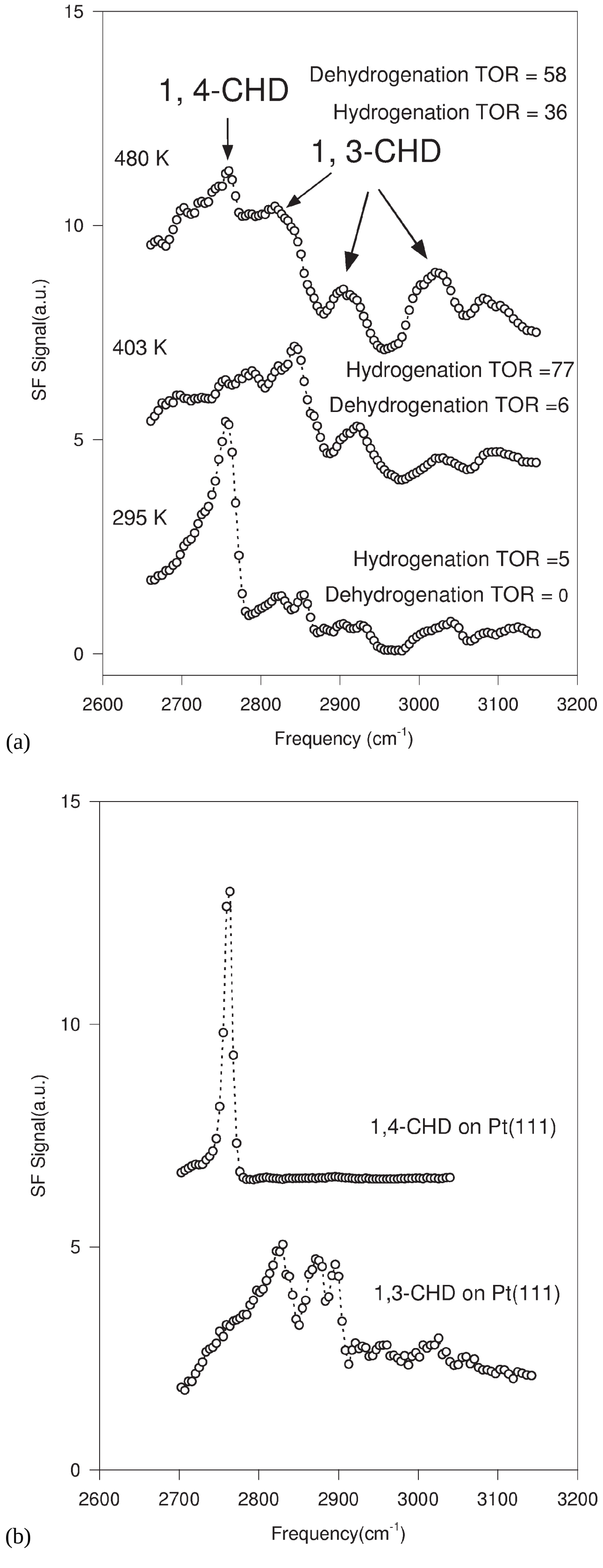

Figure 6. (a) The temperature dependence of SFG spectrum during high-pressure cyclohexene conversion on Pt(111) at 10 Torr cyclohexene/100 Torr hydrogen. The turnover rates (TOR, number of molec/platinum site/s) are also indicated in the figure. (b) SFG spectrum of 1,3-CHD and 1,4-CHD on Pt(111) in vacuum at 130 K.

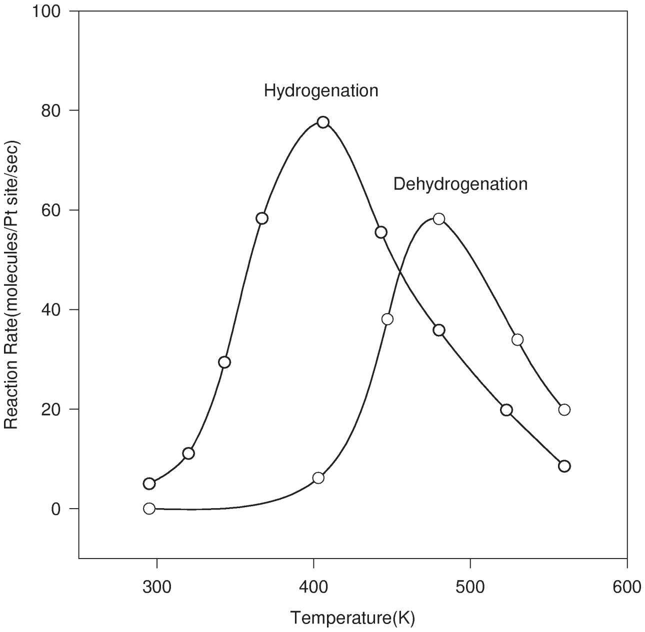

Figure 7. The temperature dependence of cyclohexene hydrogenation and dehydrogenation reactions on Pt(111) at 10 Torr cyclohexene/100 Torr hydrogen.

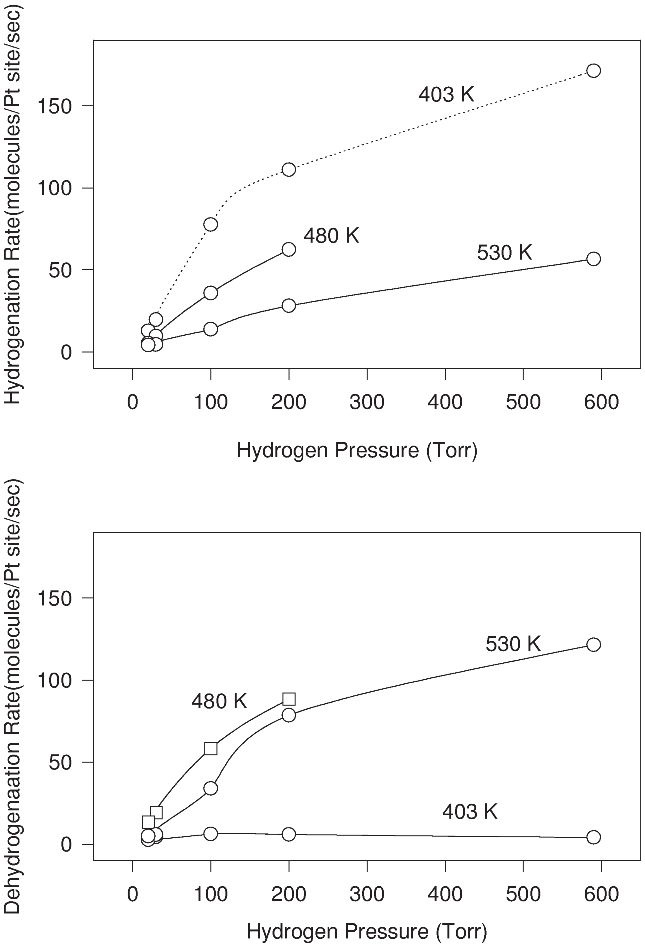

Figure 8. The hydrogen pressure dependence of both hydrogenation and dehydrogenation reactions at constant pressure of cyclohexene (10 Torr).

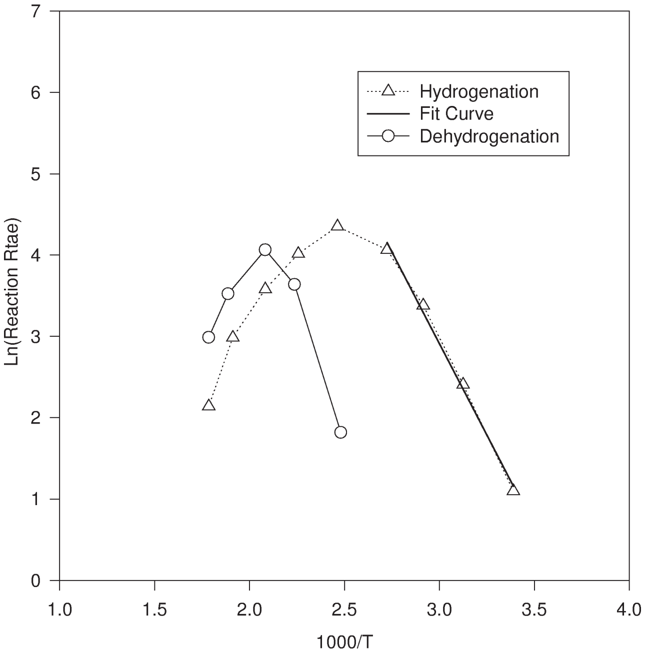

Figure 9. An Arrhenius plot of the hydrogenation and dehydrogenation reactions of cyclohexene at 10 Torr cyclohexene/100 Torr hydrogen. An activation energy of 8.9 kcal/mol for hydrogenation was obtained.

nius plot, as shown in figure 9. This activation energy is reasonable for the hydrogenation of cyclohexene. Segal et al. obtained an activation energy of ~8 kcal/mol for cyclohexene hydrogenation studies over supported platinum catalysts [28]. The measured hydrogenation rate drops quickly above 400 K, while the dehydrogenation rate increased rapidly (figure 9).

The Arrhenius behavior of the hydrogenation in this range (300–400 K) implies that the number of surface active sites for hydrogenation does not change in any significant manner in the temperature range investigated (300–400 K). Indeed, 1,4-CHD has relatively larger SFG cross section than that of 1,3-CHD on Pt(111) surface, since 1,4-CHD has stronger SFG intensity than 1,3-CHD at comparable coverage [16], and its absence in the spectrum indicates that the surface concentration of this species is very low. This allows us to conclude that 1,3-CHD is the likely surface reaction intermediate species during cyclohexene hydrogenation. The evidence found at room temperature that 1,4-CHD on the surface inhibits reactions as a full monolayer coverage is reached [11] excludes the possibility that it is an intermediate for hydrogenation in this temperature range.

To confirm the above conclusion, we carried out the hydrogenation of both 1,3- and 1,4-CHD, as shown in figure 10 (a) and (b). As expected, 1,3-CHD hydrogenates very fast with a rate of ~100 molec/site/s, while only ~5 molec/site/s was obtained for 1,4-CHD at 295 K. This correlation between the adsorbed surface species and their hydrogenation kinetics supports the above conclusion that 1,3-CHD is the chemisorbed intermediate in cyclohexene hydrogenation.

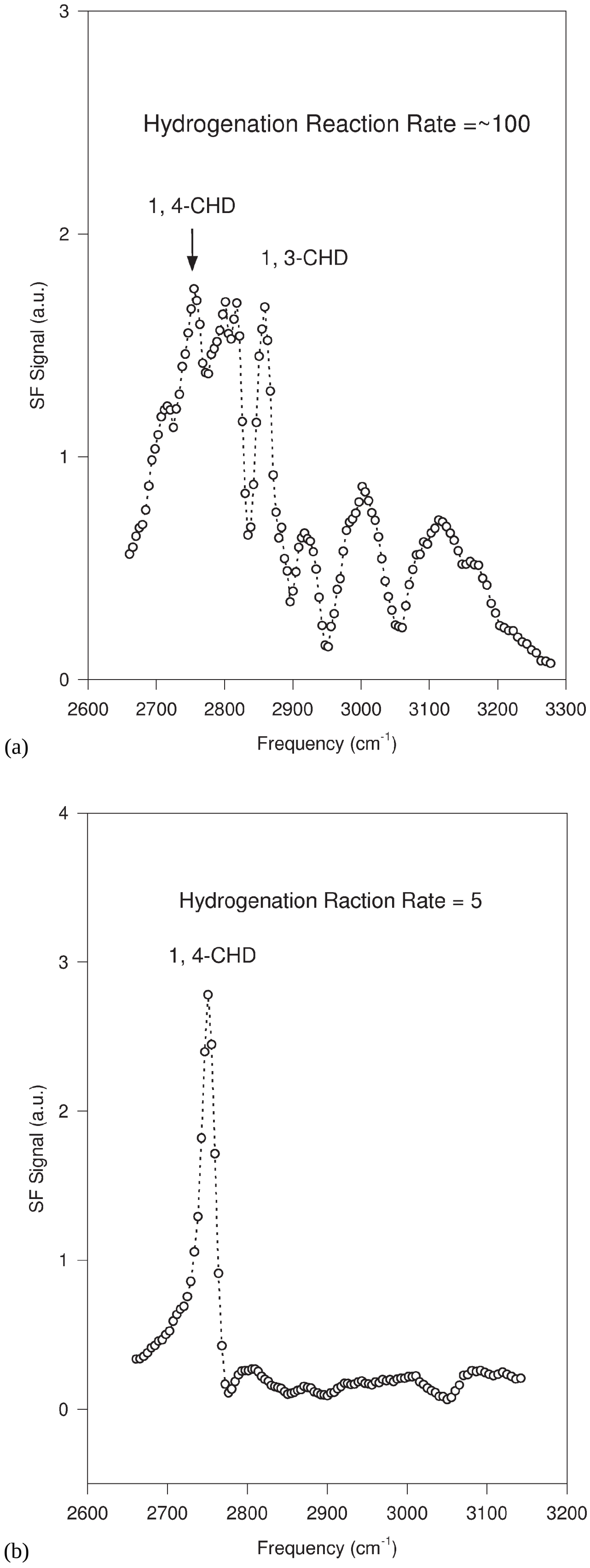

Figure 10. *In situ* SFG spectrum during high-pressure hydrogenation of (a) 1,3-CHD and (b) 1,4-CHD over Pt(111). The reaction rates are also indicated in the spectra in terms of number of molec/Pt site/s.

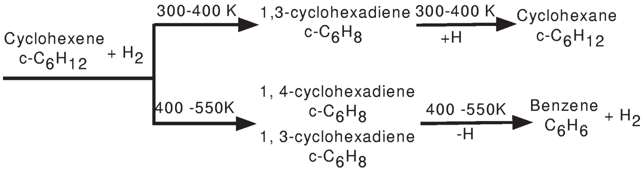

Figure 11. The proposed dominant reaction mechanism of cyclohexene conversion to cyclohexane and benzene, respectively, on Pt(111) surface at high pressures.

Above 400 K, the platinum surface carries out both hydrogenation and dehydrogenation. The dehydrogenation rate reached its peak at 480 K. This change in the rate of these two processes must be related to the change in the active surface sites for hydrogenation and dehydrogenation, respectively. Otherwise, the hydrogenation reaction would obey the Arrhenius law over the whole temperature range.

Both hydrogenation and dehydrogenation reaction rates decrease as the temperature is higher than 500 K. This could be due to the deactivation of the surface as other unreactive carbonaceous species are accumulated. It could also be possible that the lower sticking probability of cyclohexene at high temperature slows down the reactions. The reaction mechanisms that can be proposed for the hydrogenation and dehydrogenation of cyclohexene at high pressures in the 300–550 K temperature range based on our results are shown in figure 11.

4. Conclusions

Chemisorbed cyclohexene dehydrogenates to benzene in vacuum on the Pt(111) crystal surface as the temperature is increased from 130 to 330 K. π/σ- and di-σ-bonded cyclohexene and c-C_6H_9 species are the reaction intermediates. At high pressures, 1,4-CHD is the major surface species at room temperature, even in the presence of high-pressure hydrogen in the background. The other surface species is 1,3-CHD, which is recognized as one of the intermediates during high-pressure hydrogenation. Above 400 K, the surface carries out both hydrogenation and dehydrogenation reactions, and both 1,3- and 1,4-CHD surface species coexist as found by SFG. The correlation between the reaction rates and the detectable surface species indicates that both CHDs are dominant precursors for benzene formation.

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