



Hydrogenation and dehydrogenation of cyclohexene on Pt(100): A sum frequency generation vibrational spectroscopic and kinetic study

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Received 12 July 2005; accepted for publication 16 September 2005
Available online 10 November 2005

Abstract

Sum frequency generation (SFG) vibrational spectroscopy and kinetic measurements were performed during cyclohexene hydrogenation/dehydrogenation over a range of pressures (10^{-8} –5 Torr) and temperatures (300–500 K) on the Pt(100) surface. Upon adsorption at pressures below 1.5 Torr and at 300 K, cyclohexene dehydrogenates to form π -allyl c -C₆H₉ and hydrogenates to form cyclohexyl (C₆H₁₁) surface intermediates. Increasing the pressure to 1.5 Torr produces adsorbed 1,4-cyclohexadiene, π -allyl c -C₆H₉, and cyclohexyl species. These adsorbed molecules are found both in the absence and presence of excess hydrogen on the Pt(100) surface at high pressures and up to 380 K and 360 K, respectively. π -Allyl c -C₆H₉ and cyclohexyl are adsorbed on the surface up to 440 K in the absence of excess hydrogen and 460 K in the presence of excess hydrogen, at which point they are no longer detectable by SFG. Kinetic studies in the absence of excess hydrogen show that the apparent activation energy for the dehydrogenation pathway (14.3 ± 1.2 kcal/mol) is similar to that of the hydrogenation pathway (12.9 ± 0.6 kcal/mol). Different apparent activation energies are observed for the dehydrogenation pathway (22.4 ± 1.6 kcal/mol) and the hydrogenation pathway (18.8 ± 0.9 kcal/mol) in the presence of excess hydrogen.

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Keywords: Catalytic reaction; C₆ hydrocarbons; Pt(100); Pt(111); Hydrogenation; Dehydrogenation; Sum frequency generation; SFG

1. Introduction

Cyclohexene surface chemistry on single crystal platinum has received significant attention since it is considered prototypical of cyclic hydrocarbon conversion processes during naphtha reforming

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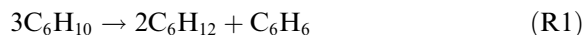
[1]. Cyclohexene is not only one of the possible reaction intermediates when cyclohexane (C_6H_{10}) is dehydrogenated to benzene (C_6H_6), but also a reactant molecule that can be either hydrogenated to cyclohexane or dehydrogenated to benzene. Cyclohexene hydrogenation/dehydrogenation on the platinum surface is found to be structure sensitive [2,3] since its turnover rates are sensitive to surface structure.

Cyclohexene adsorption on Pt(100) at low pressures ($\leq 10^{-6}$ Torr) has been studied using thermal desorption spectroscopy (TDS) [4–6], reflection absorption infrared spectroscopy (RAIRS) [4], and electron energy loss spectroscopy (EELS) [4]. Briefly, cyclohexene exists in a di- σ form on Pt(100) at 100 K. As the surface temperature is increased to 200 K, di- σ cyclohexene is converted to π -allyl c- C_6H_9 . Further increasing the surface temperature leads to dehydrogenation and benzene desorption [4]. The surface species present at low pressures/temperatures under ultra-high vacuum (UHV) may not necessarily be the same as those species that are adsorbed under catalytically relevant conditions found at high pressures/temperatures or under an excess of hydrogen. The observed surface species at various temperatures are summarized in Scheme 2(e).

Cyclohexene adsorption on the Pt(111) surface has been studied using various techniques such as TDS [6], bismuth post dosing TDS (BPTDS) [6,7], laser-induced thermal desorption (LITD) [5], high-resolution electron energy loss spectroscopy (HREELS) [4,5], RAIRS [8], and SFG [9–14] under a broad range of pressure (10^{-8} –5 Torr). Briefly, at low pressures ($\leq 10^{-6}$ Torr) on Pt(111) cyclohexene adsorbs molecularly in a di- σ form at 100 K and is dehydrogenated to π -allyl c- C_6H_9 as the surface temperature is increased to 200 K [7,8]. π -Allyl c- C_6H_9 further dehydrogenates to benzene as the surface temperature is increased up to 300 K and desorption and decomposition of benzene at temperatures ≥ 300 K [5,7,8]. Increasing the cyclohexene pressure to 1.5 Torr at 298 K interestingly results in the dehydrogenation of π -allyl c- C_6H_9 to 1,4-cyclohexadiene. Increasing the surface temperature in the absence of excess hydrogen results in hydrogenation of 1,4-cyclohexadiene to π -allyl c- C_6H_9 at 323 K. Similarly, π -Allyl

c- C_6H_9 dehydrogenates to benzene as the temperatures increase to 453 K [9]. The observed surface species at various temperatures and pressures are summarized in Scheme 2(b), (d), and (f).

In the presence of excess hydrogen (15 Torr), it was found that 1,4-cyclohexadiene and 1,3-cyclohexadiene co-exist on Pt(111) at 303 K and subsequently hydrogenate to π -allyl c- C_6H_9 at 323 K. As the surface temperature is increased to 400 K, π -allyl c- C_6H_9 dehydrogenates to 1,3-cyclohexadiene [9]. Kinetic measurements of cyclohexene hydrogenation/dehydrogenation have also been investigated on the Pt(111) surface. Yang et al. [12] have reported that cyclohexene hydrogenation occurs through two reaction pathways: disproportionation (R1) or reductive hydrogen addition (R3) by adsorbed hydrogen. The dehydrogenation of cyclohexene was reported to occur through stepwise dehydrogenation (R2) or disproportionation (R1).



In this study, we investigate catalytic reactions of cyclohexene on the Pt(100) single crystal surface with SFG vibrational spectroscopy and gas chromatography (GC) in a range of pressures (10^{-6} –5 Torr of cyclohexene) and temperatures (298–500 K) in the presence and absence of excess hydrogen (15 Torr). SFG measurements show the existence of three distinct surface intermediates on Pt(100): π -allyl c- C_6H_9 , 1,4-cyclohexadiene (C_6H_8), and cyclohexyl (C_6H_{11}). We find that cyclohexene forms both hydrogenated and dehydrogenated products in the presence and absence of excess hydrogen. Differences between the Pt(100) and Pt(111) surfaces exist as the pressure of cyclohexene and surface temperature in the presence and absence of excess hydrogen are varied. On the Pt(100) surface, π -allyl c- C_6H_9 and cyclohexyl exist on the surface until the pressure of cyclohexene is increased to 1.5 Torr at which point 1,4-cyclohexadiene is co-adsorbed with π -allyl c- C_6H_9 and cyclohexyl. π -Allyl c- C_6H_9 is the dominant surface species on Pt(111) until the cyclohexene pressure is increased to 1.5 Torr upon

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