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Reaction kinetics and in situ sum frequency generation surface vibrational spectroscopy studies of cycloalkene hydrogenation/dehydrogenation on Pt(111): Substituent effects and CO poisoning

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Abstract

The influence of substituent effects and CO poisoning were examined during the hydrogenation/dehydrogenation of cycloalkenes (cyclohexene and 1- and 4-methylcyclohexene) on a Pt(111) single crystal. Reaction rates for both hydrogenation and dehydrogenation decreased when a methyl group was added to the cycloalkene ring. The location of a methyl group relative to the C=C double bond was influential in the overall kinetics for both reaction pathways. All cycloalkenes demonstrated "bend-over" Arrhenius behavior, after which rates for hydrogenation and dehydrogenation decreased with increasing temperature (inverse Arrhenius behavior). This is explained in terms of a change in surface coverage of the reactive cycloalkene. The potential importance of hydrogen effects is discussed. Introduction of CO in the Torr pressure range (0.015 Torr) led to a decrease in turnover frequency and increase in apparent activation energy for both the hydrogenation and dehydrogenation of all cycloalkenes. Sum frequency generation (SFG) surface vibrational spectroscopy revealed that upon adsorption, the three cycloalkenes form a surface species with similar molecular structure. SFG results under reaction conditions in the presence of CO demonstrated that the cycloalkene coverage is low on a CO-saturated surface. Substituted cyclohexenes were more sensitive than cyclohexene to the presence of adsorbed CO, with larger increases in the apparent activation energy, especially in the case of dehydrogenation. A qualitative explanation for the changes in activity with temperature and the increase in apparent activation energy for cycloalkene hydrogenation/dehydrogenation in the presence of CO is presented from a thermodynamic and kinetic perspective.

Keywords: Cycloalkene; Hydrogenation; Dehydrogenation; Pt(111); Co poisoning; Substituent effects; Sum frequency generation

1. Introduction

Chemical reactions of cycloalkenes on metal surfaces have attracted considerable interest due to their importance in many aspects of heterogeneous hydrocarbon conversion chemistry including hydrogenation, dehydrogenation, ring opening, and isomerization. The hydrogenation and dehydrogenation reactions of cycloalkenes have been widely used as a model system for fundamental studies of catalysis and a testing ground for new heterogeneous catalysts [1–5]. For some cycloalkenes, their dehydrogenation reactions are considered a major step in the dehydrocyclization of n-alkanes to aromatics, an important reaction in the catalytic-reforming process [6]. Cyclohexene (C_6H_{10}) is one of most extensively studied cycloalkenes.

Cyclohexene adsorption on Pt(111) at low pressures ($<10^{-6}$ Torr) has been studied using various surface-analytical techniques, including thermal desorption spectroscopy (TDS) [7], bismuth postdosing TDS (BPTDS) [7,8], laser-induced thermal desorption (LITD) [9], high-resolution electron energy loss spectroscopy (HREELS) [9,10], and reflection absorption infrared spectroscopy (RAIRS) [11]. Cyclohexene exists in a di-σ form on Pt(111) at 100 K, converting to π-allyl c-C_6H_9 at ~200 K [8,11]. At ~300 K, π-allyl c-C_6H_9 converts to benzene. Further heating induces desorption and decomposition of benzene [8,9,11]. Cyclohexene surface reactions on Pt(111) at

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high pressure (1.5 Torr) was also studied by sum frequency generation (SFG) vibrational spectroscopy [12]. Various surface species were observed during the reactions in the range of 303–483 K. On adsorption at 303 K, cyclohexene is dehydrogenated to form 1,4-cyclohexadiene (C_6H_8). At 323 K, this species converts to π-allyl c-C_6H_9 intermediate. At temperatures above 423 K, benzene coexists with C_6H_9 on the surface. Kinetic studies of cyclohexene hydrogenation/dehydrogenation reactions on Pt(111) have also been reported [13,14].

In this study, substituent effects by methyl groups and poisoning effects of coadsorbed CO on the hydrogenation/dehydrogenation reactions of cycloalkenes (cyclohexene and 1- and 4-methylcyclohexenes) on Pt(111) were investigated. Substituent effects, concerning the chemical effect of functional groups replacing hydrogen atoms on reactivity, can greatly influence activity and selectivity in catalytic reactions [15–17]. The poisoning of catalysts, either intentionally or unintentionally, can have a dramatic effect on catalytic activity and selectivity [18–21].

An example of intentional poisoning is the addition of sulfur to platinum hydrocarbon conversion catalysts. Sulfur is added to commercial naphtha-reforming catalysts (Pt/Al_2O_3) to suppress excessive hydrogenolysis. It is postulated that sulfur adsorbs irreversibly to coordinatively unsaturated surface atoms or restructures the surface [18]. A reaction in which products adsorbs very strongly to the catalyst surface and inhibits further turnover is an example of unintentional self-poisoning. Catalyst poisons are often introduced to catalysts from feedstocks containing a low level of the poison but a sufficient level to deactivate catalysts. Few studies have been conducted on the influence of CO poisoning on hydrocarbon conversion reactions [19–23]. Adding CO in the Torr range during ethylene hydrogenation led to a doubling of the apparent activation energy on Pt(111) [21–23], whereas similar CO pressures had little influence on the apparent activation energy on Pt nanoparticle arrays [23], but both catalysts exhibited a several order of magnitude decrease in activity. Damiani and Butt [19,20] used the hydrogenolysis of methylcyclopropane as a probe reaction to investigate the structure sensitivity of the deactivation of Pt/Al_2O_3 and Pt/TiO_2 catalysts by CO. They demonstrated that larger Pt particles supported on Al_2O_3 were more sensitive to CO poisoning than smaller particles, whereas TiO_2-supported catalysts were more susceptible to CO poisoning than the Al_2O_3 supported catalysts regardless of Pt particle size.

Kinetic studies were conducted to measure reaction rates and apparent activation energies for the three cycloalkenes in the absence and presence of CO. Comparative studies between the three cycloalkenes demonstrated that the hydrogenation/dehydrogenation reaction rates were strongly affected by the existence of alkyl group and its proximity to the C=C double bond. Adding an alkyl group to the cycloalkene ring had a significant effect on overall catalytic activity but little effect on the selectivity to either product. Both reactions were poisoned by coadsorbed CO for all three cycloalkenes and led to an increase in the apparent activation energy. The change in the apparent activation energy due to CO poisoning were similar for the hydrogenation and the dehydrogenation of cyclohexene and 1-methylcyclohexene, but significantly greater for the dehydrogenation of 4-methylcyclohexene. In addition, SFG vibrational studies were carried out to identify surface intermediates during the hydrocarbon conversion reactions. Based on kinetic and SFG results, we discuss substituent and CO poisoning effects on cycloalkene hydrogenation/dehydrogenation reactions. A qualitative explanation for the changes in activity with temperature and the increase in apparent activation for cycloalkene hydrogenation/dehydrogenation in the presence of CO is discussed from a mechanistic standpoint.

2. Experimental

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 comprises a UHV chamber with a base pressure of 4×10^{-10} Torr and a high-pressure cell in which high-pressure catalysis studies were carried out. The HP cell was equipped with a reaction loop containing a recirculation pump and a septum for gas abstraction and gas chromatography (GC) analysis. For GC measurements, a recirculation pump constantly mixed the reactant and product gases in the HP cell, and periodic sampling allowed measurements of the gas-phase composition. All kinetic studies were carried out in 1.5 Torr cycloalkenes (cyclohexene and 1- and 4-methylcyclohexenes) and 15 Torr H_2 in the presence or absence of 0.015 Torr CO in the temperature range 295–530 K. Reactions were typically run for 30 min; initial turnover rates (TORs) were calculated from accumulation plots (C_6H_{12} or C_6H_6 turnover number vs time).

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 beam at 1300–3200 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 p-polarized sum frequency output from the Pt(111) crystal was collected by a photomultiplier and a gated integrator.

The theory of SFG for surface studies has been described in detail previously [24–26]. Briefly, SFG is a second-order nonlinear optical process in which an infrared laser beam at ω_{IR} is combined with a visible laser beam at ω_{VIS} to generate a sum frequency output at $\omega_{SF} = \omega_{IR} + \omega_{VIS}$. This process is allowed only in a medium without centrosymmetry under the electric dipole approximation. Platinum bulk is centrosymmetric, and its contribution to SFG is usually negligible. Isotropic gases in the HP cell do not generate SFG; only the metal surface and adsorbates on the surface can generate SFG under the electric dipole approximation. The SFG signal, I_{SF}, is related to the incident visible (I_{VIS}) and infrared (I_{IR}) beam intensities, and to the second-order susceptibility of the media ($\chi^{(2)}$), as

$$I_{SF} \propto |\chi^{(2)}|^2 I_{VIS} I_{IR}. \quad (1)$$