Dehydrocyclization of 1-hexene to benzene on $Cu_3Pt(111)$

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Even though dehydrocyclization is widely practiced in heterogeneous catalysis for the conversion of straight chain hydrocarbons into aromatic compounds, knowledge of the mechanism of this process remains limited, largely because it has not previously been possible to carry out the reaction under conditions amenable to detailed mechanistic study. We report here ultra-high vacuum studies of the dehydrocyclization of submonolayer coverages of 1-hexene to benzene on a $Cu_3Pt(111)$ single crystal surface. In these studies reflection–absorption infrared spectroscopy (RAIRS) and temperature-programmed reaction/desorption spectroscopy (TPR/D) have been used to investigate the mechanism of the reaction. The results obtained demonstrate that the mechanism involves two steps: dehydrogenation ($T = 270$ K) and additional dehydrogenation + cyclization ($T = 405$ K). The RAIRS and TPR/D results suggest that a planar intermediate with C_6H_8 stoichiometry (probably 1,3,5-hexatriene) exists on the surface between 270 and 405 K. For surface coverages of up to 12.5% of monolayer saturation the selectivity to benzene formation is 70% with the remaining 30% of the adsorbed 1-hexene dehydrogenating irreversibly to surface carbon and H_2. For higher coverages, molecular desorption commences.

Keywords: hexene; dehydrocyclization; Cu_3Pt alloy; surface; mechanism; aromatization; infrared spectroscopy; catalysis; single crystal; 1,3,5-hexatriene

1. Introduction

Dehydrocyclization of straight chain alkanes and alkenes to aromatics is an important process in the catalytic reforming of petroleum feedstocks. It is well-established that platinum [1–3] and platinum alloyed with copper [4–6], gold [7–9], and cerium [10] are among the most effective heterogeneous catalytic materials for these dehydrocyclization processes. Ultra-high vacuum studies utilizing high pressure cell techniques have shown that single crystal platinum surfaces and platinum surfaces alloyed with gold can also carry out dehydrocyclization of hexane to benzene [9,11] and heptane to toluene [12] at atmospheric pressures, but, to our knowledge, there are no reports to date where single monolayers of straight chain hydrocarbons are cyclized to aromatics. This lack of monolayer reactivity over well-defined surfaces has precluded a detailed mechanistic study of dehydrocyclization and, as a result, it has proven difficult to definitively establish the surface reaction mechanisms for these processes.

In this letter we report the dehydrocyclization of 1-hexene to produce and evolve benzene from single monolayers on a $Cu_3Pt(111)$ surface. For 1-hexene coverages up to 0.125 of monolayer saturation, 70 ± 10 % of the adsorbed molecules produce benzene at 405 K, while 30 ± 10 % decompose to deposit carbon on the surface. At higher surface coverages (above 4 L), molecular desorption of 1-hexene is also observed at ca. 240 K. Temperature-programmed reaction/desorption (TPR/D) studies in combination with reflection–absorption infrared spectroscopy (RAIRS) results provide evidence that 1-hexene dehydrogenates below 300 K to produce 1,3,5-hexatriene which is thermally stable to 405 K where it dehydrogenates and cyclizes to produce benzene.

2. Experimental

The experimental results presented here were obtained in an ultra-high-vacuum chamber with background pressure of $\sim 5 \times 10^{-10}$ Torr equipped with an Auger electron spectrometer (AES), a high-resolution electron energy loss spectrometer, a differentially-pumped quadrupole mass spectrometer, an ion gun for surface cleaning, a low-energy electron diffraction apparatus (LEED), and a setup for reflection–absorption infrared spectroscopy. A detailed description of this vacuum system is published elsewhere [13].

The $Cu_3Pt(111)$ single crystal was obtained from Material-Technologie & Kristalle GmbH (Jülich, Germany) as a circular disk (1 cm diameter and 2 mm thickness) polished to a mirror finish on one of the (111) surfaces. The crystal was mounted on a resistive heating element attached to a manipulator. The temperature of the crystal was measured by a chromel–alumel thermocouple whose junction was wedged into the hole on the side of the crystal. Crystal temperatures as low as 110 K could be achieved by cooling with liquid nitrogen.

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Heating was provided by a dc power supply (Hewlett-Packard, 6291A), controlled by a temperature programmer (Eurotherm 818 P). A temperature ramp of 3 K/s was used in the temperature-programmed desorption studies. The crystal was cleaned as described in ref. [14] by Ar^+ sputtering at 550 K for 15 min followed by annealing in UHV at 840 K for 20 min to free the surface of carbon, sulfur and oxygen as confirmed by AES.

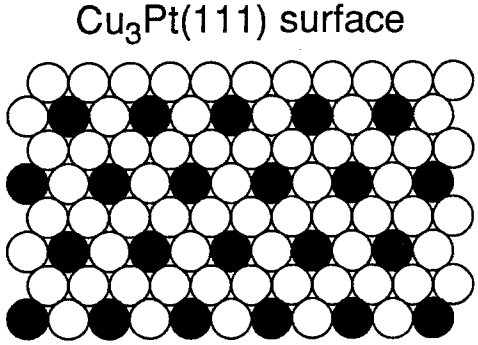
The surface structure and composition of $Cu_3Pt(111)$ has recently been studied by Wandelt and coworkers [15], and their early papers reported a (2×2) LEED pattern for this surface [15a–15c]. This is the diffraction pattern that one would expect for ideal termination of the bulk lattice, and it corresponds to a lattice of isolated Pt atoms, each surrounded by six nearest neighboring Cu atoms in the plane as shown in scheme 1.

More recent papers from Wandelt et al. report a (1×1) pattern for $Cu_3Pt(111)$ [15d–15e] which is the same as is observed here. The similarities between the bonding and reactions of CO and H_2 on the surfaces with these two different LEED patterns suggest that in both cases the surface Pt atoms are surrounded by Cu even though long-range order of the Pt atoms is absent on the (1×1) surface. Low-energy ion scattering studies indicate that the surface is enriched in copper by only 5% [15d–15e].

1-hexene (Aldrich, 99+%) was purified by several freeze–pump–thaw cycles before introduction into the chamber and the purity of the dosing gas was confirmed in situ by mass spectroscopy. All the exposures are reported in langmuirs (L), where 1 langmuir is 10^{-6} Torr s.

For the TPD experiments, the adsorbate-covered surface was positioned line-of-sight to the mass spectrometer, about 2 mm from a 2 mm diameter sampling aperture which was used to detect selectively the molecules desorbing from the center of the single crystal surface.

For the RAIRS studies, the infrared light from a FT-IR spectrometer (Perkin-Elmer 1800) is focused through a differentially pumped barium fluoride window onto the sample at an incidence angle of 82.5° from the surface normal. The reflected light in the specular direction is collected by a narrow band mercury cadmium telluride (MCT) detector (EG&G Judson, model No. J15-D14-M216-S-01M-YS-WE, Ge window, $D^* > 4 \times 10^{10}$). The optical path is purged with CO_2- and H_2O-free air generated by an FT-IR purge gas generator (Balston 75-62). Each spectrum presented here is taken with 8 cm^{-1} resolution and represents the average of several thousand scans (~4 min/1000 scans). The number of scans corresponding to each spectrum is indicated in the figure caption.



Scheme 1.

3. Results and discussion

The TPR/D results presented in fig. 1 show the evolution of masses 84 and 78 for exposure of the $Cu_3Pt(111)$ surface to different amounts of 1-hexene. The TPD peaks for mass 84 represent molecular desorption of 1-hexene as was confirmed by following masses 84 and 27 at an electron impact ionization energy 70 eV and mass 84 at an electron impact energy 9 eV[#1] (to eliminate cracking and to isolate the molecular ion [16,17]). Molecular desorption of 1-hexene is not observed for exposures less than 0.5 L. Above 0.5 L there is a linear increase in the peak area as a function of exposure. This molecular desorption occurs at 270 K for low exposures (1 L) and shifts down in temperature upon increasing the exposure. At 3 L, a second, 180 K, feature appears on the spectra. Given that the onset for second layer desorption (at 150 K; not shown) occurs for an exposure of > 4 L, the 180 K peak presumably corresponds to a second adsorption state in the monolayer.

For the exposures less than 0.5 L where no 1-hexene is evolved from the surface, benzene ($m/e = 78$) evolution is detected. Mass 78 shows a single peak at 405 K, as shown in fig. 1. The temperature of this peak is independent of exposure, and the peak area grows linearly with exposure up to a saturation value at 0.5 L. By tracing masses 78 and 77 at 70 eV electron impact ionization energy and mass 78 at 9 eV electron impact ionization energy, this peak is assigned to benzene formation and desorption. On the basis of the TPD spectra for the molecular desorption of benzene from $Cu_3Pt(111)$ which show benzene evolution at temperatures between 160 and 270 K with no decomposition, we conclude that evolution of benzene from 1-hexene at 405 K is limited by the rate of benzene formation.

1-hexene and benzene are the only gas phase hydrocarbon products detected for the interaction of 1-hexene with $Cu_3Pt(111)$. The total area of the peaks corresponding to these compounds (corrected for the mass spectrometer detection sensitivities) is plotted in the

[#1] It should be noted that these values of the electron impact ionization energy are the values from the mass spectrometer control panel. There is evidence that the actual values are slightly higher [17].

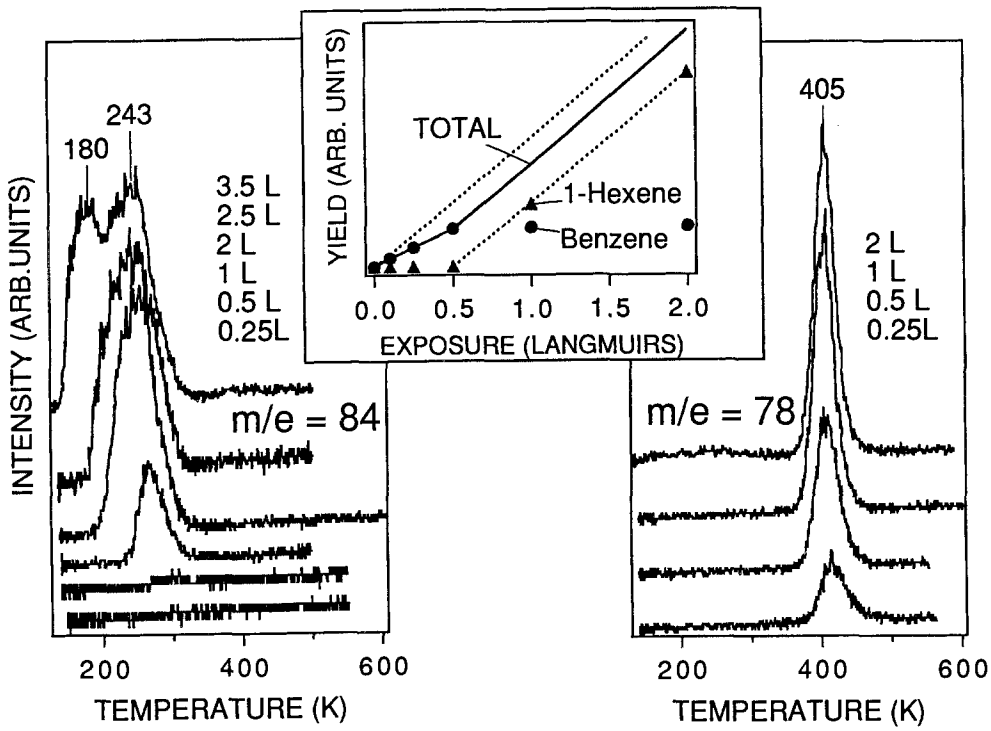


Fig. 1. TPR/D studies of 1-hexene reaction with a $Cu_3Pt(111)$ surface. The inset shows the relative yields of 1-hexene molecular desorption and benzene formation as a function of 1-hexene exposure.

inset to fig. 1. Note that the total area of these two features is not a straight line, a result which indicates (in the absence of a nonlinearity in the adsorption rate) that there are other products of the reaction. Consistent with this inference, Auger electron spectroscopy studies show that carbon remains on the surface after annealing to 840 K. The amount of carbon for exposures $\geqslant 0.5$ L corresponds to 4 ± 1 % of a monolayer of 1-hexene. Since the amount of benzene evolved corresponds to 9 ± 2 % of a saturation monolayer of 1-hexene, we conclude that for exposures less than 0.5 L, 70 ± 10 % of the adsorbed 1-hexene is converted to benzene and 30 ± 10 % decomposes to deposit carbon and evolve hydrogen. Consistent with this conclusion, we find that if saturation exposures are repeated without surface cleaning to remove carbon in between, the area of the benzene peak decreases by 30 ± 5 %.

TPR spectra of mass 2 taken after a saturation exposure of 1-hexene show two peaks as indicated in the lower panel of fig. 2. The lower temperature feature corresponds to the desorption of hydrogen whose rate of evolution is similar to the rate of H + H recombination on $Cu_3Pt(111)$ as confirmed by comparison with studies of the reaction of molecular hydrogen with this surface. The high temperature (400 K) hydrogen desorption is coincident with the evolution of benzene and presumably reflects the kinetics of the rate-determining second step in the conversion of 1-hexene to benzene.

The 2 : 1 ratio of the areas of 280 K and 400 K H_2 desorption peaks indicates, on the basis of the overall loss of six H atoms to form benzene, the loss of four H at 280 K to form a C_6H_8 intermediate which subsequently loses two more H atoms at 400 K to form benzene [#2]. We rule out 1,3- and 1,4-cyclohexadiene as this intermediate, since both of these compounds form and evolve benzene on $Cu_3Pt(111)$ below 300 K. A probable intermediate is 1,3,5-hexatriene, and similar triene species have been previously proposed as the key intermediates in catalytic dehydrocyclization [18–20].

The intermediacy of 1,3,5-hexatriene is substantiated by the RAIRS results presented in fig. 2 (top panel). This figure compares the multilayer spectrum of 1-hexene (scaled to match the size of the spectrum for a 0.5 L exposure) with the spectra of 0.5 L of 1-hexene taken at the temperatures indicated on the accompanying TPR/D spectrum. Spectrum A, taken after adsorption of 0.5 L of 1-hexene at 120 K, shows most of the intense features in the multilayer 1-hexene spectrum, confirming that at 120 K this molecule remains intact on the $Cu_3Pt(111)$ surface. When the surface is annealed to 250 K, the spectrum does not change, but when the annealing temperature is increased to 350 K, no absorption features are observed in the C–H stretching region of the IR spectrum. Since benzene has not yet formed on the surface by 350 K, these results indicate that an adsorbed intermedi-

[#2] Strictly speaking, this statement is only correct for a 100% conversion of 1-hexene to benzene. Since 30% of the 1-hexene is converted to carbon and hydrogen for this 0.5 L exposure of 1-hexene, additional hydrogen evolution *not* associated with the conversion of 1-hexene to benzene is expected. Studies are in progress to determine if this hydrogen is evolved at temperatures above 600 K.

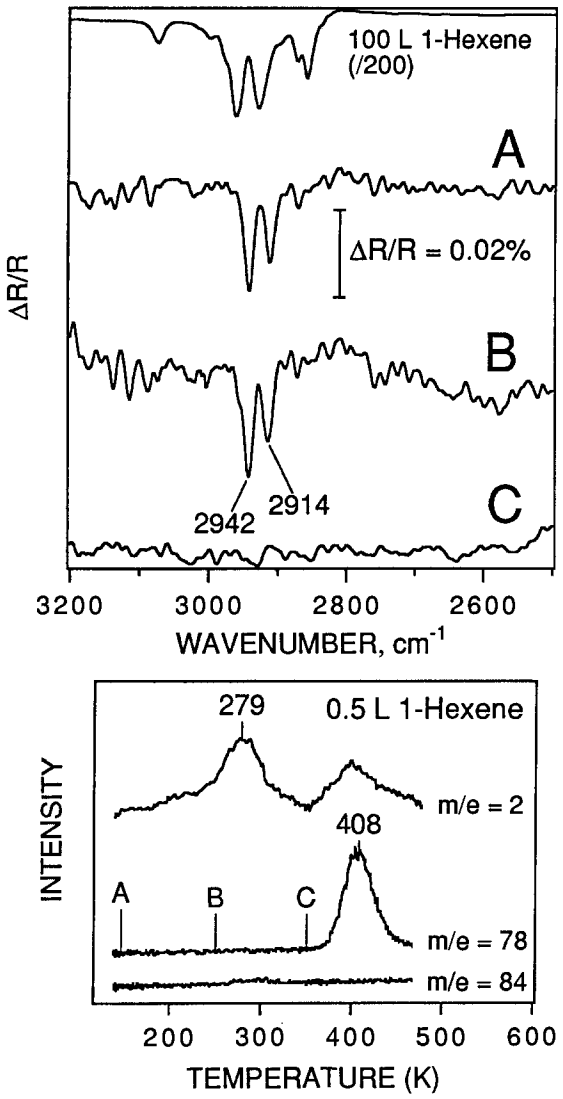


Fig. 2. Comparison of RAIRS spectra for 1-hexene dehydrocyclization to benzene on a $Cu_3Pt(111)$ surface with TPR/D results for this reaction. The multilayer 1-hexene IR spectrum (1000 scans) is compared with IR spectra for 0.5 L exposure of 1-hexene which were taken after briefly annealing the surface at the temperatures indicated in the TPR spectrum. Each of these submonolayer IR spectra represents the average over 2000 scans.

ate, undetected in the C–H stretching region by IR, exists on the surface. This observation is consistent with a planar 1,3,5-hexatriene intermediate, whose C–H bonds lie parallel to the $Cu_3Pt(111)$ surface and are therefore, as result of the surface IR selection rule [21,22], transparent in the C–H stretching region. Additional spectroscopic studies are in progress to confirm the identity of this intermediate.

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