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The kinetics of ethylene hydrogenation catalyzed by metallic palladium

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The activity of Pd(111) for ethylene hydrogenation is measured using a high-pressure reactor incorporated into an ultrahigh vacuum chamber for temperatures between 300 and 475 K, ethylene pressures between 50 and 300 Torr and hydrogen pressures from 45 to 600 Torr. The reaction rate is found to be rapid with turnover frequencies up to ~400 reactions/site/s (where rates are referenced to the atom site density on the (111) face of palladium). The measured activation energy is ~35 kJ/mol. A hydrogen reaction order of ~1.02 was found at a reaction temperature of 300 K and an ethylene pressure of 100 Torr, where the hydrogen reaction order was found to depend on temperature. A negative reaction order of ~−0.22 was found in ethylene pressure at a reaction temperature of 320 K and a hydrogen pressure of 100 Torr. The reaction rates are in good agreement with values obtained on silica-supported palladium and with other work on palladium single crystals.

KEY WORDS: ethylene hydrogenation; Pd(111) single crystal; reaction kinetics.

1. Introduction

The catalytic hydrogenation of ethylene has been studied for many years, where the general reaction pathway, involving the sequential addition of atomic hydrogen across the carbon–carbon double bond, is well established [1–8]. More recently, surface science studies in ultrahigh vacuum of ethylene on Pd(111) single crystals [9–13] and palladium nanoparticles supported on planar alumina substrates [14–17] have yielded additional insights into the chemistry at the surface. Ethylene adsorbs on Pd(111) at low coverages in a di-σ-configuration with a heat of adsorption of ~79 kJ/mol. As the ethylene coverage increases, repulsive lateral interactions between adsorbed ethylene molecules lead to a weakening of the heat of adsorption as evidenced by a significant ethylene desorption rate being detected at lower temperatures in TDP [12]. Such more weakly adsorbed ethylene is often referred to as π-bonded, although there is no direct infrared spectroscopic evidence of changes in adsorption geometry at higher coverages. In addition, the presence of sub-surface hydrogen weakens the ethylene adsorption and, in this case, π-bonded ethylene is identified on the surface using infrared spectroscopy and low-energy electron diffraction [11, 13]. It is generally assumed that more weakly bound ethylene hydrogenates more easily than more strongly bound (di-σ-bonded) ethylene implying that ethylene hydrogenation should be facilitated both by high ethylene coverages and by the presence of sub-surface hydrogen. The ethylene hydrogenation pathway has been investigated by grafting the ethyl intermediate to ethane onto Pd(111) using ethyl iodide [18]. In this case, it was found that the rate constant for the addition of the first hydrogen to form an ethyl species was smaller than that to add the second hydrogen. It should be emphasized that this does not necessarily imply that the addition of the first hydrogen is the rate-limiting step in the catalytic reaction since this also depends on the reactant coverages and the steady-state ethylene coverage is likely to be higher than that of the ethyl intermediate, thus potentially overwhelming any differences in the intrinsic rate constants.

Recent experiments with palladium nanoclusters supported on planar alumina films in ultrahigh vacuum have suggested that subsurface hydrogen reacts with adsorbed, weakly bound ethylene to yield ethane [16, 17]. A small amount of ethane is formed in temperature-programmed desorption (TPD) when ethylene is adsorbed on hydrogen-covered Pd(111), while a larger amount is produced on supported nanoclusters since, in the latter case, the hydrogen is constrained to be close to the surface. It therefore appears that sub-surface hydrogen plays a central role in ethylene hydrogenation, both as a reactant and by modifying the adsorption state of ethylene. Note that a substantial amount of ethylene is formed in TPD when acetylene is adsorbed on hydrogen-covered Pd(111) [19–21]. In this case, acetylene adsorbs more strongly on the surface than ethylene thereby increasing the desorption yield. However, in this case, the π-orbitals oriented parallel to the surface are also available for reaction with surface hydrogen, which may also contribute to the increase in ethylene yield [20].

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It has also been suggested that palladium-catalyzed ethylene hydrogenation is structure sensitive, with the (111) face being relatively inactive and, on this basis, that the activity of small nano-clusters of palladium was ascribed to the larger proportion of none-(111) facets exposed on the small nano-particles [14,15]. The catalytic activity and kinetic parameters for acetylene hydrogenation [23] and cyclotrimerization [24] have been measured using palladium in a high-pressure reactor incorporated into an ultrahigh vacuum chamber and a relatively high activity of Pd(111) single crystal model catalysts for ethylene hydrogenation has also been recently reported [25]. In the following, the results of a kinetic study of ethylene hydrogenation at elevated pressures are reported.

2. Experimental

The apparatus that was used for these experiments has been described in detail elsewhere [26,27]. Briefly, however, it consists of a bakeable, stainless-steel, ultrahigh vacuum chamber operating at a base pressure of 1×10^{-10} Torr following bakeout. It is equipped with a quadrupole mass analyzer for residual gas analysis, leak testing and TDP studies.

The apparatus also incorporates a co-axial, high-pressure reactor, which can be sealed and filled to 1 atm while maintaining ultrahigh vacuum ($\sim 2 \times 10^{-10}$ Torr) in the rest of the apparatus. This is attached to a loop and the gas recirculated by a pump. Reaction rates are measured directly from the product accumulation curves for low ($<1\%$) conversions.

The palladium sample is attached to the end of the sample manipulator and can be resistively heated to ~2000 K or cooled to 80 K by thermal contact to a liquid-nitrogen-filled reservoir. The sample is cleaned using a standard procedure, which consists of heating at 1000 K in $\sim 4 \times 10^{-8}$ Torr of oxygen and then annealing at 1200 K *in vacuo* to remove any remaining oxygen. Since the carbon KLL Auger feature is effectively obscured by a strong palladium peak, Auger spectroscopy is not particularly sensitive to the presence of small amounts of carbon on the surface so that the absence of carbon was determined by dosing the surface with oxygen and performing a TPD experiment, where the sample was judged to be free from carbon when no CO desorption was detected. The ethylene used for these experiments (Matheson, Research Grade) was transferred from the cylinder to a glass bottle and further purified by repeated bulb-to-bulb distillations and its cleanliness monitored either mass spectroscopically or using the gas-chromatograph. The hydrogen (Praxair, 99.9999%) was used directly from the cylinder. The high-pressure reactor was ballasted to 1 atm using nitrogen to ensure that the gas circulation rates were identical for all experiments.

3. Results

The rate of ethane formation from reaction between ethylene and hydrogen catalyzed by palladium was measured from the slope of the product accumulation curve for conversions less than 1%. The turnover frequencies (TOF in reactions per site per second) were normalized to the number of exposed palladium atom on a (111) surface. The temperature dependence is displayed in figure 1, which plots ln(TOF) versus $1/T$ where the reaction was carried out between 300 and 475 K. This yields a good straight line and the reaction activation energy measured from the slope yields 35 ± 1 kJ/mol. The ethylene pressure dependence was measured, initially by keeping the hydrogen pressure constant at 100 Torr, with a reaction temperature of 320 K, and by varying the ethylene pressure between 50 and 300 Torr. The resulting plot of ln(TOF) versus ln(Ethylene Pressure), where ethylene pressures are measured in Torr, is displayed in figure 2. This again yields a good straight line where the reaction order measure from the slope is -0.22 ± 0.01.

The hydrogen pressure dependence measured between 50 and 650 Torr of hydrogen at a temperature of 300 K using an ethylene pressure of 100 Torr is displayed in figure 3 as a plot of ln(TOF) versus ln(Hydrogen Pressure). This again yields a good straight line with a reaction order in hydrogen pressure of 1.02 ± 0.02. It has been found previously that the hydrogen reaction order for acetylene hydrogenation depended on temperature [28]. Accordingly, the reaction

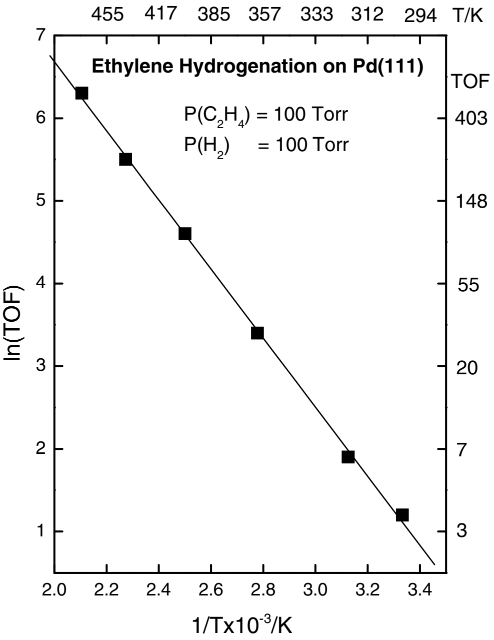

Figure 1. Arrhenius plot of ln(TOF) versus $1/T$ for ethylene hydrogenation catalyzed by palladium, with an ethylene pressure of 100 Torr and a hydrogen pressure of 100 Torr.

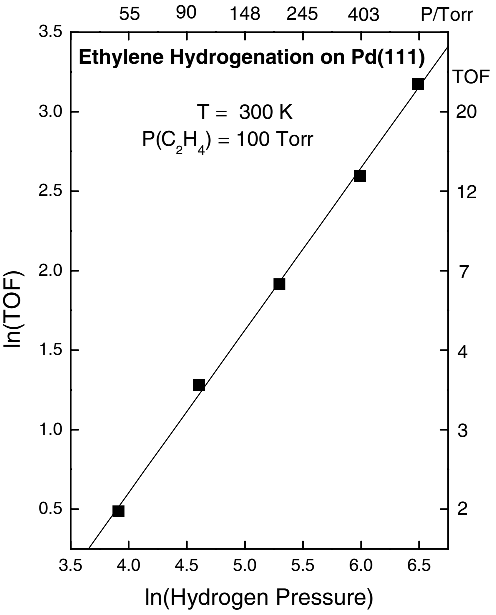

Figure 2. Plot of ln(TOF) versus ln(Ethylene Pressure) for ethylene hydrogenation catalyzed by palladium, where the ethylene pressure is measured in Torr at a reaction temperature of 320 K with a hydrogen pressure of 100 Torr.

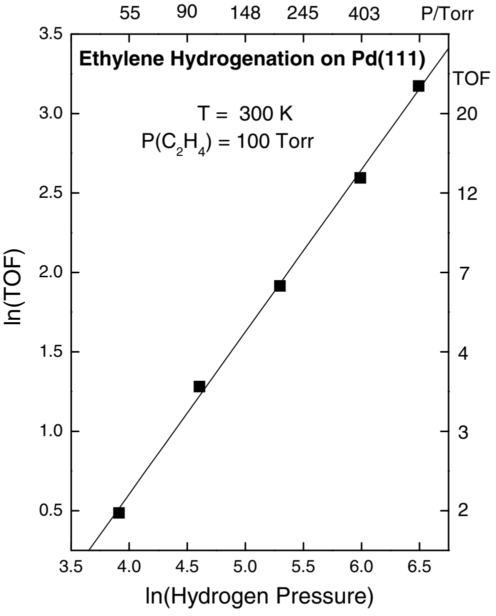

Figure 3. Plot of ln(TOF) versus ln(Hydrogen Pressure) for ethylene hydrogenation catalyzed by palladium, where the hydrogen pressure is measured in Torr at a reaction temperature of 300 K with an ethylene pressure of 100 Torr.

order in hydrogen pressure was measured as a function of temperature, and the results are displayed in figure 4. This shows that the hydrogen reaction order is indeed dependent on the reaction temperature, increasing from 1.02 ± 0.02 at 300 K to ~1.25 at 365 K.

4. Discussion

The measured reaction activation energy for ethylene hydrogenation catalyzed by Pd(111) of 35 ± 1 kJ/mol (figure 1) 320 K is in excellent agreement with values measured on silica-supported alumina (~35 kJ/mol [29]). The order in ethylene at 320 K using a hydrogen pressure of 100 Torr is −0.22 (figure 2). A negative reaction order of −0.03 was found on silica-supported palladium, and is within the range found here, but precise comparisons are difficult because this value clearly depends on reaction conditions. The hydrogen pressure dependence is greater than unity between 300 and 365 K on Pd(111) (figure 4), while a value of 0.66 was found on silica-supported palladium at a reaction temperature of 243 K [29]. Linearly extrapolating the data of figure 4 to a reaction temperature of 243 K yields a value of ~0.8, in better agreement with that measured on silica supported palladium [29]. The kinetic data of Figures 1, 2 and 3 can be summarized as:

Rate $= 8.5 \times 10^4\ P(H_2)^{1.02\ \pm\ 0.02}\ P(C_2H_4)^{-0.22\ \pm\ 0.01} \exp(-34700 \pm 800/RT)$ reactions/site/s where the pressures are measured in Torr, the activation energy in Joules, and the reaction rate is referenced to the palladium atom site density on the (111) face. These reaction kinetics are similar to those found on Pt(111) [30]. Using this equation to calculate the reaction rate under the conditions used by Rupprechter [25], using 5 mbar of H_2, 5 mbar of C_2H_4 using a Pd(111) sample leads to a value of ~0.3 reactions/site/s, in reasonable agreement with the experimental value of ~1/site/s obtained in that work.

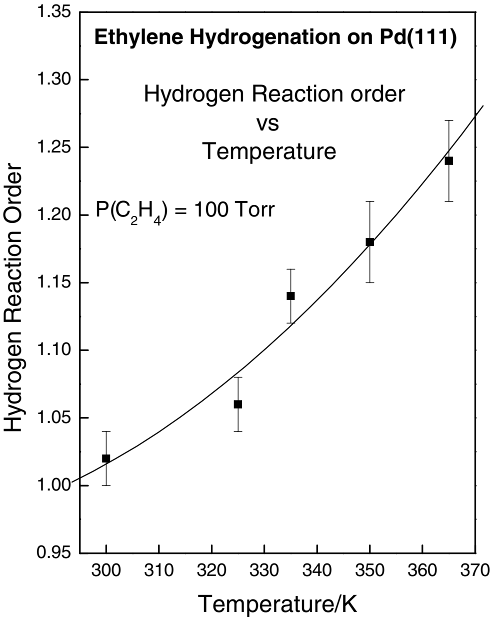

Figure 4. Plot of the hydrogen reaction order as a function of reaction temperature for ethylene hydrogenation catalyzed by palladium, where the ethylene pressure is held constant at 100 Torr.

The general ethylene hydrogenation pathway has been well established with atomic hydrogen reacting sequentially with adsorbed ethylene to form ethane [1–8] in the so-called Horiuti–Polanyi model [31,32]. The hydrogen reaction order is greater than unity at temperatures above 300 K and a value of ~0.66 has been measured at 243 K on silica-supported palladium [29]. In the case of acetylene hydrogenation, such relatively large and temperature-dependent reaction orders were rationalized by noting that the nature of the carbonaceous layer was affected by the addition of hydrogen to the reaction mixture [28]. In the absence of hydrogen, the palladium surface is covered by a vinylidene overlayer that strongly suppresses acetylene adsorption [33, 34]. As the partial pressure of hydrogen increases, a portion of the surface vinylidene converts to ethylidyne species [28]. This provides a more open surface allowing more acetylene and hydrogen to adsorb thereby increasing the catalytic rate and this effect is at least partially responsible for the large hydrogen pressure reaction orders. However, in the case of ethylene hydrogenation, ethylidyne species are formed directly from ethylene [35]. Ethylene can adsorb easily on ethylidyne-saturated Pd(111) even in ultrahigh vacuum with a saturation coverage only slightly less than on the clean surface [35]. It has been shown that the ethylidyne coverage decreases as the hydrogen pressure increases during ethylene hydrogenation [36] so that this will have an effect on the hydrogen pressure dependence in a similar way as with acetylene hydrogenation. However, in view of the fact that the ethylidyne layer only slightly inhibits ethylene adsorption onto the surface, this is likely to be a minor effect. It has however, been shown that subsurface hydrogen weakens the adsorption of ethylene from di-σ-bonded on clean Pd(111) to π-bonded when subsurface hydrogen is present [11]. It has been suggested that the more weakly bound, π-bonded ethylene hydrogenates more easily than more strongly bound di-σ-bonded ethylene so that higher subsurface hydrogen concentrations lead to higher coverages of reactive ethylene thereby leading to higher hydrogen pressure dependences.

The negative ethylene pressure dependences (figure 2) can be simply rationalized by proposing that ethylene blocks hydrogen adsorption, where this effect has been found on Pd(111) in ultrahigh vacuum. A similar blocking effect has been noted for acetylene hydrogenation where the order changes from ~−0.56 at a hydrogen pressure of 50 Torr to ~−0.8 as the hydrogen pressure increases to 400 Torr and was also ascribed to site locking by acetylene [23].

5. Conclusions

The (111) face of palladium effectively catalyzes the hydrogenation of ethylene, with hydrogen and ethylene pressure dependences that are in accord with those found on silica-supported palladium. The reaction activation energy is measured to be ~35 kJ/mol. Negative reaction orders in ethylene pressure are measured, and temperature-dependent, and positive reaction orders in hydrogen pressure are also found.

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