Naphthalene formation on $Cu_3Pt(111)$: dehydrocyclization of 4-phenyl-1-butene

Anna T. Mathauser and Andrew V. Teplyakov *

Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716, USA
E-mail: andrewt@udel.edu

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Here we report an unusual cyclization reaction leading to the formation of naphthalene from 4-phenyl-1-butene on a $Cu_3Pt(111)$ single crystal alloy surface. The two-step dehydrocyclization process is complete below 500 K and the majority of the naphthalene molecules formed are desorbed into the gas phase.

KEY WORDS: naphthalene; 4-phenyl-1-butene; thermal desorption mass spectrometry; Cu_3Pt alloy

1. Introduction

Reactions leading to the formation of carbon–carbon bonds are the foundation of numerous industrial processes. Many of these reactions are catalyzed by metals and detailed experimental studies of single crystal chemistry have already yielded significant insights into the mechanisms of these processes. One of the most interesting chemical transformations involving the formation of a carbon–carbon bond is cyclization [1]. This type of reaction produces cyclic structures that sometimes can involve a heteroatom, such as oxygen, sulfur or nitrogen. The production of complex cyclic compounds is usually performed by homogeneous processes or as a result of flame chemistry so that the final products can be purified by traditional analytical methods. However, relatively simple cyclic structures can be produced by means of highly selective heterogeneous catalysis.

Cyclization processes producing C_6 cyclic hydrocarbons have been used for several decades with the majority of products based on benzene production and its hydrogenation. Often catalysts used in reactions like that were too reactive to perform more complicated cyclization chemistry with compounds that have more than six or seven carbon atoms because these products, even when obtained on catalyst surfaces, would normally undergo further reactions or decompose at the reaction conditions, which in turn would lead to coking and quick deactivation of the catalyst.

Although a variety of materials has been used as aromatization catalysts, the vast majority of these catalysts are based on supported platinum [1–5]. Hundreds of experimental and theoretical studies of reactivity of single crystals of this metal have brought about a large amount of knowledge of kinetics, thermodynamics, steric and electronic requirements for cyclization reactions (see, for example [6–14] and multiple references therein). At the same time, chemical degradation of the desired products was significant even if relatively simple cycles were the targets of the heterogeneous process. One of the solutions to this problem was alloying platinum with other metals, which has been suggested to reduce somewhat its reactivity and increase hydrogenation rates so that aliphatic hydrocarbons could be produced. In the 1970s, de Jongste demonstrated that copper–platinum alloys are excellent aromatization catalysts [15] and by varying the alloy composition, one could govern its reactivity [16–18]. At the same time, supported Pt–Cu catalysts have been investigated with respect to hexane conversion and showed enhanced selectivity for cracking but decreased activity for nondestructive alkane reforming [19]. Unlike platinum, single crystals of copper–platinum alloys are relatively difficult to produce. Nevertheless, in the recent years, as the commercially-produced Cu_3Pt alloy has become available, there have been numerous mechanistic investigations of the catalytic abilities of this material [20–31]. Aromatization reaction was studied in detail for several C_6 hydrocarbons [32–34]. The (111) surface of the Cu_3Pt alloy has been studied extensively and it has been shown that although the reactivity of this surface is high enough for dehydrogenation or carbon–carbon bond formation reactions to occur, most of the products of these transformations could be easily desorbed from this surface and detected by mass spectrometry even at low initial coverages of reactant materials. This reactivity prompted us to investigate a long-standing problem of a possibility of heterogeneous reactions leading to the formation of large hydrocarbon molecules catalyzed by a single crystal surface.

Here we report the study of a dehydrocyclization reaction on a $Cu_3Pt(111)$ alloy surface that produces naphthalene from 4-phenyl-1-butene, as illustrated in scheme 1. The transformation takes place at 470 K, and is accompanied by the loss of two pairs of hydrogen atoms: one at about 300 K and another at 420 K. Despite partial decomposition, a significant amount of naphthalene is released into the gas phase where it is detected by mass spectrometry.

* To whom correspondence should be addressed.

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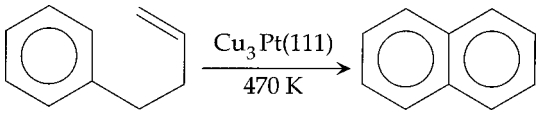

Scheme 1.

2. Experimental

The UHV chamber used in the experiment has a background pressure of 3×10^{-10} Torr. It is equipped with an ion gun for surface cleaning, an Auger electron spectrometer, a shielded mass spectrometer (Stanford Research Systems) differentially pumped by the chamber, and an apparatus for low energy electron diffraction. The Cu_3Pt single crystal (Material Technologie and Kristalle, Ulich, Germany) is a 10 mm diameter 2 mm thick disk polished to a mirror finish on one (111) surface. It was mounted onto a resistive heating element and attached to a manipulator, with capability of heating the surface to 1000 K and cooling to 120 K with liquid nitrogen. Temperature was measured by a chromel–alumel thermocouple wedged into a hole on a side of the crystal. Temperature ramp of 2 K/s was maintained for the desorption experiments by a Eurotherm 818P temperature programmer connected to a dc power supply (Hewlett–Packard 6291A). The Cu_3Pt crystal was prepared by 15 min Ar^+ (Matheson) sputtering followed by 20 min annealing to 820 K [26]. This procedure results in the stoichiometric bulk terminated surface structure of the $Cu_3Pt(111)$ single crystal where each Pt atom is surrounded by copper atoms, without significant surface enrichment by either component [26]. The cleanliness and ordering of the surface was confirmed by AES and LEED. 4-phenyl-1-butene (Aldrich, 99%) sample was subjected to several freeze–pump–thaw cycles in order to remove trapped gases. Its purity was then tested by comparing the spectrum obtained *in situ* against the standard literature mass spectrum. The compound was introduced into the chamber and adsorbed onto the crystal at 120 K. Naphthalene (Aldrich, 99%) was introduced into the vacuum chamber through the leak valve. Although naphthalene is solid, it has a high enough vapor pressure for one to be able to use such an arrangement. The purity of naphthalene was checked *in situ* by mass spectrometry and the obtained mass spectrum was compared against literature data. In the TPD studies the adsorbate-covered crystal was positioned in the line-of-sight with respect to the mass spectrometer, approximately 3 mm from a 4 mm diameter sampling aperture, allowing for an accurate detection of species desorbing from the center of the crystal surface. All the exposures are reported in langmuirs (1 L $= 10^{-6}$ Torr s) and recalibrated with respect to the monolayer coverage of a compound dosed as explained below.

3. Results and discussion

Before attempting to study the dehydrocyclization of 4-phenyl-1-butene, we needed to gather some information about the adsorption and chemical reactivity of the expected

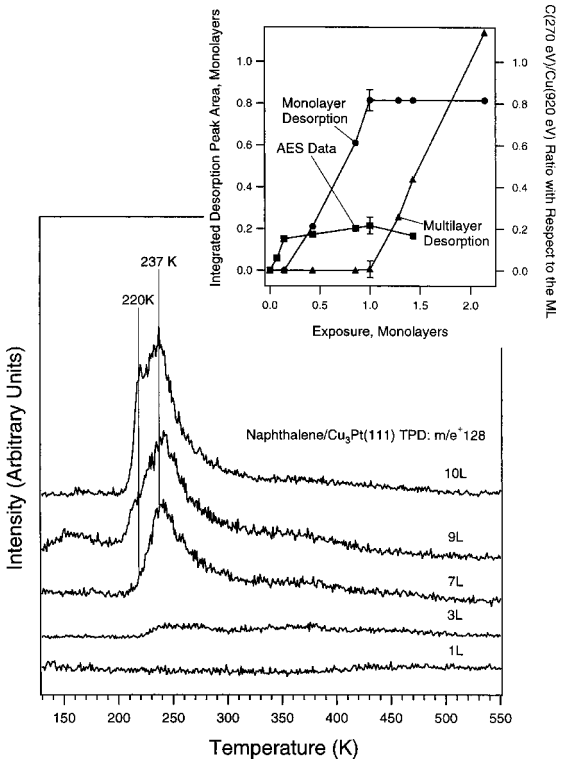

Figure 1. Temperature-programmed desorption studies of naphthalene on a $Cu_3Pt(111)$ surface. The inset shows the balance of TPR/D and AES yields calibrated with respect to the monolayer.

product of this reaction, naphthalene. The temperature-programmed desorption studies of naphthalene on a $Cu_3Pt(111)$ surface are summarized in figure 1. Thermal desorption traces of $m/e^+ = 128$ as a function of the original dose suggest that the majority of naphthalene molecules desorb from this surface around 237 K. The only hydrocarbon product desorbing from the surface into the gas phase was naphthalene. Some decomposition was registered by Auger electron spectroscopy and the summary of the AES studies is presented in the inset to figure 1, where the original dose is recalculated with respect to the monolayer coverage. For convenience, we will refer to the coverage just below that required for the formation of naphthalene multilayer to start, as the *monolayer* coverage. The calibration of the AES signal was possible by analyzing the spectra of the clean $Cu_3Pt(111)$ surface dosed with the exposures of naphthalene up to a monolayer coverage at 125 K. With the assumption that the sticking probability at 125 K is one and using the monolayer coverage of 7 L, as determined from the thermal desorption studies, the AES response for decomposed naphthalene molecules was calibrated. The inset to figure 1 clearly shows that approximately 80% of the monolayer naphthalene desorbs into the gas phase with some of the monolayer molecules undergoing decomposition. This percentage is changing as a function of the initial naphthalene coverage reaching 80% only when a full monolayer is adsorbed.

The fact that naphthalene molecules could desorb into the gas phase after adsorption on a $Cu_3Pt(111)$ surface brings

about two interesting points. First, it should be noted that such metals as Pt, Pd or Ni, are often used for *hydrogenation* of complex cyclic compounds [35–38] but are rarely studied in a form of single crystal for investigating the mechanisms of *formation* of large hydrocarbons. A very interesting chemistry of C_6 hydrocarbons on model palladium catalysts is described in [39]. However, the reactivity of palladium that allows for such transformations as hydrogenolysis prevents the use of similar catalytic surfaces for synthesizing such complex structures as naphthalene. At the same time, the single crystal of the Cu–Pt alloy is reactive enough to perform the chemistry similar to that on other transition metals. Moreover, its reactivity is moderate enough so that the majority of the complex C_{10} hydrocarbon molecules can still desorb from the surface. The second point is the consequence of the first one and is related to the possibility of using thermal desorption as a tool to monitor the production of naphthalene by dehydrocyclization process on a single crystal surface. Since the majority of adsorbed naphthalene molecules can be safely desorbed upon thermal annealing, the reactions leading to the formation of such complex hydrocarbon compounds can be studied in ultrahigh vacuum and, moreover, these reactions might be useful for real industrial heterogeneous catalytic processes.

Surface transformations of 4-phenyl-1-butene are summarized in figure 2. When molecular desorption of this compound is followed by mass spectrometry ($m/e^+ = 132$), no desorption is observed up to 3 L of initial coverage. A 7 L exposure shows that the multilayer peak is just forming at about 215 K. Thus 6 L dose can be considered a monolayer saturation coverage. Similarly to the naphthalene studies described above, we will refer to the coverage just below that required for the formation of 4-phenyl-1-butene multilayer to start as the *monolayer* coverage. The production of naphthalene from the alloy surface was registered at 471 K. Interestingly, even small initial coverages of 4-phenyl-1-butene are enough to release some naphthalene into the gas phase, although the decomposition process does compete with this desorption. The formation of naphthalene was additionally confirmed by monitoring the evolution of $m/e^+ = 74$, 102, 126 and 127 as a function of temperature. It should be noted that the 4-phenyl-1-butene mass spectrum contains very little of the 74, 102, 127 and 128, and no 126 trace. H_2 ($m/e^+ = 2$) TPR/D study shows two peaks, shifting from 295 to 306 K and 418 to 427 K as the coverage is increased from 1 to 7 L, corresponding to the loss of two pairs of hydrogen atoms upon dehydrogenation and cyclization reactions. Hydrogen desorption spectra do not show any significant changes upon further increasing the initial coverage of 4-phenyl-1-butene. Consistent with this mechanism, the ratio of the two hydrogen desorption peaks is 1.0 ± 0.15 throughout all the experiments reported here. (It should be noted that naphthalene decomposition seems to occur in two steps releasing hydrogen at similar temperatures. However, the exact mechanism of naphthalene decomposition could not be established based on the results presented here.) Carbon remains on the alloy surface after thermal annealing as a result of the decomposition. It appears that the decomposition is a combination of two processes: (1) direct decomposition of a fraction of the 4-phenyl-1-butene molecules, and (2) decomposition of a fraction of naphthalene molecules after successful formation of naphthalene, as was suggested by the TPR/D and AES studies of naphthalene on a $Cu_3Pt(111)$ surface presented above. The balance of decomposition, dehydrocyclization, and molecular desorption of 4-phenyl-1-butene is shown in the inset for figure 2. This balance was deduced from exposing fixed pressures of naphthalene and 4-phenyl-1-butene to the mass spectrometer to determine the sensitivity and by calibrating the AES response by adsorbing the monolayer coverages of both compounds at cryogenic temperatures, where the sticking coefficient for both hydrocarbons was assumed to be one. The inset for figure 2 suggests that the percentage of surface reactions is a function of the initial coverage of 4-phenyl-1-butene. However, at the one monolayer coverage, 50% of the initial dose of 4-phenyl-1-butene desorbs back into the gas phase, while the surface transformations of the rest of the molecules produce naphthalene and surface carbon at a ratio of approximately 3 to 2 within our error of measurement. Thus, naphthalene can be produced from the dehydrocyclization process on a $Cu_3Pt(111)$ surface. It is released into the gas phase where it can be detected by mass spectrometry. The het-

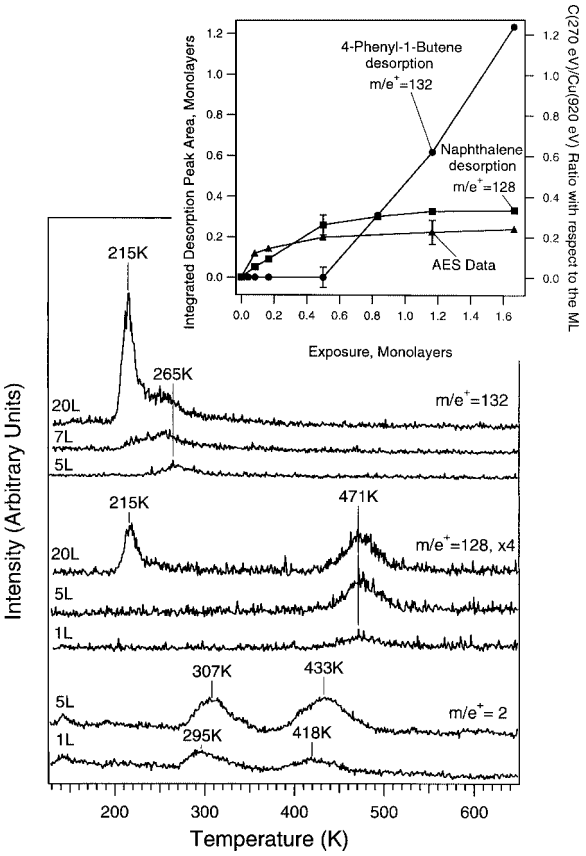

Figure 2. Temperature-programmed desorption/reaction studies of 4-phenyl-1-butene on a $Cu_3Pt(111)$ surface. The inset shows the balance of TPR/D and AES yields calibrated with respect to the monolayer.

erogeneous reactions like the one described herein have the potential for being very useful in production of large hydrocarbons and further studies of chemical transformations of long-chain aliphatic hydrocarbons are under way.

One more interesting point can be learned from the studies of H_2 ($m/e^+ = 2$) evolution during chemical reaction of 4-phenyl-1-butene on the $Cu_3Pt(111)$ surface as a function of the initial dose of 4-phenyl-1-butene. All the hydrogen molecules are desorbed into the gas phase below 450 K. At the same time, reaction-limited naphthalene desorption does not start until approximately 450 K. According to the literature [32–34], the dehydrocyclization reaction for C_6 linear hydrocarbons is described as a two-step process: (1) loss of the hydrogen atoms leading to the formation of hexa-σ-bonded hexatriene-like intermediate, and (2) cyclization accompanied by the loss of two more terminal hydrogen atoms. The second step of this process is actually a combination of two steps. In the previous reports [32–34] the evolution of hydrogen produced by the loss of the two terminal hydrogen atoms from the hexatriene intermediate was too close to the temperature of the thermal reaction/desorption of the final product, benzene, to distinguish these two steps. However, slightly higher temperature for the evolution of naphthalene formed from 4-phenyl-1-butene in our studies allows us to make a conclusion about the actual rate-determining step in cyclization processes on this surface. Since all the hydrogen released by 4-phenyl-1-butene desorbs well below the temperature of reaction-limited desorption of naphthalene, it is clear that the formation of carbon–carbon bond rather than the loss of two terminal hydrogen atoms from the hexatriene-like intermediate is the rate-limiting step of the dehydrocyclization process.

4. Conclusions

The dehydrocyclization reaction of 4-phenyl-1-butene on a $Cu_3Pt(111)$ surface was studied by thermal desorption mass spectrometry and Auger electron spectroscopy. It was shown that the main reaction product was naphthalene desorbing from the surface at 470 K. The minor pathway for the surface reaction of 4-phenyl-1-butene was decomposition as confirmed by AES. This study confirms the generality of the dehydrocyclization processes on single crystal surfaces and suggests that large hydrocarbon molecules can successfully undergo this transformation on a $Cu_3Pt(111)$ surface with a high percentage of the product desorbing into the gas phase. Rate-determining step for this reaction was found to be the carbon–carbon bond formation.

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