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Hydrocarbon conversion on palladium catalysts

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Abstract

The reaction pathways for acetylene trimerization and hydrogenation, and ethylene hydrogenation, catalyzed by palladium, are explored using a range of surface-sensitive techniques. Reflection–absorption infrared spectroscopy (RAIRS) and low-energy electron diffraction (LEED) show that ethylene is di-σ-bonded on clean Pd(1 1 1), but forms a π-bonded species on a hydrogen pre-covered surface, where the transformation is induced by sub-surface hydrogen. Catalytic ethylene hydrogenation proceeds on an ethylidyne-covered Pd(1 1 1) surface, and it is found that ethylene can still adsorb onto palladium in spite of the presence of an ethylidyne overlayer, and is still in a di-σ-configuration. The rates of ethylidyne formation, and removal by hydrogen are measured independently, where the latter rate is found to be first order in hydrogen pressure. The ethylidyne coverage is measured under reaction conditions as a function of $P(H_2)/P(C_2H_4)$ and found to decrease to ∼1/3 of saturation. Benzene is formed from acetylene on clean Pd(1 1 1) via a metallocyclic C_4H_4 intermediate. This further reacts with a third acetylene to form benzene. However, catalytic cyclotrimerization proceeds in the presence of a carbonaceous layer, which consists of vinylidene species ($CH_2{=}C{=}$). Thus, at high pressures, benzene is formed by reaction between acetylene adsorbed on the vinylidene-covered palladium surface and adsorbed vinylidene itself. The addition of high pressures of hydrogen to the reaction mixture forms a more open surface covered by a mixture of ethylidyne and vinylidene species, rationalizing the observed increase in the benzene formation rate with the addition of hydrogen.

Keywords: Hydrogenation; Cyclotrimerization; Pd(1 1 1) model catalysts; Reflection–adsorption infrared spectroscopy; Low-energy electron diffraction; Ethylene; Acetylene; Hydrogen; Ethylidyne; Vinylidene

1. Introduction

Palladium-catalyzed acetylene cyclotrimerization and alkene and alkyne hydrogenation provide ideal candidates for fundamental investigations of catalytic reaction pathways. This is because these reactions proceed in ultrahigh vacuum where, for example, benzene is formed in temperature-programmed desorption when a Pd(1 1 1) single crystal is saturated with acetylene [1], and adsorbed atomic hydrogen reacts with acetylene or ethylene to yield ethylene and ethane, respectively [2]. In addition, palladium single crystals catalyze these reactions at high pressures with identical kinetics to those of supported systems.

Palladium-catalyzed hydrogenation of ethylene and acetylene are classical catalytic reactions that have been studied for many years. Early on it was established that adsorbed atomic hydrogen adds across the double or triple bond of the adsorbed hydrocarbon [3–14], in the so-called Horiuti-Polanyi model. These hydrogenation reactions were extensively studied in the classical work of Bond [12] where temperature-dependent hydrogen reaction orders of unity or greater are measured, while the order in alkene or alkyne was found to be negative. The latter effect can be rationalized by assuming that hydrogen adsorption is blocked by the alkene or alkyne, while there is no clear explanation for the hydrogen pressure dependences. It was later discovered that a Pt(1 1 1) single crystal model ethylene hydrogenation catalyst was covered by ethylidyne species during reaction [13], although these react with hydrogen too slowly to account for ethylene formation and were proposed to merely act as spectator species.

More recently, it has been demonstrated that theoretical strategies can be used to calculate catalytic rates [15–18]. This has been achieved by calculating heats of adsorption

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and activation energies quantum mechanically using density functional theory (DFT) and by using these energies as inputs into Monte Carlo calculations to predict reaction rates [19]. Such calculations agree extremely well with measured catalytic rates for acetylene hydrogenation. However, energies calculated by DFT are only accurate to a few kiloJoules per mole, and pre-exponential factors were assumed to be "normal" values, for example, $1 \times 10^{13}\,s^{-1}$ for first-order reactions. Such a good agreement between calculated and measured global rates may therefore arise from a cancellation of errors and does not guarantee that it correctly reproduces all of the elementary reaction steps. Nevertheless, these results do indicate that theory has developed to the point at which realistic connections can be made between theory and experiment.

Acetylene cyclotrimerization was first referred to (to our knowledge) in 1915 [20]. Subsequent studies introduced the proposition that one of the roles of the catalyst was to provide a structural template for benzene synthesis [21], as well as lowering the reaction activation energy. This notion was later borne out experimentally where various tailored surface structures could be fabricated by carefully cutting single crystals to form faces with known orientations [22]. These experiments clearly demonstrated that the hexagonal (1 1 1) face of palladium was far more active for the synthesis of benzene from acetylene than others [23,24].

In the early 1980s, it was shown that a monolayer of acetylene chemisorbed on Pd(1 1 1) reacted to form benzene, a result published almost simultaneously by three groups [1,25–27]. Although the reaction, in this case, is not catalytic, this discovery provided an ideal test system for studying a reasonably complicated organic synthetic reaction pathway in some detail, using a wide array of surface-sensitive strategies. Subsequently, several surfaces were found to catalyze the same reaction [28–31].

The following paper outlines how surface science strategies have resulted in the discovery of various surface species on the (1 1 1) face of palladium and how their roles in the catalytic reaction have been identified. This surface analytical information has been used to paint a picture of the working, catalytically active surface, postulate plausible catalytic reaction pathways, and test them.

2. Experimental methods

A wide range of ultrahigh vacuum experimental strategies was used to attack the problem of understanding the catalytic pathways. These include high-pressure catalytic reactions to monitor reaction kinetics at high-pressures [32] and temperature-programmed desorption (TPD) to monitor similar effects in ultrahigh vacuum [1,27]. Surface species have been scrutinized by X-ray and ultraviolet photoelectron spectroscopies [1]. More recently, laser-induced thermal desorption (LITD) [33–35] and nuclear magnetic resonance spectroscopies [36] have been used to monitor the nature of the surface species. Two techniques deserve particular mention. The first is photoelastic-modulation reflection–absorption infrared spectroscopy (PEM-RAIRS) [37–40], which is used to measure the species present on the surface in the presence of a high pressure (in the Torr range) of reactants, and the second is low-energy electron diffraction (LEED) [41]. As conventionally applied, the analysis of surface structures using LEED requires the presence of an ordered overlayer, which, since many systems, in particular small hydrocarbons on metal surfaces, do not form ordered overlayers, has limited its applicability. Attempts to measure overlayer structures from the diffuse background scattering induced by the presence of a disordered adsorbate have been hampered by the weakness of the diffuse background signal [42]. It has however been demonstrated that the intensities of the (1 × 1) Bragg spots are modified by the presence of a disordered overlayer by about two orders of magnitude more than the intensity of the diffuse background scattering [43,44]. This therefore can be measured more easily than the background scattering and has proven very effective in measuring structures of disordered overlayer of small hydrocarbons on Pd(1 1 1) surfaces and allowed the results of these structure determinations to be compared with DFT predictions and infrared measurements.

3. Results and discussion

3.1. *Ethylene hydrogenation: the structure and chemistry of ethylene on clean and hydrogen-covered Pd(1 1 1)*

Measurement of the catalytic ethylene and hydrogen pressure dependences for ethylene hydrogenation yields hydrogen reaction orders slightly larger than unity, and negative reaction orders in ethylene pressure [12]. The structure of ethylene on Pd(1 1 1) has been investigated using RAIRS where adsorbed ethylene yielded vibrational features at ~1103 and $2900\,cm^{-1}$. Using a correlation diagram constructed using the frequencies of organometallic analogs, it was found that ethylene on clean Pd(1 1 1) was di-σ-bonded [46]. The structure of a disordered overlayer of ethylene was also measured on Pd(1 1 1) from the LEED *I*/*V* curves of the substrate (1 × 1) Bragg spots [47]. In this case, a global structural search was carried out by calculating the Pendry *R*-factor by allowing one carbon to move over 21 points within a reduced surface Wigner-Seitz cell, and simultaneously varying the azimuthal angle and height. The molecule was constrained to be parallel to the surface with a C–C bond length fixed at 1.45 Å. The best-fit structure was then used as an input into a tensor-LEED program [48] in order to optimize the structure. The resulting structural parameters are displayed in Table 1 and the structure depicted in Fig. 1. This reveals that ethylene is indeed di-σ-bonded on Pd(1 1 1) and adsorbed on a bridge site. It has been found previously using LEED that tilted ethylenic species form on Pt(1 1 1) surfaces [49]