

Adsorption kinetics on chemically modified or bimetallic surfaces

Cite as: J. Chem. Phys. **100**, 664 (1994); <https://doi.org/10.1063/1.466931>

Submitted: 25 May 1993 . Accepted: 15 September 1993 . Published Online: 31 August 1998

Chen Xu, and Bruce E. Koel



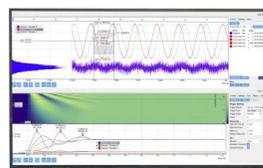
View Online



Export Citation

Challenge us.

What are your needs for
periodic signal detection?



Zurich
Instruments

Adsorption kinetics on chemically modified or bimetallic surfaces

Chen Xu and Bruce E. Koel

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482

(Received 25 May 1993; accepted 15 September 1993)

Surface adatom modifiers that act as promoters or poisons on transition metal catalysts can have a large influence on adsorption kinetics along with their influence on adsorption energetics. Accounting for this effect requires recognition of the role of a new kind of intrinsic precursor — *the modifier precursor state*. A mathematical description of the adsorption kinetics of molecules on chemically modified or bimetallic surfaces incorporating this state has been derived based on Kisliuk's statistical model [P. Kisliuk, *J. Phys. Chem. Solids* **3**, 95 (1957)]. The resulting equation can be used to explain satisfactorily data on CO adsorption kinetics on chemically modified (Cl-, P-, S-, H-, O-, and K-precovered) Pt(111) surfaces. This concept should have broad implications for many systems in heterogeneous catalysis, such as bimetallic and alloy surfaces and coadsorbed layers, and for the multicomponent surfaces that are involved in materials growth and processing.

I. INTRODUCTION

Because of its importance as the first elementary reaction step in heterogeneous catalysis, the kinetics of adsorption have been studied extensively and many excellent reviews are available.¹⁻⁴ Nevertheless, most studies have been limited to adsorption on simple surfaces comprised of a single component, e.g., clean Pt(111). Since most metal heterogeneous catalysts are in fact bimetallic or alloy catalysts, and since dramatic alterations in the catalyst chemistry occur by addition of chemical modifiers (as promoters or poisons) to the metal surfaces, there has been a steady drive toward fundamental studies of such systems. Data from recent investigations on bimetallic and chemically modified surfaces have been reviewed.⁵⁻⁷ One finds that a complete mathematical description of adsorption kinetics on these surfaces is still lacking. Usually, for the case of nondissociative adsorption and no adsorption onto the modifier, the influence of the second component or surface modifier on the adsorbate sticking coefficient has been taken into account using the following equation:

$$S_M = S(1 - m\theta_M), \quad (1)$$

where S and S_M are the sticking coefficients on the clean surface and on the surface precovered with a modifier (second component), respectively, θ_M is the modifier coverage, and m is the parameter describing how many sites are blocked by one adatom of the modifier. In this paper, we will show that this equation can be used only under the assumption of a Langmuir isotherm and therefore gives an incorrect description of the sticking coefficient in most cases. We will extend a previous treatment of precursor mediated adsorption kinetics⁸ to include chemically modified surfaces and derive an equation describing the coverage and temperature dependence of the sticking coefficient. For brevity, we will limit this paper to consider only molecular chemisorption on two-component surfaces. However, our approach can also be adapted for dissociative

chemisorption and multicomponent surfaces and should have broad application in a variety of gas-surface reactions.

II. THEORY

Impinging on the surface, a molecule can be elastically or inelastically scattered. If the molecule loses enough of its kinetic energy to the surface via excitation of surface phonons or electronic transitions, or through relaxation via vibrational and rotational energy transfer within the molecule, the molecule can become trapped on the surface. The loss of kinetic energy perpendicular to the surface is the determining factor for trapping.¹⁻⁴ The translational energy component parallel to the surface does not need to be lost necessarily for the molecule to become trapped. In this case, a mobile trapped species occurs on the surface. The molecule can be trapped either directly into a chemisorbed state or into a weakly bound (physisorbed) precursor state. Once becoming trapped into the precursor state, the molecule can then desorb, chemisorb, or diffuse to a second site (in the case of a mobile precursor). Two different precursor states are usually distinguished—intrinsic and extrinsic. An intrinsic precursor exists above an unoccupied site and is usually indicated by a strong dependence of the initial sticking coefficient on the surface temperature. An extrinsic precursor exists above an occupied site and was originally introduced to explain the coverage independence of the sticking coefficient at small adsorbate coverages. Another experimental indication of the role of an extrinsic precursor is a cosine scattering distribution in molecular beam experiments which are used to calculate the trapping coefficient. However, as pointed out recently by Harris and Luntz,⁹ in cases of strong chemisorption, care must be taken about interpreting a cosine scattering distribution since translational to rotational and normal to parallel energy conversions can also cause a substantial energy scrambling in the interaction between the molecule and surface.

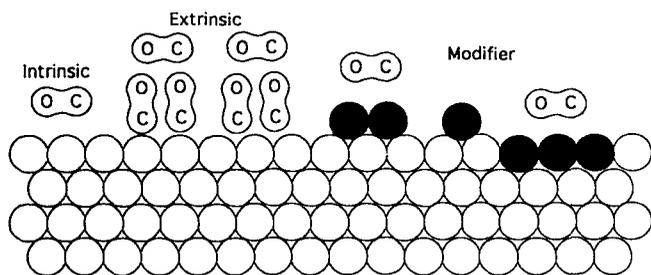


FIG. 1. Three different precursor states on a chemically modified surface.

The concept of a precursor state was originally introduced by Langmuir¹⁰ and Lennard-Jones¹¹ to explain a coverage-independent sticking coefficient at small coverages. The presence of an extrinsic precursor is especially necessary to explain the coverage independence; an intrinsic precursor cannot account for it. Two different approaches have been used to describe precursor-mediated adsorption kinetics: (1) a statistical model by Kisliuk,⁸ and (2) a kinetic model by Becker and Hartman,¹² Ehrlich,¹³ and Gorte and Schmidt.¹⁴ Under identical assumptions, both approaches give identical results.¹⁵ Therefore we will limit the following discussion only to the statistical model.

Precursor states generally have been thought to be weakly bound, mobile, molecular states. The molecule is trapped temporarily on the surface by long-range physisorption (van der Waals) forces. If an extrinsic precursor exists on the clean surface (on top of an adsorbed molecule), it is certainly reasonable to assume that a *modifier precursor state might also exist on top of a modifier adatom*. Such a state might also exist on top of a second, "inert" metal component in an alloy. This precursor is different than both intrinsic and extrinsic precursors and its importance has not been discussed before to our knowledge. In comparison to the intrinsic precursor, the modifier precursor cannot be converted to a chemisorbed molecule and has therefore, in most cases, a longer lifetime than the intrinsic precursor. Its contribution to the sticking coefficient is determined only by the ratio of the migration probability to the desorption probability. The modifier precursor exists on the surface even at zero coverage of the adsorbate and certainly influences the initial sticking coefficient, while the extrinsic precursor has no influence on the initial sticking coefficient. In most cases, the desorption probability of the modifier precursor should be lower than that for the extrinsic precursor due to a larger interaction with the modifier compared to the adsorbed molecule. The three different precursor states that we consider are illustrated in Fig. 1.

Assuming the existence of a modifier precursor, we will derive an equation to describe the coverage and temperature dependence of the sticking coefficient based on the formulation provided by the Kisliuk model.⁸ The terms used in our derivation are defined below and we have used the same term as in the Kisliuk derivation whenever possible:

P_a —the probability that a physisorbed (trapped) molecule above an empty site becomes chemisorbed;

P_b —the probability that a physisorbed (trapped) molecule above an empty site desorbs;

P_c —the probability that a physisorbed (trapped) molecule above an empty site will diffuse to an adjacent site;

P'_b —the probability that a physisorbed (trapped) molecule over a filled site occupied by the molecule desorbs;

P''_c —the probability that a physisorbed (trapped) molecule over a filled site occupied by the molecule will diffuse to an adjacent site;

P'''_b —the probability that a physisorbed (trapped) molecule above a filled site occupied by a surface modifier atom desorbs;

P''''_c —the probability that a physisorbed (trapped) molecule above a filled site occupied by a surface modifier atom will diffuse to an adjacent site;

P_{a1} —the probability of chemisorbing on the first site¹⁶

$$P_{a1} = (1 - \theta - \theta_M) P_a; \quad (2)$$

P_{b1} —the probability of desorbing from the first site

$$P_{b1} = (1 - \theta - \theta_M) P_b + \theta P'_b + \theta_M P'''_b; \quad (3)$$

P_{c1} —the probability of diffusing to a second (adjacent) site

$$\begin{aligned} P_{c1} &= 1 - P_{a1} - P_{b1} \\ &= 1 - P_a - P_b + \theta(P_a + P_b - P'_b) + \theta_M(P_a + P_b - P''_b). \end{aligned} \quad (4)$$

The probability of chemisorbing on a second site P_{a2} , desorbing from the second site P_{b2} , and diffusing to a third site P_{c2} can be described similarly by the following equations:

$$P_{a2} = P_{c1} (1 - \theta - \theta_M) P_a, \quad (5)$$

$$P_{b2} = P_{c1} [1 - \theta - \theta_M] P_b + P'_b + \theta_M P''_b, \quad (6)$$

$$\begin{aligned} P_{c2} &= P_{c1} - P_{a2} - P_{b2} \\ &= P_{c1} [1 - P_a - P_b + \theta(P_a + P_b - P'_b) + \theta_M(P_a + P_b - P''_b)] \\ &= P_{c1}^2. \end{aligned} \quad (7)$$

The measured sticking coefficient is a sum of the probabilities to become chemisorbed on all of the sites

$$\begin{aligned} S &= P_{a1} + P_{a2} + P_{a3} + \dots \\ &= P_a (1 - \theta - \theta_M) (1 + P_{c1} + P_{c1}^2 + \dots) \\ &= \frac{P_a (1 - \theta - \theta_M)}{1 - P_{c1}} \\ &= \frac{P_a (1 - \theta - \theta_M)}{P_a + P_b - \theta(P_a + P_b - P'_b) - \theta_M(P_a + P_b - P''_b)}. \end{aligned} \quad (8)$$

For $\theta = \theta_M = 0$, the initial sticking coefficient on the clean surface is given by

$$S_0 = \frac{P_a}{P_a + P_b}. \quad (9)$$

The relative sticking coefficient S/S_0 can be calculated using the following equation:

$$S/S_0 = \left(1 + \frac{\theta}{1-\theta-\theta_M} K' + \frac{\theta_M}{1-\theta-\theta_M} K'' \right)^{-1}, \quad (10)$$

where

$$K' = \frac{P'_b}{P_a + P_b} \quad \text{and} \quad K'' = \frac{P''_b}{P_a + P_b}. \quad (11)$$

Equation (10) describes the coverage dependence of the relative sticking coefficient on both the adsorbate and modifier surface concentration. The temperature dependence of the sticking coefficient is involved in the various probabilities P_i as shown below.

Now we turn to two special cases. First, when the modifier coverage is zero, i.e., $\theta_M = 0$, Eq. (10) reduces to

$$S(\theta)/S_0 = \left(1 + \frac{\theta}{1-\theta} K' \right)^{-1}. \quad (12)$$

This equation is identical to the original Kisliuk equation⁸ which describes the adsorbate coverage dependence of the relative sticking coefficient. Second, when the adsorbate coverage is zero, i.e., $\theta = 0$, Eq. (10) reduces to

$$S_0(\theta_M)/S_0 = \left(1 + \frac{\theta_M}{1-\theta_M} K'' \right)^{-1}. \quad (13)$$

This equation describes the dependence of the adsorbate initial sticking coefficient on the modifier concentration.

Using the same normalization factors as in Ref. 8 and an Arrhenius form for the rate, the various probabilities P_i can be described as follows:

$$\begin{aligned} \sum P_i = P_a + P_b + P_c = 1, \quad \sum P'_i = P'_b + P'_c = 1, \\ \sum P''_i = P''_b + P''_c = 1, \end{aligned} \quad (14)$$

$$\begin{aligned} P_j &= \frac{\nu_j \exp(-E_j/kT)}{\sum \nu_i \exp(-E_i/kT)}, \\ P'_j &= \frac{\nu'_j \exp(-E'_j/kT)}{\sum \nu'_i \exp(-E'_i/kT)}, \\ P''_j &= \frac{\nu''_j \exp(-E''_j/kT)}{\sum \nu''_i \exp(-E''_i/kT)}. \end{aligned} \quad (15)$$

If we insert Eq. (15) into Eq. (8) or Eq. (10), we will have a closed equation describing the dependence of the sticking coefficient on adsorbate coverage, modifier coverage, activation energies and pre-exponential factors of the

individual processes, and the surface temperature explicitly.

III. RESULTS AND DISCUSSION

A. CO adsorption kinetics on modified metal surfaces

Most investigations of the influence of heteroatoms or surface modifiers on adsorption kinetics have been carried out for CO adsorption on transition metals, and so we will limit our discussion here to this type of system. The initial sticking coefficient of CO, S_0^{CO} , on most transition metals is very high (near unity). A CO-coverage-independent sticking coefficient up to a CO coverage of $\theta_{\text{CO}} = 0.2-0.3$ has often been found. With a further increase in the CO coverage, the CO sticking coefficient S^{CO} decreases gradually to zero at saturation coverage. The initial sticking of CO on transition metals often shows a very small or even no temperature dependence.¹⁷⁻²⁰ The generally accepted description used to explain this finding is that CO adsorbs onto the surface via direct adsorption into the chemisorbed state, influenced only by the presence of an extrinsic precursor. The influence of the extrinsic precursor state is indicated by the coverage independence of the sticking coefficient. The negligible effect of an intrinsic precursor state is consistent with the temperature independence of S_0^{CO} and is the limiting case of the general statement of $P_a \gg P_b$ (i.e., $\nu_a e^{-E_a/kT} \gg \nu_b e^{-E_b/kT}$) (Refs. 6, 11 and 21-23) as discussed in more detail below. An alternative explanation of the temperature independence of the initial sticking coefficient would be that $E_a = E_b$. However, direct experimental evidence for this has never been found. Also we point out that ν_a is usually smaller than ν_b because of the large entropy increase associated with desorption and thus P_a must be smaller than P_b if $E_a = E_b$. Therefore, this rationale predicts the initial sticking coefficient to be smaller than 0.5 from Eq. (9), which is certainly not the case for CO adsorption on most transition metals.

The presence of surface modifiers often causes a strong temperature dependence of the initial sticking coefficient and a change in the coverage dependence of the sticking coefficient.⁶ The initial sticking coefficient shows a different dependence on the modifier coverage depending on the surface temperature. The adsorption kinetics of CO on K-modified Pt(111) (Ref. 20) and Pd(100) (Ref. 24) surfaces has been studied recently. In these experiments, the dependence of S_0^{CO} on the K-precoverage θ_K was determined either using direct kinetic or temperature programmed desorption (TPD) uptake methods. Results from both of these studies are reproduced in Fig. 2. It can be seen that S_0^{CO} shows only a very small or no dependence on θ_K up to $\theta_K = 0.25-0.35$ and then decreases gradually to zero. These findings were correlated to a transition of "ionic" K to "metallic" K (either through a site change or change in electronic structure). In order to explain the dependence of S_0^{CO} on θ_K using the above argument, a sharp transition from ionic to metallic K adatoms at a particular θ_K must be assumed. This is quite plausible, but

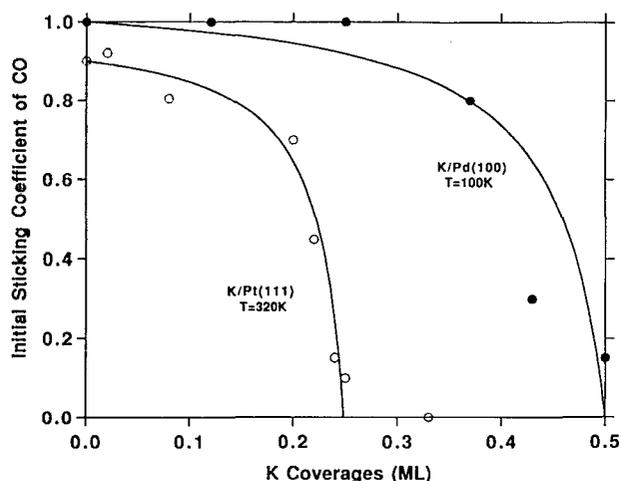


FIG. 2. The initial sticking coefficient of CO on K-precovered Pt(111) (Ref. 20) and Pd(100) (Ref. 24) surface at various K coverages, reproduced from Refs. 20 and 24. The solid curves are fits to the data using Eq. (19).

a gradual, continuous transition from a partially ionic to metallic phase with increasing K coverage has often been observed on Pt(111).^{5,26} An abrupt change in the chemical nature of K has been found only on Ag(100).^{25,26}

Results very similar to those shown in Fig. 2 have been found also for C₂H₄ on Bi-precovered Pt(111) (Ref. 27), and for CO on Ni(100) precovered with Bi (Ref. 28) and with electronegative modifiers at low temperatures (~100 K). For example, the adsorption kinetics of CO on S-modified Ni(100)²⁹ were studied using TPD uptake measurements at several sulfur precoverages, θ_S . For $\theta_S < 0.3$, the initial sticking coefficient of CO is independent of θ_S and is near unity. For $\theta_S \geq 0.3$, S_0^{CO} falls below unity. On O- (Refs. 20 and 30), H- (Ref. 20), Se-, and S- precovered Pt(111) (Refs. 31–33) surfaces and Sn/Pt(111) surface alloys³⁴ S_0^{CO} was found to be independent of modifier precoverage up to $\theta_M = 0.25$ or even higher. In some cases, these findings were previously attributed to island formation of the modifier.^{6,20} Within this interpretation, there are still modifier-free areas of the surface up to a certain critical modifier coverage and, therefore, the adsorptive properties of the clean surface are preserved. This explanation is not very satisfying either. Even if the modifier forms islands, the probability of incident molecules impinging on the modified surface increases with the modifier concentration. According to simple site blocking theory [see Eq. (1)] the molecule impinging on the site of the modifier cannot become chemisorbed. Therefore, we expect a linear decrease of the initial sticking coefficient in these cases too.

At higher temperature (300 K), the dependence of S_0^{CO} on the modifier (Cl, P, or S) precoverage shows a Langmuirian behavior and can be described well with Eq. (1).³⁵

The finding that the CO initial sticking coefficient on modified surfaces is a strong function of the surface temperature in contrast to the temperature independence of S_0^{CO} on the clean surface is very important. This certainly

relates to the different modifier-coverage dependence of S_0^{CO} at different temperatures. A strong decrease of S_0^{CO} with increasing temperature on modified surfaces always has been found.^{6,33,34} This decrease has been attributed previously to a reduced lifetime of the intrinsic precursor state because of the electronegative modifier which prevents the diffusion of CO and reduces the binding energy of CO on the surface,⁶ but this contradicts the direct adsorption mechanisms of CO on Pt(111). These studies and all of the systems discussed in this section point to a need to improve our understanding of adsorption kinetics on modified surfaces.

B. Temperature dependence of the initial sticking coefficient on clean and chemically modified surfaces

The temperature dependence of $S_0(\theta_M)$ is contained in Eq. (13) and can be rewritten in the following form:

$$S_0(\theta_M) = \frac{P_a}{P_a + P_b} \left(1 + \frac{\theta_M}{1 - \theta_M} K'' \right)^{-1} \\ = \frac{\nu_a \exp(-E_a/kT)}{\nu_a \exp(-E_a/kT) + \nu_b \exp(-E_b/kT)} \\ \times \left(1 + \frac{\theta_M}{1 - \theta_M} K'' \right)^{-1}. \quad (16)$$

For a clean surface, Eq. (16) reduces to

$$S_0 = \frac{\nu_a \exp(-E_a/kT)}{\nu_a \exp(-E_a/kT) + \nu_b \exp(-E_b/kT)} \\ = \frac{1}{1 + (\nu_b/\nu_a) \exp[-(E_b - E_a)/kT]}. \quad (17)$$

Using Eq. (17), the temperature independence of S_0 can be explained either by (1) the desorption activation energy from the intrinsic precursor state is the same as to the activation energy for conversion from the intrinsic precursor to the chemisorbed state ($E_a = E_b$); or (2) the rate constant for the intrinsic precursor becoming chemisorbed is much larger than the rate constant for the molecule desorbing from the intrinsic precursor ($\nu_a e^{-E_a/kT} \gg \nu_b e^{-E_b/kT}$). From transition state theory, ν_b must be larger than ν_a because of the large entropy increase associated with desorption. Therefore, the second explanation requires that $E_b \ll E_a$. Within the context of the first explanation, we do have an intrinsic precursor, but the equivalence of the two activation energies prevents a temperature dependence. In the second case, we don't have a real intrinsic precursor state. Because every molecule trapped in an intrinsic precursor state immediately becomes chemisorbed, the sticking coefficient is only determined by the trapping coefficient which often does not depend or only depends slightly on the surface temperature.⁴ Therefore, S_0 is temperature independent. Only an intermediate situation between these two limiting cases can show a temperature dependent initial sticking coefficient. For CO on most transition metals, the second explanation ($E_b \ll E_a$) is pre-

ferred.^{6,11,21-23} This is due probably to the fact that CO adsorbs very strongly on transition metals (except for Ag, Cu, and Au) with no appreciable energetic barrier.

As reviewed in Sec. III A, the presence of a surface modifier causes a strong temperature dependence of the

initial sticking coefficient $S_0(\theta_M)$ in contrast to the behavior of S_0 on the clean surface. How can we understand this change? Since S_0 is temperature independent, K'' is the only temperature dependent term in Eq. (13). K'' can be expressed as follows:

$$\begin{aligned}
 K'' &= \frac{P_b''}{P_a + P_b} \\
 &= \frac{v_b'' \exp(-E_b''/kT)}{\sum v_i'' \exp(-E_i''/kT)} \cdot \frac{\sum v_i \exp(-E_i/kT)}{v_a \exp(-E_a/kT) + v_b \exp(-E_b/kT)} \\
 &= \frac{1}{1 + (v_c''/v_b'') \exp[-(E_c'' - E_b'')/kT]} \cdot \frac{\sum v_i \exp(-E_i/kT)}{v_a \exp(-E_a/kT) + v_b \exp(-E_b/kT)}. \quad (18)
 \end{aligned}$$

First, let us look at the first term in Eq. (18). The temperature dependence is determined by the difference in activation energies for migration and desorption of the precursor on top of the modifier. The typical physisorption energy of CO is between 7 kJ/mol [condensation energy of CO (Ref. 36)] and 19 kJ/mol [on Ag (Ref. 37)] and the migration activation energy of the precursor is about 30% of its binding energy (equal to the physisorption energy). Therefore, $(E_c'' - E_b'')$ is a few kilojoules per mole and a strong temperature dependence of the first term is expected between 100–300 K ($kT = 0.83$ – 2.5 kJ/mol). From Eq. (18), it is seen that K'' increases with increasing temperature.

The second term shows a complicated temperature dependence. Since $P_a \gg P_b$ ($E_a \ll E_b$) for CO on transition metals, most adsorbed molecules on the clean surface become chemisorbed as mentioned before, and the migration probability from the clean surface must also be negligible. In this case, the second term reduces to unity, independent of temperature. The first term is therefore the only temperature dependent term. If the migration probability from the clean surface is not negligible, the second term reduces to $1 + (v_c''/v_b'') \exp[-(E_c'' - E_a)/kT]$ because of $v_a \exp(-E_a/kT) \gg v_b \exp(-E_b/kT)$ for CO on transition metals. Since $E_a \ll E_b$ and $E_c \approx 0.3E_b$, $E_c - E_a$ must be larger than zero. Increasing the surface temperature will again cause an increase of K'' . In both cases, a strong temperature dependence of $S_0(\theta_M)$ is expected on modified surfaces. A decrease of $S_0(\theta_M)$ with increasing temperature is expected from Eq. (16) and the above analysis of K'' in Eq. (18), in good agreement with experimental results in the literature as reviewed briefly in Sec. III A. Physically, this means that since a molecule in the modifier precursor state can only either desorb or move to an empty site (where it is highly likely to chemisorb at zero adsorbate coverage) and since the activation energy for migration is always smaller than the activation energy for desorption, an increase in the surface

temperature causes a much stronger increase in the desorption rate constant than that for migration out of the modifier precursor state. Therefore, a decrease of $S_0(\theta_M)$ with increasing temperature should be seen on modifier-precovered surfaces.

C. Dependence of the initial sticking coefficient on the modifier concentration

The dependence of $S_0(\theta_M)$ on the modifier concentration as described by Eq. (13) is very similar to the original Kisliuk equation.⁸ The only difference between these two equations is that the adsorbate coverage θ is replaced by the modifier coverage θ_M , and the probability of desorption from the extrinsic precursor on top of an adsorbate is replaced by the probability of desorption from the modifier precursor on top of the modifier. Physically, this means that the precursor on top of the modifier prevents a linear decrease of $S_0(\theta_M)$ with increasing modifier coverage, just as in the case of a clean surface where the extrinsic precursor prevents a linear decrease of the sticking coefficient with increasing adsorbate coverage. It is therefore no wonder that experiments have often observed a similar dependence of the initial sticking coefficient on the modifier coverage as observed for the sticking coefficient on the adsorbate coverage.

The experimental results in Fig. 2 can be fit using Eq. (13). Since m is not equal to 1 for K on Pt(111) and Pd(100), Eq. (13) must be rewritten to

$$S_0(\theta_M)/S_0 = \left(1 + \frac{m\theta_M}{1 - m\theta_M} K'' \right)^{-1}. \quad (19)$$

The results are given as the solid line in Fig. 2. The best fits were obtained by $m=4$ and $K''=0.095$ for Pt(111) and $m=2$ and $K''=0.089$ for Pd(100). The fitting parameter K'' should not be taken too seriously because many as-

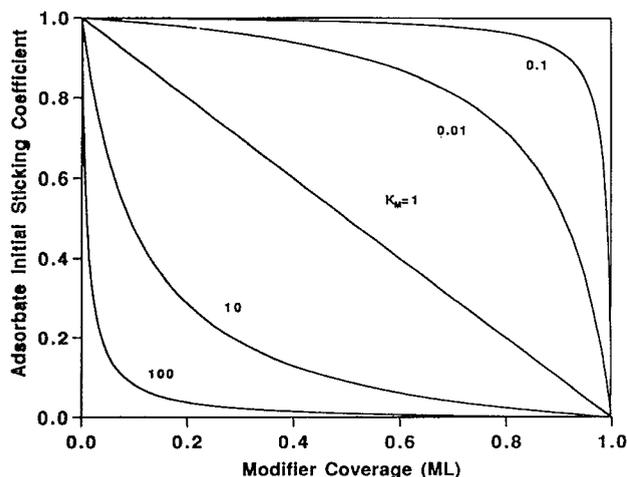


FIG. 3. The dependence of the initial sticking coefficient on the modifier coverage as given by Eq. (13) for various K'' values.

sumptions have been made. This agreement should only demonstrate the validity of our equation to explain the modifier coverage independence of the initial sticking coefficient at small modifier coverage.

The calculated dependence of $S_0(\theta_M)$ on the modifier coverage for several values of K'' is shown in Fig. 3. The initial sticking coefficient decreases linearly with increasing modifier concentration for $K''=1$, and for this condition, Eq. (1) can be used to describe the dependence of $S_0(\theta_M)$ on the modifier coverage. In all other cases, where the modifier precursor state plays a role, $S_0(\theta_M)$ does not scale linearly with the modifier coverage. When K'' is smaller than unity, the modifier holds the precursor on top of it long enough for transfer to occur to an empty site to possibly become chemisorbed; the initial sticking coefficient decreases much more slowly with increasing modifier coverage than one would expect from Eq. (1). When K'' is larger than unity, desorption from the modifier precursor is very efficient and an additional desorption pathway for the precursor on top of the empty site is also open, i.e., migration of the precursor from an empty site to a modifier-precovered site and then desorption. This causes a much faster decrease with increasing modifier coverage than one would expect from Eq. (1). (Physically, this process is not very probable and therefore, no experimental result has been observed for this case to our knowledge.)

Turning again to some of the existing experimental results described in Sec. III A, we can now understand the experimental findings. In all of the systems investigated, an initial sticking coefficient independent of modifier coverage is found at a modifier coverage of $\theta_M=0.25-0.5$ at low temperature. This is due to the great propensity of CO to be trapped in the modifier-precursor state at the temperature used in most experiments (the extrinsic precursor, i.e., the precursor on top of adsorbed CO, has a similarly long lifetime at these temperatures, which causes the CO coverage-independence of S^{CO} on the unmodified surface). In going to higher temperature, K'' increases, as discussed before, and can eventually reach unity. In this case, a linear

decrease of the initial sticking coefficient is observed for CO on C-, P-, or S-precovered Pt(111) at 300 K.³⁵ In contrast to the studies on K/Pd(100), the adsorption kinetics of CO on K-modified Pt(111)²⁰ were studied at 320 K. In this case, the influence of the modifier precursor is less important than at lower temperatures and the size change due to the ionic to metallic transition of K, as discussed in our previous explanation of this data, could still play an important role. However, the analysis presented herein certainly complicates this simple interpretation.

IV. SOME ADDITIONAL NOTES

Until now, we have assumed implicitly that the trapping coefficient is unity. However, a trapping coefficient below unity has been observed often.¹⁻⁴ The trapping coefficient can also vary from the clean surface to a modified surface because of the change of the surface atom effective mass and the physisorption well depth. Therefore, a quantitative analysis of experimental results must incorporate the various trapping coefficients in the above equations. This can be done easily.

In the above discussion, we also neglected lateral interactions between the adsorbates, between adsorbates and modifier adatoms, and between modifier adatoms. Similar approaches as used for clean surfaces by Cassuto and King³⁴ can be adapted to describe all of the lateral interactions on modifier precovered surfaces too.

The last note we want to make is that the desorption kinetics on bimetallic and modifier-precovered surfaces will certainly be influenced by the presence of the modifier precursor state. This role has not been considered before either. However, the incorporation of the effects of the modifier precursor can be done analogously to that introduced for the precursor role on a clean surface.^{38,39}

V. CONCLUSION

The concept of a modifier precursor has been introduced. A molecule impinging on an inert (for chemisorption) modifier adatom or surface atom can be trapped in a physisorption well above the modifier and influence the adsorption kinetics considerably. Both experimental and theoretical evidence for the presence of this third precursor (in addition to intrinsic and extrinsic precursors) has been presented. The equation derived by incorporating the effects of the modifier precursor has been used to explain the experimentally observed dependence of adsorbate molecule initial sticking coefficients on the modifier coverage and the surface temperature. The concept of the modifier precursor should not only be limited to adsorption kinetics and, e.g., a complete interpretation of desorption kinetics on modified surfaces must also consider the effect of the modifier precursor.

ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division.

- ¹C. R. Arumainayagam and R. J. Madix, *Prog. Surf. Sci.* **38**, 1 (1991).
- ²J. A. Barker and D. J. Auerbach, *Surf. Sci. Rep.* **4**, 1 (1984).
- ³M. P. D'Evelyn and R. J. Madix, *Surf. Sci. Rep.* **3**, 1 (1984).
- ⁴M. A. Morris, M. Bowker, and D. A. King, in *Comprehensive Chemical Kinetics*, edited by C. H. Bamford, C. F. T. Tipper, and R. D. Compton (Elsevier, Amsterdam, 1984), Vol. 19.
- ⁵*Physics and Chemistry of Alkali Metal Adsorption*, edited by H. P. Bonzel, A. M. Bradshaw, and G. Ertl (Elsevier, Amsterdam, 1989).
- ⁶M. P. Kiskinova, *Poisoning and Promotion in Catalysis Based on Surface Science Concepts and Experiments* (Elsevier, Amsterdam, 1992).
- ⁷C. T. Campbell, *Annu. Rev. Phys. Chem.* **41**, 775 (1990).
- ⁸P. Kisliuk, *J. Phys. Chem. Solids*, **3**, 95 (1957).
- ⁹J. Harris, and A. C. Luntz, *J. Chem. Phys.* **91**, 6421 (1989).
- ¹⁰I. Langmuir, *Chem. Rev.* **6**, 451 (1929).
- ¹¹J. E. Lennard-Jones, *Trans. Faraday Soc.* **28**, 333 (1932).
- ¹²J. A. Becker and C. D. Hartman, *J. Phys. Chem.* **57**, 157 (1953).
- ¹³G. Ehrlich, *J. Phys. Chem.* **60**, 1388 (1956).
- ¹⁴L. D. Schmidt, in *Topics in Applied Physics*, edited by R. Gomer (Springer, Berlin, 1975), Vol. 4.
- ¹⁵W. H. Weinberg, in *Kinetics of Interface Reaction*, edited by M. Grunze and H. J. Kreuzer (Springer, Berlin, 1986).
- ¹⁶The exact equation should be $P_{a1} = (1 - n\theta - m\theta_M)P_a$. For brevity, we set $n = m = 1$. However, this assumption does not influence the derivation qualitatively. For n and m not equal to 1, very similar results can be obtained— n and m can be added simply to the final equation.
- ¹⁷R. J. Behm, G. Ertl, and V. Penka, *Surf. Sci.* **160**, 387 (1985).
- ¹⁸T. Engel, *J. Chem. Phys.* **69**, 373 (1978).
- ¹⁹H. Pfnür, and D. Menzel, *J. Chem. Phys.* **79**, 2400 (1983).
- ²⁰L. Q. Jiang, and B. E. Koel, *Surf. Sci.* **273**, 273 (1992).
- ²¹J. C. Kiskinova, in *New Trends on CO Activation*, edited by C. Guzzi (Elsevier, Amsterdam, 1991).
- ²²J. C. Campuzano, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, edited by D. King and D. P. Woodruff (Elsevier, Amsterdam, 1984).
- ²³L. K. Verheij, J. Lux, A. B. Anton, B. Poelsema, and G. Comsa, *Surf. Sci.* **182**, 390 (1987).
- ²⁴A. Berkó, and F. Solymosi, *J. Chem. Phys.* **90**, 2492 (1989).
- ²⁵H. B. Nielsen, U. Burghaus, G. Broström, and E. Matthias, *Surf. Sci.* **234**, L271 (1990).
- ²⁶J. A. D. Matthew, F. P. Netzer, and G. Astl, *Surf. Sci.* **259**, L757 (1991).
- ²⁷R. G. Windham, B. E. Koel, and M. T. Paffett, *Langmuir* **4**, 1113 (1988).
- ²⁸M. E. Jones, and B. E. Koel (to be published).
- ²⁹E. L. Hardegee, P. Ho, and J. M. White, *Surf. Sci.* **165**, 488 (1986).
- ³⁰A. Szabo, M. Kiskinova, and J. T. Yates, Jr., *J. Chem. Phys.* **90**, 4604 (1989).
- ³¹S. Johnson and R. D. Madix, *Surf. Sci.* **108**, 77 (1981).
- ³²M. Kiskinova, A. Szabo, and J. T. Yates, Jr., *J. Chem. Phys.* **89**, 7599 (1988).
- ³³M. Kiskinova, A. Szabo, and J. T. Yates, Jr., *Surf. Sci.* **226**, 237 (1990).
- ³⁴C. Xu, and B. E. Koel (to be published).
- ³⁵M. Trenary, K. J. Uram, and J. T. Yates, Jr., *Surf. Sci.* **157**, 512 (1985).
- ³⁶*CRC Handbook of Chemistry and Physics*, edited by R. C. Weast, 54th ed. (The Chemical Rubber Co., Boca Raton, FL, 1973).
- ³⁷G. McElhiney, H. Papp, and J. Pritchard, *Surf. Sci.* **54**, 617 (1976).
- ³⁸A. Cassuto and D. A. King, *Surf. Sci.* **102**, 388 (1981).
- ³⁹R. Gorte and L. D. Schmidt, *Surf. Sci.* **76**, 559 (1978).