Kinetics of Chemical Reactions on Solid Surfaces: Deviations from Conventional Theory

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ABSTRACT

Isothermal kinetic measurements on elementary steps between species adsorbed on solid surfaces have highlighted significant deviations from conventional kinetic theories. In particular, it has been found that neighboring adsorbates modify the energetics of surface reaction in ways not explained by macroscopic kinetic models. The free energy barriers associated with transition state theory can be expanded to include coverage-dependent terms, but that does not account for local effects due to surface islanding. Changes in surface concentrations also lead to changes in adsorption geometries, and even to different adsorbate−surface bonding. Future Monte Carlo simulations and other theoretical approaches to describe surface kinetics need to include these factors.

1. Introduction

According to collision theory, the rate of elementary chemical reactions depends mainly on two parameters: the frequency of collisions among reacting molecules, and the probability that those collisions result in a chemical transformation.[1,2] In the case of two different reactants, A and B, in an homogeneous mixture (or where at least one of them has high mobility), the rate of reaction can be written simply as

$$R = k[A][B] \qquad (1)$$

where k is a macroscopic reaction constant representing the average of individual reaction probabilities—cross sections—for each collision over all possible energies and geometrical configurations (and [A] and [B] are the concentrations of the reactants). Alternatively, transition-state theory equates the rate of a bimolecular reaction to the number of activated complexes formed.[3,4] That number is estimated by assuming that the complex is in equilibrium with the reactants, and by using statistical mechanics to calculate the corresponding equilibrium constant. Again, for a homogeneous system, the same rate law (eq 1) is obtained, except that the reaction constant is now expressed in terms of the partition functions of the reactants and activated complex and the activation enthalpy.

The theories mentioned above have been quite successful in explaining the chemical kinetics of many systems, in particular of reactions occurring in dilute gaseous mixtures. However, such success has relied in great part on the assumption that reaction rate constants depend only on the properties of the reactants, and that the effect of the surrounding environment can be neglected. Unfortunately, in condensed matter, this is a crude approximation that rarely holds. In the following review, we point to some of the deviations from conventional chemical kinetic theories that result from the influence of coadsorbates on the rate of surface chemical reactions.

The development of a plethora of new surface-sensitive techniques in the past few decades has led to an explosion in research of surface phenomena.[5] In terms of surface chemistry, a large number of chemisorbed species have been fully characterized, both in terms of their electronic and geometrical properties and with respect to their reactivity.[6] The field of surface kinetics, however, has not advanced at the same pace. Kinetic parameters have been most often estimated by temperature-programmed desorption (TPD) spectroscopy, a technique in which desorbing species are detected by mass spectrometry during heating of the surface.[7] Unfortunately, the variations in temperature in those experiments lead to simultaneous changes in surface concentrations, so those two variables become correlated in ways not easy to separate during data analysis. The difficulties in extracting kinetic parameters from such experiments have become evident even in simple systems, such as the unimolecular desorption of small chemisorbed species.[8−10]

Accurate kinetic studies require the careful and independent control of as many variables as possible. This is now viable on surfaces because of the availability of molecular beam techniques, which can be used under well-controlled conditions. At an extreme, kinetic measurements could be carried out via small perturbations around an equilibrium (or steady-state) condition,[11,12] but that requires the reaction to be reversible. More typically, isothermal measurements may be performed systematically as a function of initial coverage, beam flux, and temperature, even in the case of irreversible processes.[13,14] We in our laboratory have developed a variation of the so-called King and Wells method[15,16] in which effusive collimated beams are directed onto single-crystal surfaces while the temporal evolution of both reactants and products are followed by mass spectrometry.[17,18] After appropriate calibrations, both surface concentrations and reaction rates can be extracted from those data as a function of time, and from those, rate laws can be determined. The basal planes of single crystals are used

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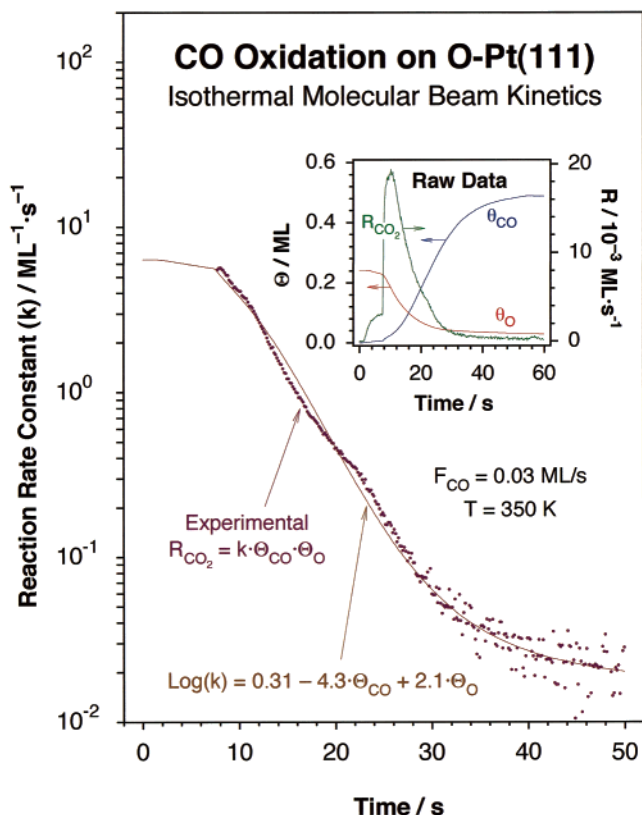* Phone: (909) 787-5498. Fax: (909) 787-3962. E-mail: francisco.zaera@ucr.edu.

FIGURE 1. Inset: time evolution of the CO and oxygen surface coverages (θ_{CO} and θ_O) and of the rate of carbon dioxide production (R_{CO_2}) during the isothermal oxidation of carbon monoxide on an oxygen-precovered Pt(111) surface, as measured by using a molecular beam technique.[19] Main frame: time evolution of the reaction rate constant k calculated from the data in the main frame by using conventional kinetic theories. The breakdown of those theories for surface reactions is apparent by the 3 orders of magnitude change seen for k over time. Such variations may be accounted for by a linear dependence of the activation energy of the reaction on the surface coverages of O and CO, as suggested by the fit also provided in this figure, but not if a full set of experiments with different starting conditions is considered.

as solid substrates to minimize the complexities introduced by multiple adsorption sites. Below we discuss some of the information extracted from studies using that approach.

2. Surface Kinetics as a Function of Surface Coverages

A typical example of the kind of information acquired by our studies of surface kinetics using effusive molecular beams is illustrated by the data in Figure 1.[19] Displayed in the inset of that figure is the rate of production of carbon dioxide as a function of time for the case of a carbon monoxide beam impinging on an oxygen-precovered platinum (111) single-crystal surface kept at a constant temperature ($T = 350$ K). Also shown there is the calculated temporal evolution of the surface concentrations of the adsorbed CO molecules and oxygen atoms, the reactants. Figure 1 shows that the rate of CO_2 production is maximized when significant concentrations of both

CO and O are present on the surface, as expected, and decreases if the coverage of any of the two species is depleted. However, it is also clear that the quantitative behavior deviates significantly from that predicted by eq 1. Specifically, the reaction rate constant estimated by using that equation changes by almost 3 orders of magnitude as the reaction progresses (Figure 1, main-frame).

Kinetic deviations from eq 1 such as those illustrated in Figure 1 have been long recognized in surface science, in particular in connection with desorption processes.[20-22] As already suggested above, it is not possible to neglect intermolecular interactions in high-density systems, such as those encountered with adsorbates on solid surfaces. This problem has been typically addressed by considering the activation energy for desorption to be coverage-dependent. Because it has been found that desorption kinetics can often be described by a monotonically changing activation barrier, the coverage dependence of such barrier has in many cases been empirically described as linear. This approach also works well for the description of the results from individual bimolecular kinetic experiments in our study on the oxidation of carbon monoxide with atomic oxygen on platinum surfaces: note the excellent fit of the logarithm of the reaction rate constant to a linear equation in the coverages of CO and atomic oxygen shown in Figure 1. It, however, fails dismally when collectively considering the kinetic data obtained as a function of initial oxygen coverage and CO beam flux.[19]

A number of more elaborate models have been used to described the kinetic changes observed experimentally as a function of surface coverages, many starting from the original transition state theory.[3,4] The general idea behind those models is depicted in the energy diagram as a function of reaction coordinate displayed in Figure 2. There, the reaction rate constant is described in terms of an equilibrium between the reactants (left-hand side minimum) and the transition state at the top (saddle point) of the potential energy curve. This energy surface changes with varying surface coverages, because the intermolecular interactions among adsorbates affect the energies of both the reactants and the activated complex. Those changes manifest themselves in the reaction constant via changes in the Gibbs free energy ($\Delta G^{\ddagger}$) of the barrier.

What is needed, then, is an adequate description of the dependence of $\Delta G^{\ddagger}$ on the conditions of the reaction. Several attempts have been made to accomplish this, mainly by using statistical mechanics. Perhaps the simplest reported approximation made to address this issue is the mean field approach originally introduced by Bragg and Williams.[23] However, their model is acknowledged to be often inadequate, because it does not take into consideration the correlation between distributions of molecules on the surface.[24] A better approach is to expand the free energy term in a virial series,[25,26] a method that has the advantage of treating energetic and entropic factors on an equal footing, but that is still limited to low coverages. Much more widely used is the so-called quasi-
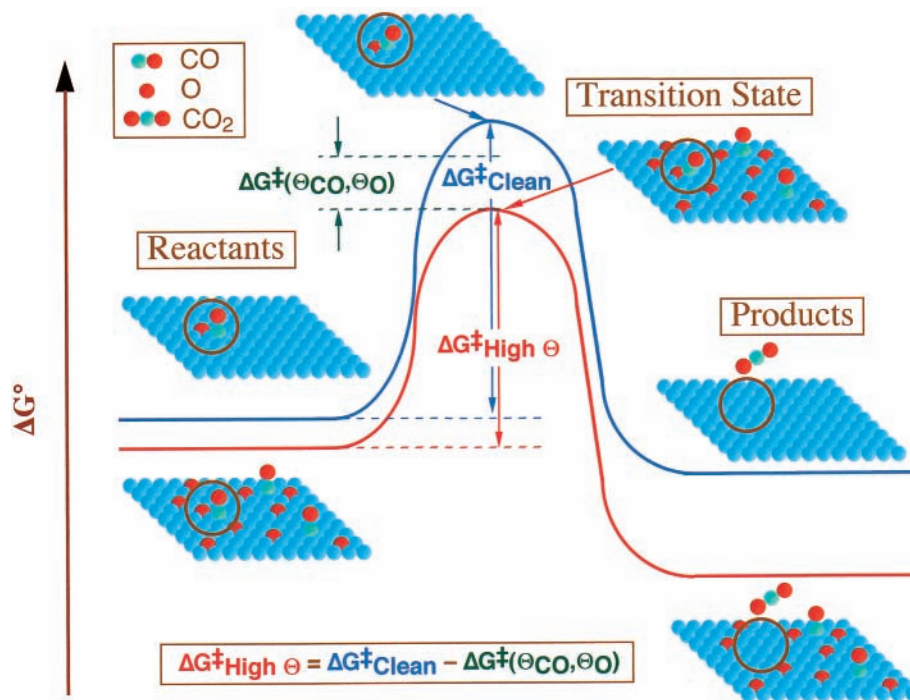
$$\Delta G^{\ddagger}_{High \, \Theta} = \Delta G^{\ddagger}_{Clean} - \Delta G^{\ddagger}(\Theta_{CO}, \Theta_O)$$

FIGURE 2. Schematic representation of the one-dimensional potential energy surface for the oxidation of CO with adsorbed oxygen atoms on a metal surface as a function of reaction coordinate. This diagram illustrates how that potential energy surface changes with varying coverages of the reactants and how that results in different activation barriers. The inclusion of the dependence of the energetics of reaction on the presence of neighboring adsorbates allows for the extension of transition-state theory to the description of surface reactions. An accurate description of that dependence, however, still remains a challenge.

chemical approximation, which could be considered as an extrapolation of the virial expansion to higher densities,[24] and which comes in different variants. Goymour and King have included all lateral interactions in the differential heat of desorption,[8] but both Adams[27] and Zhdanov[28] have described the rate constants in terms of probabilities of distributions of particles on surfaces. Kevan has introduced a transfer matrix technique to better represent the neighboring clusters of adsorbates in activation barrier calculations on surfaces.[24,29]

Unfortunately, derivations of analytical expressions based on statistical mechanics are quite difficult, and their extension to bimolecular surface reactions is almost impossible. More critical, statistical mechanics models still average the chemical properties of the surface over different local ensembles. This ignores possible changes in reaction kinetics due to different sample preparations or reaction histories. The importance of such effects is illustrated in Figure 3, where significantly different results are reported for the oxidation of CO on Pt(111) with the same average coverages of reactants on the surface.[30] There, two different preparation methods were used to deposit atomic oxygen on the platinum surface, allegedly leading to the random distribution of the adsorbates in one case (Figure 3, top) and to the formation of surface islands in the other (Figure 3, bottom). The results from that work show an ∼4-fold increase in reactivity in the latter case. Additional experiments corroborate the existence of kinetically distinct types of oxygen atoms on the Pt(111) substrate, even though they all sit in identical sites at the start of the reaction.[19,30] The development of those

states was explained by a lowering in the reaction activation barrier of reaction due to O—CO interactions within the carbon monoxide adsorbed inside the oxygen islands.

In our opinion, the best theoretical way to address the kinetic problems originating from local fluctuations in coverages of adsorbed species is by using Monte Carlo simulations.[31,32] Monte Carlo algorithms are relatively easy to set up and are ideally suited to include such local effects.[33–35] A few papers have already reported computer simulations on simple reactions, such as the CO oxidation described here, but they so far have only attempted to reproduce TPD traces;[36] that does not represent a particularly stringent test. Moreover, some simulations have included hypotheses later contested, like the assumption of preferential reactivity at the perimeter of adsorbate islands.[37] There is still much room for improvement in terms of theoretical studies of surface reaction kinetics, especially as better quality (isothermal) experimental data become available.

3. Role of Surface Adsorbate Islanding

Another example in which a seemingly simple reaction displays complex surface kinetics is that of the reduction of nitrogen monoxide on Rh(111) single-crystal surfaces.[38–40] For one, the desorption and decomposition of NO show two different kinetic regimes, at least in part because of the deposition of nitrogen and oxygen atoms on the surface.[41] The problem is simplified somewhat during steady-state NO reduction processes, because there the use of a reducing agent (CO in our studies) removes the
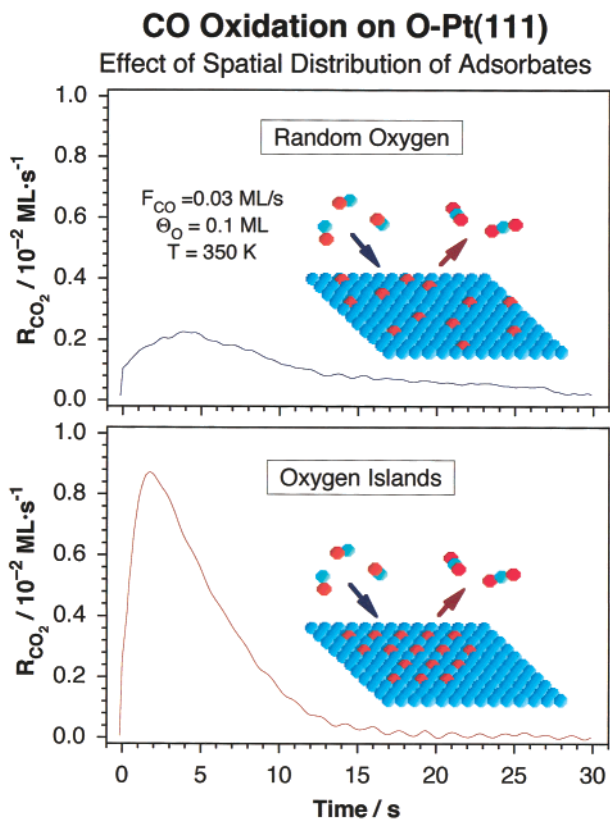
CO Oxidation on O-Pt(111)
Effect of Spatial Distribution of Adsorbates

NO+CO/Rh(111) Conversion
Role of Surface Nitrogen

FIGURE 4. Nitrogen steady-state coverages as a function of beam composition during the reduction of NO by CO on a Rh(111) surface. Two types of kinetically different nitrogen species were identified in those experiments: a strongly bonded nitrogen, the coverage of which was calculated from TPD data (left inset); and weakly bonded N, with coverages estimated from data obtained by blocking the beam during the steady-state portion of the kinetic runs (right inset).[43] In the main frame, it is shown that the second species is the one that correlates with the steady-state reaction rates.[42]

FIGURE 3. Oxidation kinetics for carbon monoxide on oxygen-covered platinum single-crystal surfaces illustrating the importance of the spatial distribution of the adsorbates in determining reaction rates.[30] Two different sample preparation methods were used to obtain a random distribution of O atoms on the surface in one case (top) and a clustered arrangement in ordered surface islands in the other (bottom). Large differences in rates were observed between the two cases, although both kinetic runs started with the same average concentrations of oxygen and CO on the surface. This example highlights the role that neighboring adsorbates play in modifying both the energetics of the reacting species and the rates of reaction.

surface oxygen immediately as it is produced.[42] Nevertheless, two kinetically different adsorbed nitrogen atoms are seen in that system,[43] as illustrated by the data in Figure 4. On one hand, there is a buildup of a critical coverage of N atoms on the rhodium substrate before steady state is reached.[44] A constant nitrogen coverage is then retained by the surface during the catalytic reduction of NO by CO; this can be measured by TPD experiments afterward (Figure 4, left inset). In contrast, a small amount of N_2 desorption is detected right after the interception of the molecular beam feeding the surface reaction (Figure 4, right inset). The data in the main frame of Figure 4 indicate that it is this second "weakly bonded" nitrogen, the one associated with the steady-state reaction rates.

Isotope-labeling experiments have proven that the two types of nitrogen atoms referred to above are, in fact, the same surface species but in different local environments. In particular, all of the "strongly bonded" nitrogen atoms (the first type, detected by TPD) are eventually removed from the surface during the steady-state conversion of NO with CO. Figure 5 shows the temporal dependence of this
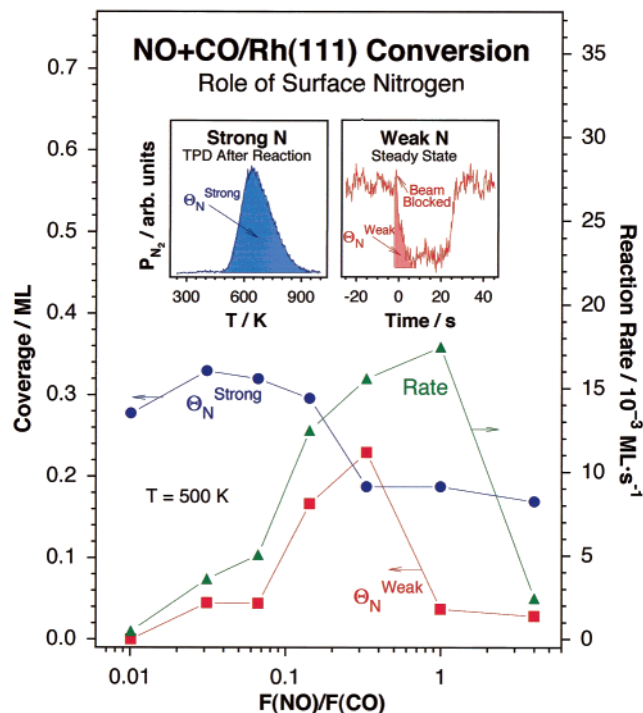
removal, as measured by replacing ^{14}NO with ^{15}NO during the NO catalytic reduction runs.[43] The kinetics of the isotopic switching can be explained by the formation of atomic nitrogen surface islands and by the preferential conversion of the atoms at their periphery. That model is also supported by the nonstatistical isotopic distribution of nitrogen atoms in the N_2 that desorbs in post mortem TPD experiments.[45,46] Such island formation has a significant influence in the mechanism of the catalytic reduction of NO. Specifically, it was found that the removal of the ^{14}N surface atoms after isotopic switching occurs exclusively via the formation of $^{14}N^{15}N$; no appreciable $^{14}N^{14}N$ is made at any stage of the reaction with ^{15}NO.[47] The implication is that molecular nitrogen is produced not by recombination of two surface nitrogen atoms, as commonly believed, but via the formation of an N−NO intermediate.[39,47,48] The decomposition of N_2O on rhodium surfaces is, indeed, much faster than any of the other steps involved in the catalysis of NO reduction.[49]

4. Nature of the Reacting Surface Species

Island formation is one reason similar surface species may display different kinetic behavior. A change in adsorption geometry with changing surface coverage is another. This is a common phenomenon. For instance, carbon monoxide generally adsorbs onto metals with its molecular axis
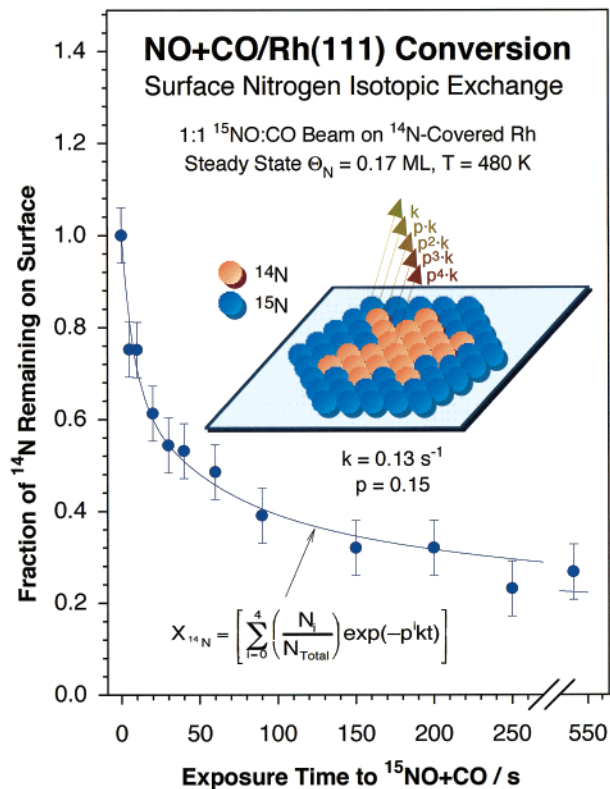
FIGURE 5. Fraction of ^{14}N from the total nitrogen adsorbed on the surface during the steady-state conversion of NO on Rh(111) as a function of the time elapsed after replacing the $^{14}NO + CO$ beam with an equivalent $^{15}NO + CO$ mixture (solid circles).[39,43] The original ^{14}N is slowly displaced by new ^{15}N via a complex kinetics involving the formation of surface islands. The model used to describe this behavior is depicted in the inset, and the results are reported as a solid line in the main frame. Only the outer nitrogen atoms are available for reaction, and are converted to molecular nitrogen not by direct recombination, but rather via a reaction with new incoming NO molecules to form a N−NO intermediate.[47] This example illustrates how island formation and other inhomogeneities in the distribution of adsorbates can complicate the kinetic picture of surface reactions.

FIGURE 6. Data from infrared studies on the adsorption of cinchonidine from a carbon tetrachloride solution onto a platinum surface.[60] Cinchonidine is a chiral molecule used to modify platinum catalysts in order to add enantioselectivity to its hydrogenation activity. Three distinct concentration regimes were identified in our uptake experiments: below 5%, between 5 and 20%, and above 20%, which correspond to no adsorption, a flat-lying bonding geometry on the surface, and a tilted configuration, respectively. The figure displays the signal intensities of the key infrared features corresponding to the flat-lying (solid circles) and tilted (solid squares) geometries as a function of cinchonidine concentration in the carbon tetrachloride solution and shows how they correlate well with reported changes in activity and enantioselectivity of a platinum catalyst modified with 10,11-dihydrocinchonidine toward the hydrogenation of ethyl pyruvate (open diamonds).[77] Adsorption geometry changes induced by variations in surface concentration can profoundly affect the kinetics of surface reactions.

perpendicular to the surface, but may tilt at low coverages on some specific substrates.[50−52] Alkyl chains and other hydrocarbons are also known to reorient as the surface becomes more crowded, presumably because the gain in energy from a van der Waals attraction with the surface is offset by intermolecular interactions.[53−55] These geometrical changes can affect the reactivity of surface species, as, for instance, in the case of hydrocarbon moieties on transition metals, in which extensive decomposition at low coverages gives way to some hydrogenation as the surface concentration is increased.[56−59]

An interesting example of the role of surface coverage on adsorption geometry and reactivity is shown in Figure 6.[60] Those data refer to studies on the bestowal of enantioselectivity to platinum catalytic surfaces by the adsorption of cinchonidine, a chiral alkaloid modifier.[61] Our in situ infrared results show that the performance of the cinchonidine/platinum system is optimized by a flat-lying adsorption geometry of the aromatic ring of the modifier and that th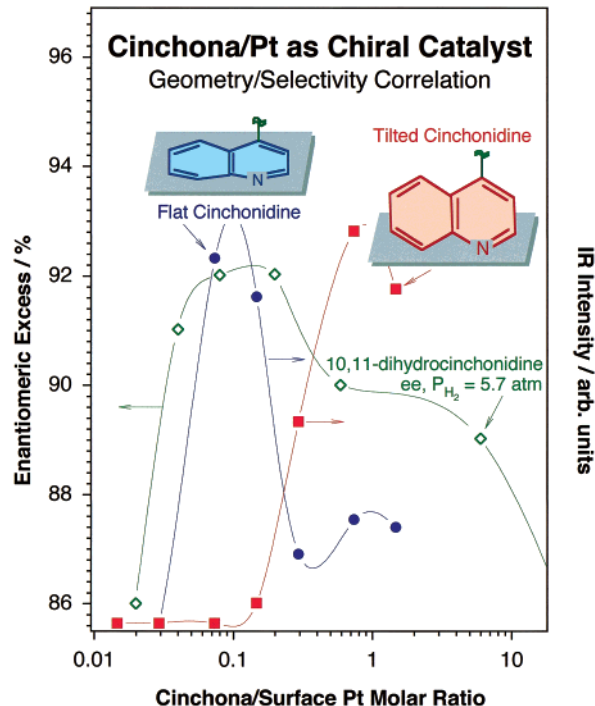at geometry depends strongly on the concentration of the modifier in the solution. This is a particularly complex system in which the nature of the solvent and the stereo arrangement of the different constituting groups of the modifier around the chiral center also contribute to determining adsorption geometries as well as the activity and enantioselectivity of the catalytic system.

An equally dramatic effect of surface coverage on surface reactivity is seen in the catalytic hydrogenation of unsaturated hydrocarbons over transition metals.[57,59,62−65] In those systems, the very nature of the adsorbate−substrate interaction changes with increasing coverage. Figure 7 displays data on the adsorption of propylene on Pt(111) to illustrate this point.[66,67] On most clean transition metals, the adsorption of olefins leads to a rehybridization of the olefin to a strongly bonded di-σ species: the infrared spectrum of di-σ propylene on Pt(111) is shown in the right inset of Figure 7.[66] At higher coverages, however, a second, weaker π interaction becomes apparent (left panel of Figure 7).[66] The difference in adsorption
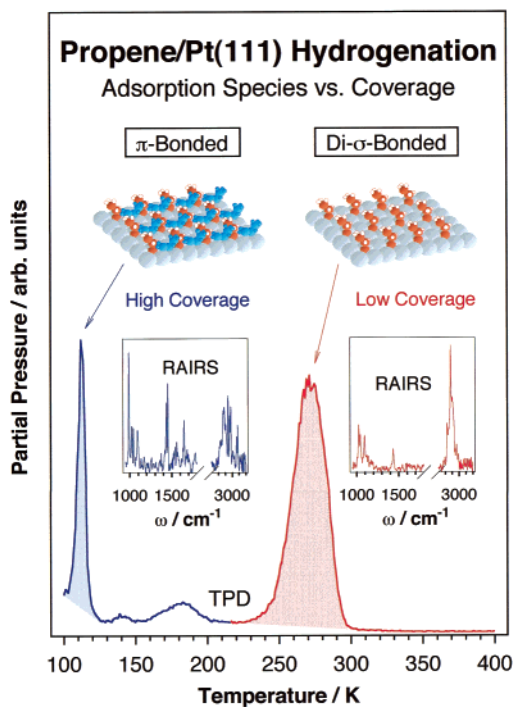
FIGURE 7. Evidence for the formation of adsorbed species with different surface bonding during the uptake of olefins on metals as their coverage increases. The example presented here corresponds to propylene on Pt(111). The insets display the significantly different infrared spectra corresponding to di-σ (right) and π (left) bonding,[66] and the main frame shows the accompanying temperature-programmed desorption data, with its two distinct peaks for the two different species.[67] The more weakly π-bonded olefin that builds up at high coverages is the one believed to participate in catalytic hydrogenation.[62] Interestingly, though, both species appear to be interchangeable. What surface concentration is supposed to be considered in the kinetic analysis of that reaction?

FIGURE 8. Inset: raw isothermal kinetic data for the uptake of ethylene on clean Pt(111) at 250 K, obtained by using our collimated molecular beam setup.[71] The surface first becomes saturated with one-fourth of a monolayer of strongly di-σ bonded ethylene within the first 10–15 s of dosing, but after that, a small amount of more weakly π-bonded ethylene adsorbs reversibly. The reversible species can be allowed to desorb and re-adsorb by turning the molecular beam off and on (as indicated by the spikes seen after 20 s). Kinetic measurements on hydrogen-precovered surfaces highlighted the direct correlation between the coverage of this second type of ethylene and the reaction rate for hydrogenation of ethylene to ethane (main frame).

strength between those two species is clearly manifested by the two distinct peaks in the molecular TPD spectrum (main panel of Figure 7), which correspond to desorption energies of about 7 and 16 kcal/mol for the π and di-σ species, respectively.[67]

The significance of the existence of two types of adsorption for olefins on metals is that the surfaces used in the catalytic conversion of hydrocarbons are coated with carbonaceous species immediately after exposure to the reaction mixture.[64,68–70] Our molecular beam kinetic work on the ethylene/Pt(111) system has revealed that it is the weakly bonded π olefin that adsorbs onto such covered surfaces the one that intervenes directly in the hydrogenation process.[71] The inset in Figure 8 shows raw data from those experiments pointing to the reversible uptake of a small amount of ethylene after saturation of the clean Pt(111) surface with the olefin, and the main frame points to the almost linear dependence of the ethylene hydrogenation rate on the surface coverage of this weakly π-adsorbed intermediate.

An interesting question arises in connection with the identity of the different species seen in a given system as a function of coverage. It is not clear if, as the coverage is increased beyond the point where the nature of the adsorption changes, all molecules become adsorbed onto
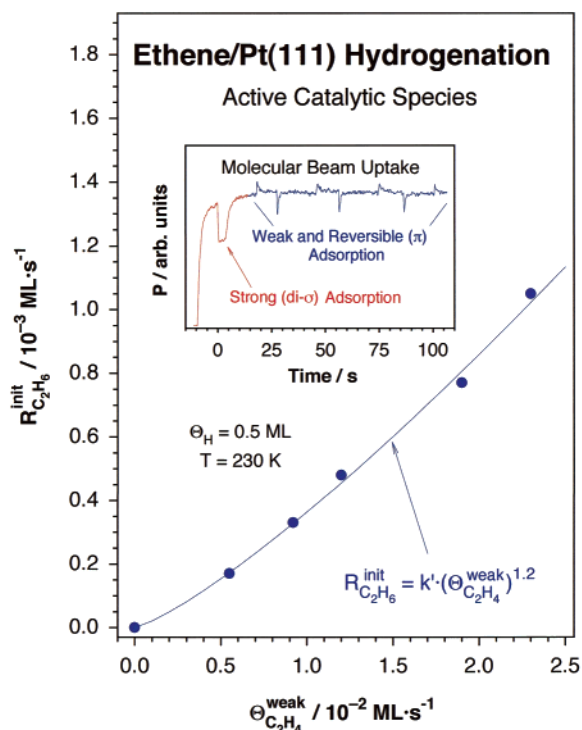
an equivalent new state or if they sequentially fill two or more distinct sites with different adsorption energies. The answer to that quandary may be different, depending on the system being considered. In the case of the formation of compressed layers, as with CO on Pt(111), the first scenario is the most likely.[9] The weakly and strongly adsorbed olefin states reported above can be easily exchanged upon exposure to additional gas-phase molecules,[71] suggesting that they also all change adsorption sites collectively. On the other hand, a more complex behavior is seen with CO on Fe(100), in which no interconversion occurs between the α and β or between the α_1 and α_2 CO states, but where significant mixing is observed between the α_2 and α_3 states.[72] What surface concentration of the reacting species should be considered when describing reaction kinetics in the high coverage regime?

5. Thoughts for Future Studies

The use of molecular beams to measure surface kinetics has already led to the identification of a number of deviations from classical kinetic theory. Those deviations are still in need of proper accounting by theory. It is our

belief that one of the best approaches in this quest is the use of Monte Carlo kinetic simulations, perhaps in combination with quantum mechanic calculations of the energetics of surface ensembles of adsorbates. Some interesting reports have already appeared in the literature in this direction.[73] It is also crucial that computational calculations on adsorption energies and activation barriers consider the effects of surface coverages and local adsorbate distributions.[74]

New approaches are also needed in connection with the search for accurate kinetic measurements in catalysis. In terms of the use of molecular beams, one of the main limitations at this point is that there are currently no designs available for the generation of the high-flux beams needed to reproduce nondemanding reactions, such as hydrocarbon hydrogenation, in their catalytic steady-state.[75] Recall that the weakly adsorbed species believed to intervene in those processes are short-lived and are likely to build up on the surface in detectable amounts only under the high impinging frequency conditions that prevail in atmospheric pressure environments. This problem could conceivably be addressed by new designs with pulsed beams or nanoliter-size reactors.[59] Finally, it is also important to identify and characterize active reaction intermediates in situ during catalytic reactions. In this context, there has been a renewed interest in the use of optical spectroscopies for surface studies.[76] A combination of pulsed molecular beams with in situ spectroscopies could lead to the characterization of the chemistry of weakly adsorbed transient intermediates and to the direct correlation of the surface concentration of those species with their reaction rates.

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