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Ethylene Adsorption on Platinum: Kinetics, Bonding, and Relevance to Catalysis

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It has been long recognized that adsorption energies of molecules on solids can display a strong dependence on surface concentration.[1,2] In many cases, that correlation is linear,[3] but abrupt drops in energy beyond a critical coverage (usually corresponding to an ordered overlayer) are also common.[4] Two explanations can be cited for this behavior. On one hand, adsorbates may bond in new, weaker adsorption sites as the early surface states become filled.[5] Alternatively, an increase in adsorbate−adsorbate interactions may collectively modify the adsorption energy of all of the surface species.[6] Whether all adsorbates are displaced into a new single state or the incoming molecules fill new distinct sites as the surface coverage increases depends on the system being considered. In the case of the formation of compressed layers, as with CO on Pt(111), the first scenario is the most likely.[6] With CO on Fe(100), however, no interconversion between the various CO states is seen, suggesting separate adsorption sites.[7] Here we introduce results from experiments on the kinetic behavior of unsaturated hydrocarbons on transition metals indicating an intermediate behavior where, upon saturation, additional molecules initially adsorb into a weak precursor state, but later force their neighbors to rearrange and open up a stronger adsorption site.

The experiments were carried out on a Pt(111) single crystal held under ultrahigh vacuum (UHV) by using a variation of the so-called King and Wells method, where effusive collimated beams are directed onto the surface, while the temporal evolution of both reactants and products is followed by mass spectrometry.[8,9] Both reaction rates and surface concentrations are then extracted and correlated from the raw data after appropriate calibration.[10] Figure 1 displays typical results from such experiments, in this case for the uptake of ethylene on a hydrogen-predosed Pt(111) surface at 230 K. A constant uptake rate, corresponding to a sticking probability of close to 90%, is observed up to a coverage of about 0.06 monolayers (ML), after which the rate of adsorption decreases monotonically until reaching saturation around 0.11 ML (after about 50 s of continuous exposure to the beam). It is also seen that subsequent blocking and unblocking of the ethylene beam at later times during the same experiment result in the reversible desorption and readsorption of a small fraction of the surface ethylene, respectively.

Two interesting observations can be highlighted from Figure 1. The first is that, while the rate of ethylene readsorption depends linearly on its surface coverage (a behavior explained by a simple probabilistic model developed many years ago by Langmuir),[2,11] the reversible desorption deviates from linearity. The data in Figure 1 were fitted to an Arrhenius rate law with a coverage-dependent activation energy amounting to an intermolecular repulsion of about 15 ± 5 kcal/mol·ML, as is also suggested by experiments on the temperature dependence of the reversible adsorption (data not shown). The data reported here were obtained on hydrogen-covered surfaces to better mimic olefin hydrogenation conditions, but similar behavior was observed on clean Pt(111) (data not shown).

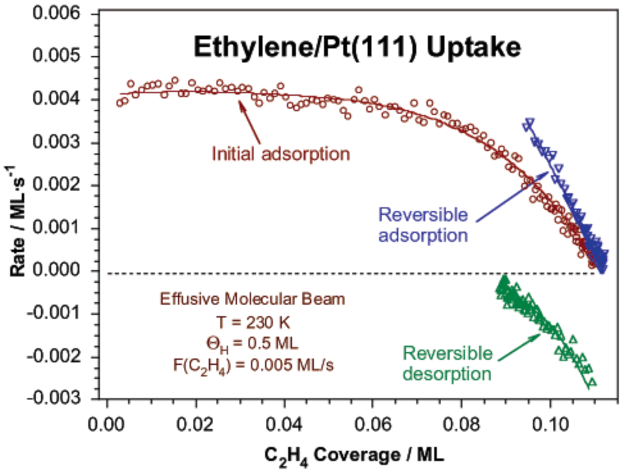

Figure 1. Uptake kinetics for ethylene adsorption on a hydrogen-predosed ($\Theta_H = 0.5$ ML) Pt(111) surface at 230 K, as measured by using a molecular beam setup.[8] These data provide information about the irreversible initial adsorption into a di-σ state (○), as well as on the rates of reversible desorption (△) and readsorption (▽) from the second π state that develops at high coverages. Two observations are worth noticing from this figure: (1) the rate of readsorption at any given coverage is much higher than that seen in the initial uptake; and (2) the behavior of the rate of reversible desorption versus coverage indicates a strong intermolecular repulsion.

The second important observation from Figure 1 is that the rate of readsorption at any given coverage is significantly higher than that seen during the initial uptake. For instance, at 230 K, the initial rate of adsorption at an ethylene coverage of 0.10 ML is only about 0.0017 ML/s, but after at least one cycle of desorption from the reversible state it reaches a value of about 0.0025 ML/s. This implies that noticeable changes take place on the surface in the interim between the two processes (a period of time of at least 20 s). The desorption and readsorption kinetics are reproducible once the first cycle is completed.

To probe the kinetic behavior of the initial (irreversible) and reversible adsorption states of ethylene on Pt(111) further, additional isotope switching experiments were performed. Figure 2 shows the time evolution of the surface concentration of normal ethylene (C_2H_4) during its uptake on the hydrogen-covered Pt(111) surface, as well as those of normal (C_2H_4) and perdeuterio (C_2D_4) ethylene after switching to a C_2D_4 beam, all at 230 K. The data prove that most of the adsorbed C_2H_4 can be displaced by new incoming C_2D_4, but that this takes significantly longer times than those needed to reach saturation during the initial uptake. Additional analysis indicates that the initial rate of C_2D_4 adsorption on the C_2H_4-covered

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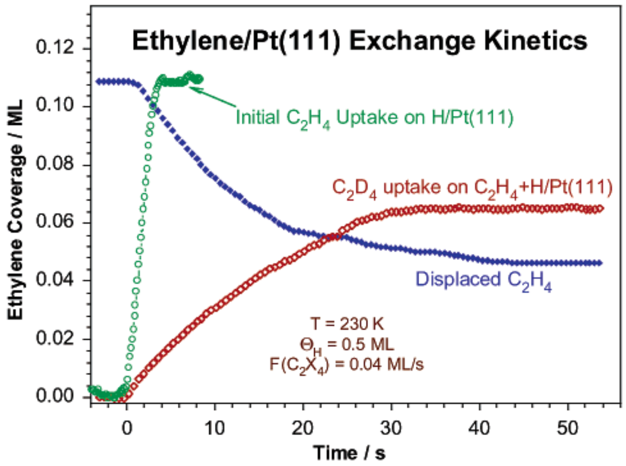

Figure 2. Temporal evolution of the surface concentration of normal ethylene (C_2H_4) during its uptake at 230 K on a hydrogen-predosed Pt(111) surface (○), as well as those of C_2H_4 (◆) and C_2D_4 (◇) after switching to a C_2D_4 beam. The time scale was reset in the latter case to zero at the time of the switch to be able to overlap both sets of data. Significant isotope exchange is possible in this system, but at a much slower rate than that of the initial adsorption.

surface at 230 K amounts to about 0.015 ML/s, less than one-half of the initial uptake rate for C_2H_4 (0.035 ML/s). More importantly, there is a 2−3 s delay between the switching on of the C_2D_4 beam and the point at which desorption of the displaced C_2H_4 starts (data not shown); this time is needed to replenish the population of the reversibly adsorbed ethylene. The displacement of adsorbates by other gases has been seen in the past,[12] only that in this case an interconversion between two different adsorption states is required. Also worth noticing is the fact that the isotopic displacement does not follow any simple rate law, but asymptotically approaches an intermediate isotopically mixed layer. Some degree of heterogeneity within the ethylene monolayer may explain this kinetic observation.[13,14]

The picture that emerges from these results is one in which two types of kinetically different olefin adsorption states are present on the surface. The nature of those two states has been studied extensively in the past.[1,15,16] It has been determined that, on most clean transition metals, olefins initially rehybridize upon adsorption into di-σ bonded species.[17,18] It has also been observed that, at higher coverages, a second, weaker π interaction becomes apparent.[19] This latter π bonding has been detected both under vacuum[20] and in situ during catalysis[21] and has been shown to be the state that intervenes directly in catalytic hydrogenation processes.[10,13] The new results reported here indicate that the π high-coverage state is indeed kinetically different from the initial di-σ species, adsorbing more weakly and reversibly on the covered surface. More importantly, the data in Figure 2 prove that interconversion between the two adsorption states is possible, albeit at a relatively slow rate. One possible explanation for this behavior is that at high coverages new ethylene molecules initially adsorb into a weak precursor state, possibly a small surface opening within the slightly disordered first monolayer. Some of those molecules then desorb rapidly back into the gas phase, but others exert a strong repulsive force on their neighbors, slowly displacing them from their original bonding configurations to form a new local molecular ensemble, perhaps even an extended compressed layer. The coverage dependence of the desorption rates and the different kinetics in the initial uptake and the subsequent readsorptions in Figure 1 provide support for this model. Such displacements may also aid in the scrambling of the adsorbates manifested by the isotopic switching experiments illustrated in Figure 2.

Our interpretation of the molecular beam results reported here helps better understand the mechanism of catalytic olefin hydrogenation. It has been established that alkane production in those processes involves reactant molecules adsorbed in the presence of a strongly bonded carbonaceous layer, of ethylidyne in the case of ethylene.[22] Additional studies have corroborated that it is the weakly (π) bonded species that participates directly in this catalysis.[16,23] On the basis of the observations discussed above, it can be suggested that, under reaction conditions, a small amount of the olefin first adsorbs weakly on top of the carbonaceous layer that builds up at the start of the catalytic process, but then forces the neighboring moieties from that layer to open up a stronger binding state where the hydrogenation to the alkane can take place. It has in fact been shown that ethylidyne acquires limited mobility under reducing conditions[18,24] and also that the kinetics of the hydrogenation of ethylene to ethane can be described in terms of the concentration of the reversibly adsorbed species. Both results are consistent with our proposal.[10]

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