TOPICAL REVIEW

The role of precursor states in adsorption, surface reactions and catalysis

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Abstract
Among the many concepts which have been developed in surface science to explain the nature of adsorption, the role of weakly-held intermediate states, so-called precursor states, is one of the most important. The kinetics of precursor-mediated adsorption is described, together with examples showing how significant such effects can be, not just in adsorption itself, but also in surface reactions on crystals and on model-supported catalysts.

1. Introduction
The purpose of this paper is to review aspects of our understanding of surface reactivity, in particular relating this to the involvement of relatively short-lived, intermediate states, often called ‘precursor’ states, in the kinetics. In part it was presented as a paper at the Interdisciplinary Surface Science Conference held at Reading University in 2009 (ISSC17), in honour of Professor David King's contribution to surface science. Hence this paper relates to his contribution to our understanding of adsorption and surface reactivity, particularly regarding the role of precursor states in adsorption. It is the case that almost all, if not all, catalytic reactions carried out on the industrial scale rely on the chemisorption of the reactant on the surface, so that significant bond transformation can take place. This occurs via reactant bond weakening, and the transfer of atoms, either internally within the molecule (isomerization reactions, for instance) or between molecules/atoms. The surface mediates this process by forming the adsorbed state. In what follows I will first outline the basic kinetics of adsorption, then go on to show how these are modified by the consideration that a weakly-held state of the reactant (such as a physisorbed species) can be involved in the process. I will then give some examples which show the great importance of such a precursor state for dictating the rates of surface reactions and catalysis.

2. Reaction kinetics and surface reactions

2.1. Simple rate equations
We need to define some simple relationships, which relate to adsorption kinetics which are described in section 2.2.
Elementary rate equations (that is, those taking place in a single step, as shown in reaction (i)) are of the general form

\[ x \rightarrow z + y \quad (i) \]

where \( x \) is the reactant concentration, \( t \) is time, \( n \) is the order of reaction and \( k \) is the constant of proportionality between rate and concentration, and is the rate constant.

If a reaction takes place in two sequential steps as follows:

\[ x \xrightarrow{1} I \xrightarrow{2} z + y \quad (ii) \]

then the equation becomes slightly more complicated:

\[ \frac{dI}{dt} = k_2[I] \quad (2) \]

where \([I]\) is the intermediate concentration and \( k_2 \) is the rate constant for step 2. In principle this rate may vary in a moderately complicated way, depending on the relative values of the rate constants for step 1 and step 2. If step 2 is relatively fast, then the rate becomes dictated by step 1 and the concentration of the intermediate then remains low and fairly constant during most of the course of the reaction. Under such circumstances the time dependence of the rate can be solved by the steady-state approximation and is given by

\[ \frac{dI}{dt} = x_0(1 - e^{-kt}) \quad (3) \]

where \( x_0 \) is the starting concentration of reactant. In a number of cases the first step is an equilibrium one, as follows:

\[ x \Leftrightarrow I \xrightarrow{2} z + y \quad (iii) \]

Then the kinetics are modified to

\[ \frac{dI}{dt} = K k_2 x \quad (4) \]

where \( K \) is the equilibrium constant for step 1 (equal to the ratio of forward and back rate constants).

### 2.2. Surface reactivity and adsorption

A number of famous early scientists recognized the importance of surfaces in some types of reactions and in catalysis, and the latter term itself originally being coined by Berzelius to describe a particular (and at the time thought to be peculiar [1]) type of reactivity, and it is now widely used in the English language, beyond its original scientific definition. Faraday, in particular, noted the importance of clean Pt surfaces for efficient catalysis and the negative effects of certain gases which could act as poisons for the hydrogen–oxygen reaction [2]. One of the most well-known kinetic relationships in this field is that of Langmuir, whose work was stimulated by the attempts to understand the working of tungsten filament light bulbs (he was employed by General Electric) with the ultimate aim of improving their efficiency. The result was the Langmuir adsorption isotherm [3], describing equilibrium adsorption, and it is based on simple adsorption and desorption steps proceeding at equilibrium:

\[ x_g + s \rightarrow x_a \quad (iv) \]

\[ x_a \rightarrow x_g + s \quad (-iv) \]

with subscripts g and a referring to gas phase and adsorbed species, respectively, while \( s \) is an adsorption site at the surface. The adsorption rate then is

\[ R_a = \frac{dx_a}{dt} = k_1 P (1 - \theta) \quad (5) \]

where \( \theta \) is a dimensionless, relative quantity, representing the fractional coverage of the surface by adsorbate, relative to the maximum coverage at saturation, \( P \) is the gas pressure of the reactant and \( k_1 \) is the rate constant for reaction \((iv)\). In terms of what follows, we will define the sticking probability, \( S \), as

\[ S = \frac{R_a}{R_a^0} = S_0 (1 - \theta) \quad (6a) \]

or, for dissociative adsorption, which requires two surface sites:

\[ S = \frac{R_a}{R_a^0} = S_0 (1 - \theta)^2 \quad (6b) \]

where \( R_a^0 \) is the impingement rate of molecules with the surface, \( R_a \) is the adsorption rate and \( S_0 \) is the zero coverage value of the sticking probability. The corollary of equation \((5)\) for desorption \((\text{-iv})\) is

\[ R_d = k_{-1} \theta. \quad (7) \]

If the system is at equilibrium with steady-state, constant coverage, then it follows that

\[ \theta = KP/(1 + KP) \quad (8) \]

where \( s \) is a surface site required for adsorption (whose coverage \( = 1 - \theta \)), \( P \) is the equilibrium pressure of \( x \) in the gas phase and \( K \) is the adsorption equilibrium constant (the ratio of adsorption and desorption rate constants). This is the usual form of the Langmuir adsorption isotherm for non-dissociative adsorption.

It is important to consider carefully what we mean by the definition in equation \((6a)\). In practical terms \( R_a \) relates to adsorption into a state which is long-lived with respect to the timescale of the experiment. If desorption rates back into the gas phase are high, then what is measured is the net sticking probability into the adsorbed state, which may be significantly lower than the absolute sticking probability. Indeed, if desorption rates are high then the apparent net sticking probability may be close to zero, even though adsorption is taking place, and this is discussed further in section \(3.1\). Aspects of this have been considered in more detail by Burghaus [4].

Of more importance for reactivity is the Langmuir equation, describing simple surface reaction kinetics. This is a pre-equilibrium situation akin to that in section \(1\), but the difference here is the limitation of the amount of the intermediate due to the limited number of sites, \( s \), which are available at the surface:

\[ x + s \Leftrightarrow I_s \rightarrow z + y \quad (v) \]
squares, all rate constants $k_1 = k_2 = 1$, $k_{-1} = 0$, that is, no pre-equilibrium, a series reaction; squares, all rate constants $= 1$; triangles, $k_1 = k_{-1} = 1$, $k_2 = 0.1$, that is, step 2 is slow and rate-determining.

The kinetic result is

$$\frac{dz}{dt} = k_1 k_2 P / (k_{-1} + k_2 + k_1 P). \quad (9)$$

The form of this is different from the general case of pre-equilibrium where the reactivity has normal order dependence and the reactants do not appear in the denominator of the rate equation and, as shown in figure 1, the rate can be seen to occur at high reactant pressures; that is, it then becomes zero order. Note that the Langmuir equation above (equation (9)) is essentially the same as that for the famous Michaelis–Menten equation for enzyme catalysis, derived at about the same time as the Langmuir equation [5]. Note that, even though this is the simplest possible case of a surface reaction, equation (9) is already rather complicated, with three rate constants involved.

At this point we need to consider more about the nature of adsorption itself, since the Langmuir equation is based on the simplistic premise that molecules hit a surface and either adsorb if sites are free at the point of impact, or do not if the sites are already blocked. As we know the situation is rather more complex than that.

2.3. Chemisorption and physisorption

We now know very well that adsorption is not a simple collision event where a molecule hits a surface and either sticks or bounces back into the ether. It is a much more complex process and the reader is directed to a number of recent reviews which go into more detail regarding the kinetics and dynamics of the interaction of an approaching molecule with the surface than can be considered here [6–9].

Historically the contribution of Lennard-Jones represents another seminal point in our understanding of adsorption, since he considered adsorption from a theoretical point of view [10]. He drew the kind of adsorption potential scheme which is now reproduced in a huge number of research talks and undergraduate courses, which shows that adsorption can proceed in two stages, and that there is a relatively weak interaction with the surface at long distance, known as physisorption (figure 2(a)). Here polarization effects cause a dipolar interaction with the surface which leads to an attraction and lowering of potential energy in the system. At closer approach electronic repulsion causes the potential energy to increase again and so a potential ‘well’ is present, which means that the approaching molecule can be ‘trapped’ into this state for some time and physisorb. If we consider a molecule such as oxygen, then we can imagine putting in the bond dissociation energy to split the molecule to atoms. If these atoms approach the surface, then the potential diminishes continually upon close approach until ‘touch-down’, at which point electron transfer has occurred to form a chemical bond between the surface and the atom; it is chemisorbed. At the point at which the physisorption and chemisorption curves cross it is now well known from experiment and theory that real physical curve-crossing for many systems is facile, and so transfer from the physisorbed molecule to the chemisorbed atomic state can occur readily and with high probability. For instance, on most transition element surfaces the sticking probability of oxygen into atomic states occurs with a probability greater than 0.1.

Figure 2 is essentially a one-dimensional picture of the surface, whereas molecules and surfaces especially are very much three dimensional in their electronic structure. Thus, there are difficulties encountered by the approaching molecule since not all collisions are of the right orientation to favour adsorption. The reader is referred to the concept of ‘early’ and ‘late’ barriers to dissociation of molecules, relating to whether the actual dissociation process occurs at long or short distance from the surface. Figure 3 shows a more detailed, hypothetical example of the potential curves above from the work of Darling [11], but a number of authors are developing an ever more detailed description of such multi-dimensional potential profiles using not only empirical methods, but also DFT and ab initio methods (see, for instance, [12–14]).

2.4. ‘Precursor states’, ‘transients’, ‘intermediates’

Following on from the considerations above, it is clear that chemisorption can be preceded by physisorption and that this state, and the energetics of its adsorption, must play an important role in the adsorption process. This can also have significant technological consequences, since heterogeneous catalysis, one of the major facilitating technologies of the 20th century, occurs through reactions between chemisorbed species. Thus the mechanistic scheme described above in (v) seems, in general, to be an inadequate description of the process, since it only involves the chemisorbed intermediate. Instead we need to elaborate the scheme as follows:

$$x ⇔ P + s \rightarrow I_a \rightarrow z + y \quad (vi)$$
where we use the symbol $P$ to represent the physisorbed state, though we may more generally refer to it, as many others before have, as the ‘precursor’ state (see below). However, we need some clarification of what we mean by a precursor state, in particular because there are also other, related terms around in the literature, such as the ‘transient’ state [15] (not to be confused with the ‘transition’ state, as in the Eyring theory of reaction kinetics [16]) and surface intermediates.

At this stage let us make a very simple definition of the ‘precursor state’ as a species which has thermally accommodated to the surface temperature, but which has a short, but nevertheless significant, lifetime on the surface compared to the lifetime of the strongly adsorbed state $I_a$. The precursor can exist over both filled and empty sites on the surface. $I_a$ may either be the final adsorbed state or may proceed to product formation. Many measurements in surface science do not proceed to products $z$ and $y$ in scheme (vi) (although we will describe some that do below) and so $I_a$ is indeed often the final state of the adsorption measurement and $I_a$ is essentially stable and long-lived. A better description than the simple Lennard-Jones 1D picture (which in itself is extremely useful) and which gives extra insight into the role of these precursors is shown in figure 4. There is usually a much more shallowly corrugated potential parallel to the surface plane, shallow enough to allow mobility in the precursor state, which can then dramatically affect adsorption kinetics.

A distinction from ‘transient’ or even ‘transition’ states is that these can be chemisorbed species, occupying specific adsorption sites at the surface (though the ‘transient’ can also have some mobility on the surface [15]), whereas the precursor does not occupy chemisorption sites.

Now let us examine the kinetic consequences of this consideration. The rate of formation of the intermediate
adsorbed state is
\[ \frac{d[I_a]}{dt} = k_2 \theta_p (1 - \theta) \]  
(10)
and, invoking the steady-state approximation for the coverage of the precursor state, then
\[ \frac{d[I_a]}{dt} = k_2 K_p P_X / (1 + K_p P_X) \]  
(11)
where \( K_p \) is the equilibrium constant for the first step. The effect of this on adsorption rates is shown in figure 5. Although the involvement of such a precursor will affect the adsorption kinetics somewhat (in general, reducing the adsorption rate due to desorption of molecules from the precursor state), the basic Langmuir ideas apply, that is, the precursor cannot chemisorb on a filled site, and, as figure 5 shows, the sticking coefficient (proportional to rate) will decrease linearly with increasing coverage, assuming constant, low steady-state coverage in the precursor state.

However, it was found very early on that the sticking probability (and hence adsorption rate, equation (6a)) did not follow the simple decrease with increasing coverage which might have been expected, an early example being shown in figure 6 from the work of Becker and Hartman [17] for nitrogen adsorption on a W film, together with results from King et al for planar W(100) [18] and a stepped surface, W(320) [19]. Here it is evident that the sticking probability stays much higher than might be expected on the basis of the Langmuir considerations, for instance, at 0.4 monolayer coverage on the (100) surface the adsorption rate is far higher (\( S / S_0 = 0.7 \)) than might be expected on the basis of the relatively few remaining clean pair sites on the surface (it should be 0.03). The more complex nature of adsorption had already been recognized in 1933 by Taylor and Langmuir [20] who proposed the idea that diffusion in a weakly-held layer had a role in adsorption; this was needed in order to explain the high sticking probability of Cs on tungsten, even as coverage approached saturation. In seminal papers in 1957 Kisliuk, working at Bell Labs, presented an analytical approach to understanding such high adsorption rates [21, 22]. He quantified the importance of diffusion in the ‘precursor’ state (which he considered to be physisorbed), and in two elegant
papers he outlined the mathematical application of such an idea, which is pictorially outlined in figure 7. Here it is considered that there are two types of precursor which have mobility in this weakly-held state—‘intrinsic’ (that over an empty chemisorption site) and ‘extrinsic’ (that over a filled site) [23]. The adsorption rate then depends upon the rate of adsorption from the intrinsic state and the rate of diffusion of the extrinsic state to empty sites where it can adsorb. Summing all these probabilities results in a simple modification to the Langmuir-type adsorption rate as follows:

\[
S = S_0 \left[1 + \left(\frac{K_p \theta}{1 - \theta}\right)\right]^{-1}.
\] (12)

The resulting dependence of \(S/S_0\) upon coverage of the adsorbate is given in figure 8 for a variety of values of \(K_p\). Here it can be seen that the equation reduces to the simple Langmuir form of equation (6) when \(K_p = 1\) (that is, no role of the precursor), whereas when \(K_p\) is very small there is a very large precursor effect and \(S\) stays high to very high coverage. The so-called precursor state parameter \(K_p\) is given by basic probabilities as follows:

\[
K_p = S_0 P_{de}/P_{ai}
\] (13)

where the probabilities are defined as shown in figure 7. Clearly the lower the desorption probability from the extrinsic precursor, the more chance it has to diffuse to an adjacent empty site and thereby chemisorb (\(K\) small). This strongly relates to the nature of the adsorption potential and the relative barriers between adsorption and desorption from precursor states. In terms of figure 2(a), the relative sizes of the desorption barrier from the precursor state (equal to the adsorption heat, \(\Delta H_p\)) and the barrier to chemisorption (equal to \(E_a\)) dictate the adsorption rate, and especially the temperature dependence, which depends upon the difference between the two, as follows [18]:

\[
\alpha/S_0 - 1 = (A_d/A_a) \exp(-\Delta H_p - E_a)/RT).
\] (14)

Here \(\alpha\) is the thermal accommodation coefficient into the precursor state, and \(A_d\) and \(A_a\) are the prefactors for desorption and chemisorption from the precursor state. In general, if the apparent activation energy \((\Delta H_p - E_a)\) is positive (that is, the crossover point of physisorption and chemisorption curves is below the zero potential) then the initial sticking probability decreases as temperature increases, whereas if the reverse is the case (that is, the crossover is as in figure 2) the initial sticking increases with increasing substrate temperature.

King et al developed these ideas further in their studies of the dissociative adsorption of nitrogen on tungsten surfaces referred to above and in figure 6 [18, 19]. In particular, in order to describe the sticking curves completely, they had to
that is, the crossover point is at section 2.2, but King initial sticking probability decreases with increased surface state parameter and is given by

\[ \frac{S}{S_0} = (1 + K(1/\theta_{\text{so}} - 1))^{-1}. \]

This is apparently simple, except that the distribution of pair sites, \( \theta_{\text{so}} \), is given from statistical analysis in terms of the quasi-chemical approximation and has a complex dependence on atomic coverage:

\[ \theta_{\text{so}} = 1 - \theta - \left[ 2\theta(1-\theta)/\left(1-4\theta(1-\theta)(1-\exp(-\omega/kT))\right) \right]^{1/2} + 1 \]

where \( \omega \) is the pairwise interaction energy between nearest-neighbour sites. For W(100) they found the apparent activation energy described in equations (14) above to be 18 kJ mol\(^{-1}\), that is, the crossover point is at \(-18\) kJ mol\(^{-1}\), and the initial sticking probability decreases with increased surface temperature. In most cases the sticking probability that was measured was the ‘net’ sticking probability described in section 2.2, but King et al showed that \( S \) could be determined in some cases, even in the region where desorption rates become significant, by the use of isotopic mixing [24]. See Burghaus for a more detailed discussion of these approaches and of further refinements, including ways of differentiating ‘net’ and ‘absolute’ sticking probabilities [4].

Note that, in a number of publications [24–26], King and his colleagues have developed these ideas further, in particular applying them to the desorption process, something we are not considering in detail here. However, precursor effects are indeed also important in desorption and can lead to significant broadening of desorption curves and slowing of desorption rates (largely due to the possibility of readsorption from the precursor during the process). Gorte and Schmidt used a classical chemical kinetic approach [27, 28] to examine the effects of the precursor state, with a variety of reaction schemes and precursor roles, on desorption profiles. Similarly, Kreutzer et al [29, 30] have recently refined and extended these ideas in a number of elegant papers, and have also applied the precursor ideas to both adsorption and desorption.

From the considerations above we can estimate, in a general way, the extent of diffusivity in precursor states. We can express the number of ‘hops’, \( N_h \), that a molecule makes on the surface from the ratio of the Frenkel lifetime on the surface before desorption (\( \tau_{\text{des}} \)) to the lifetime for the hopping process (\( \tau_{\text{diff}} \)):

\[ N_h = \frac{\tau_{\text{des}}}{\tau_{\text{diff}}} = \frac{k_{\text{diff}}}{k_{\text{des}}} = \frac{A_{\text{diff}}}{A_{\text{des}}} \exp((E_{\text{des}} - E_{\text{diff}})/RT) \]  

where we have also expressed the lifetimes in terms of inverse rate constants and their Arrhenius expansion. Further, if we assume \( A_{\text{des}} \sim A_{\text{diff}} \), and that the diffusion activation energy is \( 1/3 \)rd of the desorption energy, which is the approximate relationship from experimental determinations, then we can derive the data shown in table 1 for a particular desorption energy which might be typical of physisorbed states (in this case I have happened to use 38 kJ mol\(^{-1}\)). Even though the lifetime of such a state at ambient temperature is very low, less than one microsecond, nonetheless it can diffuse over many sites, \( \sim 30000 \) of them! We can re-interpret this in terms of a lateral extent of diffusion by using the concept of the ‘diffusion circle’ [31–33]. Here we simply consider the hops as distributed in a circle around the landing site on the surface (figure 9), and so we can describe the extent of the diffusion by the radius of this circle, that is:

\[ r \sim (N_h / \pi)^{1/2}. \]  

Of course, this is a somewhat simplistic approach, but it is useful to give an idea of the average diffusivity. In reality this diffusion is not a step function, as in figure 9, but is a distribution related to Fickian diffusion, that is:

\[ \langle x^2 \rangle = Dt. \]  

And so the extent of diffusion from the landing site is related to the square root of the time of residence at the surface:

\[ x_{\text{rms}} = (Dt)^{1/2}. \]

We can then plot the probability of diffusion in terms of the differential of this equation with respect to time, that is

\[ dx_{\text{rms}}/dt = c t^{-1/2} = d / x_{\text{rms}} \]

where \( c \) and \( d \) are constants. This gives the type of distribution shown in figure 10, with a big decrease in the probability

### Table 1. The temperature dependence of diffusivity in the precursor state.

| \( T (K) \) | \( N_h \) | \( \tau_{\text{des}} (s) \) | \( r \) (sites) |
|---|---|---|---|
| 200 | \( 4 \times 10^6 \) | \( 8 \times 10^{-4} \) | 12000 |
| 300 | \( 3 \times 10^4 \) | \( 4 \times 10^{-7} \) | 90 |
| 500 | 450 | \( 10^{-9} \) | 12 |

include the influence of lateral interactions between atoms in the chemisorbed layer. This strongly affects the distribution of pair-unoccupied sites which are required for the dissociation. The sticking-coverage dependence includes the precursor state parameter and is given by

\[ \frac{S}{S_0} = (1 + K(1/\theta_{\text{so}} - 1))^{-1}. \]
of finding the diffusing molecule away from the landing site. These diffusion concepts will be developed further in the following sections.

3. Precursor states in action

In what follows I will describe various examples, mainly from the work in our own laboratory, which show the important role of precursor states in adsorption itself, but which also show that they can play a critical role in surface reactions (that is, reactions in which the adsorbate transforms to another state and/or yields gas phase products).

3.1. An important example of simple precursor effects: CO adsorption on transition metals and the CO oxidation reaction

Figure 11 shows a sticking probability curve for the adsorption of CO on Pd(110) [34], which is just used as an example of what is generally seen for sticking curves for CO adsorption on transition metals, particularly late transition elements such as the precious metals. There is no doubt that CO adsorbs molecularly, and it desorbs again in TPD with a peak at \(~450\) K. However, it is clear that the behaviour is non-Langmuirian and that the sticking stays high as the coverage increases, only decreasing significantly at high coverages. Using equations (12) above yields a value for the precursor state parameter \(K\) of 0.13, indicating a significant effect and hence the large curvature of the sticking plot. It is unlikely in this case that there is an intrinsic precursor state, and that adsorption is efficient above empty sites, since the CO molecule experiences a continual attraction to the surface up to the bottom of the chemisorption well, that is, it is more like the potential energy representation in figure 2(b). Instead, the sticking stays high because of an extrinsic precursor, that is, CO can physisorb over filled sites where it cannot chemisorb, and can then diffuse to nearby empty sites.
3.2. Mobile precursors can ‘seek and find’ the active site

As mentioned in section 2.2, the sticking probability measured may indeed be a net sticking probability if the desorption rate from the adsorbed state is significant during the timescale of the measurement. Thus, although the apparent sticking probability becomes close to zero in figure 11(f) at a temperature of 470 K and a coverage of ∼0.1, this is due to a high rate of desorption from the chemisorbed state at that temperature.

Curve shapes of the type shown in figure 11 seem to be very general for CO adsorption, at least for the transition elements. Thus similar curve shapes are seen for adsorption on Rh(110) [35], Cu(110) [36, 37], Ir(110) [38] and W(320) [39], for instance.

Because the precursor is so important in adsorption then it can also play a major role in reactions such as CO oxidation. It has been shown that the precursor state for CO has a strong influence on the nature of the CO oxidation reaction on metal single crystals. Thus for Rh(110) CO adsorption itself is precursor-influenced, but so also is the CO oxidation reaction, and including the precursor state in the kinetic model was essential to modelling CO oxidation over a wide range of reaction temperature [40].

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One of the first papers to identify the importance of steps in adsorption was that of Singh-Boparai et al. They examined the adsorption of nitrogen on a stepped W surface—the (320) plane, which consists of mostly the (110) terraces with 20% (100) type steps [19]. The near-close-packed (110) plane has been shown to be very unreactive to N2 dissociation (s ~ 0.01) [41, 42], though even this may be due to the presence of a low density of steps on the surface, whereas the (100) is active (s ~ 0.6) [18, 19], as shown in figure 6 above. Thus, naively, we might expect the sticking probability to reflect the fraction of (100) sites and be ~0.1. However, the precursor effect is clearly evident from the very high sticking probability and curvature of the sticking probability as the coverage increases, as shown in figure 6, again is very different from what is expected from Langmuirian kinetics, especially for dissociation ([1−θ]2 dependence). The details of this system can be found elsewhere [19], but it is interesting to note that there are two mobility effects in these data, as shown in figure 12. The precursor has the mobility to find the active sites for dissociation, which are at the step edges, but the dissociated atoms are also mobile (and may be ‘hot’ atoms [43]) and can populate the (110) sites which are inactive for direct adsorption from the gas phase. In this way not only the (100) sites, but all of the sites on the surface become populated efficiently.

The basic equation above had to be modified to fit the kinetics for W(320) in order to incorporate the fraction of active sites, the step sites, for dissociation, as follows:

\[ S/S_0 = (1 + K(1/\gamma \theta_{co} - 1))^{-1} \]

where \( \gamma \) is the step site fraction, in this case 1/3.

3.3. Mobile precursors result in enhanced surface reaction rates: acid–base reactions at surfaces

The examples given above were for relatively simple adsorption processes, that is, adsorption without a surface reaction taking place. We will now consider situations in which the precursor state interacts with another species with which it reacts—in the following cases acid–base reactions. First of all, let us consider the reaction between pre-adsorbed oxygen atoms (the base) and gas phase formic acid. The sticking probability of formic acid on the clean Cu(110) surface is low, at ~0.1 [44, 45], but upon pre-adsorption of oxygen atoms the reaction probability is very high at 0.82 (see figure 13) [44, 46]. This is because it is difficult for the formic acid to dissociate on the clean surface sites, but the oxygen atoms are able to strip off the acidic hydrogen to produce adsorbed formate in the following way, much more efficiently, via a physisorbed formic acid molecule:

\[ \text{HCOOH} \rightarrow \text{HCOOH}_{p} \]

\[ \text{HCOOH}_{p} + \text{O} \rightarrow \text{HCOO}_{a} + \text{OH}_{a}. \]

As figure 13 shows, the initial sticking probability is very high, but remains constant over a long part of the reaction process until almost all the oxygen is used up—due to the mobility of formic acid in the precursor state which enables it to ‘seek out’ the remaining oxygen atoms, even as their coverage becomes very low. This is even more clearly manifested if only a very small amount of oxygen is dosed onto the surface. Even with only 0.03 monolayers of pre-adsorbed oxygen atoms, the initial sticking probability of formic acid is still 0.82. Again, this is
due to precursor molecules diffusing on the surface and finding the sparsely distributed oxygen atoms with high efficiency.

We were able to examine this effect in even more detail for isopropanol, where we could measure the sticking at low pre-coverages of oxygen atoms as low as 0.008 monolayers, figure 14 [31]. This is a truly remarkable promotion of the reaction event by pre-adsorbed oxygen, whereby the net sticking probability is close to 0 on the clean copper surface, but is increased to 0.75 with a very low pre-coverage of oxygen atoms, and demonstrates the extreme mobility of the alcohol molecules in the weakly-held layer. Indeed, the effect may be more extreme than even this implies because it is known that oxygen adsorbs into a peculiar structure on Cu(110)—forming long strings of Cu–O on the surface [47, 48]. It has been shown that, for similar reactions with methanol, only the oxygen atoms at the end of these chains are the active ones for the reaction [49–51], so the diffusion circle picture is like that shown in figure 15, with a wide spacing between the active oxygen atoms on the surface—a rough estimate gives a spacing of ~20 lattice sites between them. Clearly then, since the initial sticking probability is still high at 0.008 ML of pre-adsorbed oxygen atoms, there is little desorption of the precursor species over that distance before it finds an active site and reacts.

This reaction of formic acid was modelled in some detail for the case where 0.25 monolayers of oxygen was pre-adsorbed, and an essential part of the modelling was the precursor state influence on the adsorption required to fit the flat plateau of the sticking versus time shown above [52]. This is a difficult system to model over a range of adsorption temperatures because reaction products also form during the reaction (CO₂, H₂ and H₂O) and the stoichiometry of the reaction varies with temperature. Further, the active sites are located at the oxygen atomic sites, so that the reaction rate modelling has to include oxygen coverage, in the correct functional form, as follows:

\[ R_1 = A_1 \times \exp\left(\frac{-E_1}{RT}\right) \times \left(1 + \frac{K \times [1 - \theta_O]}{\theta_O}\right)^{-1}. \]

A very good fit of this approach to the data is seen in figure 16; the change of stoichiometry with temperature and the change in product ratios from the formate reaction with oxygen could be fitted by the understanding of the formate stability and the importance of precursor state adsorption which has been obtained from surface science investigations from several groups [44–46, 53–55]. The modelling of the dependence of the product evolution on temperature is shown in figure 17 and the fit is good, showing that the overall reactions are as follows.
Figure 16. Theoretical modelling of formic acid uptake curves at a variety of adsorption temperatures upon a Cu(110) surface with 0.25 monolayers of oxygen pre-adsorbed [52].

Figure 17. Product evolution during the reaction of formic acid with 0.25 ML of oxygen atoms pre-adsorbed on Cu(110) as a function of surface temperature using a molecular beam reactor (solid points) and modelled (open points).

At intermediate temperatures where the formate can decompose (to ~400 K) the reaction is

$$2\text{HCOOH} + \text{O}_a \rightarrow \text{CO}_2 + \text{H}_2 + \text{H}_2\text{O}$$

whereas at higher temperatures the reaction moves to

$$\text{HCOOH} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$

and by 680 K the reaction proceeds almost exclusively in this manner. The main reason for the difference relates to the formate stability. At the lower temperatures the formate decomposes only slowly, so that a second formic acid molecule can react with the OH formed from the primary reaction, before a hydrogen is liberated from the formate by decomposition. In contrast, at higher temperatures, the formate decomposition is fast and so H atoms from the formate decomposition react with OH before another formic acid molecule does [52].

Figure 18. XPS measurements of the uptake of oxygen onto Zn(0001) from the work of Roberts et al [56]. It shows the large sticking increase when ammonia is incorporated into a gas feed compared with the pure O$_2$ case.

Roberts et al [56, 15, 57, 58] have reported surface processes which are a kind of inverse of the reactions above, that is, oxygen adsorption itself is enhanced via the precursor state. Oxygen is not pre-adsorbed, but precursors are pivotal in enabling high reaction rates to be seen. In particular, they investigated the reaction between oxygen and ammonia on Zn(0001). Oxygen adsorption on the clean surface was found to be very slow (the estimated sticking probability was $\sim 10^{-3}$), yet it was enhanced to a very high value when both oxygen and ammonia were co-dosed, figure 18 [56, 15]. It was proposed that this was due to a mobile, reactive, precursor molecular oxygen ‘O$_{\delta - 2}$’ species, which interacted with ammonia in the weakly-held state, enabling facile O$_2$ dissociation, and hence a higher net sticking probability for oxygen into a long-lived state.

3.4. Precursor states can ‘seek and find’ the active site II—finding nanoparticles on model catalysts and high area catalysts

Some considerable time ago Boudart et al reported some unusual findings for the adsorption of hydrogen on Pyrex glass and later for the oxidation of CO on model Pt catalysts supported on $\alpha$-alumina [59, 60]. Basically, they found that the reaction rate for CO oxidation was much higher than they expected on the basis of the measured fractional coverage of the catalyst surface by Pt particles. This latter finding reflected some earlier related findings of higher adsorption rates than might be expected from gas pressures on catalyst particles, mooted to be due to diffusion from the surrounding support area [61, 62]. These were explained by Boudart in terms of a reverse spillover of CO from the support to the metal, invoking the ‘collection zone’ concept, which is discussed below.

In recent times surface science, in relating to catalysis, has moved to the production of model materials, for instance, nanoparticles have been deposited on well-defined support surfaces, either single-crystal oxides [63, 64] or thin film oxides [65, 66]. As a result some surface studies have revisited this point of the collection zone, though note that it has also been outlined in terms of the ‘diffusion circle’ described above,
as a shorthand way of describing the extent of diffusion of a precursor state on a surface [67]. In a series of elegant works by Matolin et al [94] there was a noted enhancement of the sticking of CO on model-supported Pd catalysts, using several different types of support material [52, 53, 68–71]. Here they associated the enhancement with the ability of CO, adsorbed into a precursor state within the capture zone of the Pd nanoparticles, to migrate to the Pd, and they incorporated this idea into a formulation for the sticking. This essentially consists of two parts—that due to molecules directly adsorbing on the Pd particles, and that arising from those adsorbed weakly in the capture zone. For the situation in which metal nanoparticles are well separated and capture zones do not overlap:

$$S_t = (S_s X_d (2r + X_d) + S_{Pd} r^2) r n$$

where $S_t$ is the measured sticking probability, $S_s$ is that for CO on the support, $S_{Pd}$ that on the metal particles of radius $r$, $n$ is the particle density and $X_d$ is the extent distance of the capture zone from the Pd particle. Even though this has many assumptions incorporated into it (homogeneous particle size distribution, a finite limit to the capture zone (see the end of section 2.4)) they nonetheless could model the adsorption with reasonable success.

Henry et al [72, 73, 63] also developed these kinds of ideas and have carried out molecular beam measurements, extending beyond adsorption to the reactive catalytic situation. They emphasize the importance of taking into account the extent of the capture zone effect when trying to interpret the effects of particle size on catalytic reactivity, for instance for the CO/NO reaction on Pd/MgO(100) model catalysts [73]. The capture zone can result in higher reaction rates than expected from the Pd coverage on the support MgO, but the extent itself depends on the density of the particles on the surface. A number of theoretical descriptions have evolved [74–76], and Zhdanov and Kasemo [76] have applied Monte Carlo modelling to the effect of the diffusion zone around nanoparticles on the bistability profiles (rate versus reactant pressure variation) of bimolecular surface reactions. There can be dramatic shifts of the maximum to lower reactant pressure due to such effects.

Bowker et al measured the adsorption of CO on Pd nanoparticles (of ~4 nm diameter) [67] and found an enhancement of the sticking probability of CO by a factor of ~5 over what would be expected from the areal coverage of the surface by Pd nanoparticles. This is due to the influence of the precursor state, and this effect is shown in figure 19 and schematically shown in figure 20. Here the adsorption is of two main types—direct adsorption on the nanoparticles, plus that from a diffusing flux of CO via the precursor state on the support. Note that the adsorption of CO on oxides is generally weak, usually ~20–50 kJ mol$^{-1}$, and so the lifetime at ambient temperature is very short. The best fit to the data in this case was obtained with 38 kJ mol$^{-1}$ binding energy; the lifetime is ~a tenth of a microsecond at 300 K, and so the radius of the ‘diffusion circle’ on the support would be ~2 nm. Thus the particle (of approximate cross-sectional area 12 nm$^2$) would capture CO molecules from an area on the support of approximately four times its own area, and hence the significant enhancement of the CO sticking which is seen in these kinds of measurements. In figure 20 the Boudart idea of the collection zone is also shown which reflects this effectively higher cross section for adsorption on to the particles, and the diffusion circle is just another way of expressing this idea.

The idea of the collection zone is a good one, but we must remember that there will not be an isotropic distribution
of precursor molecule concentration on a surface with active nanoparticles around, as pointed out by Henry et al [72]. As shown in figure 21 there will be ‘draining’ of the CO in the vicinity of the nanoparticles since, on the support, the coverage will be determined by the gas phase equilibrium, dictated by adsorption and desorption, as follows:

\[
CO_g \rightarrow CO_p
\]

\[
CO_p \rightarrow CO_g
\]

whereas when a particle is nearby there is an additional kinetic process draining the precursor CO coverage as follows:

\[
CO_p \rightarrow CO_{a,Pd}
\]

This results in the depletion of the precursor state illustrated schematically in figure 21. What this shows is a depletion around the particles from the concentration far from the particle (the level in the middle of the region between particles). Of course, the adsorption situation is non-steady state and is dominated by the kinetics of the chemisorption onto the metal nanoparticles, and so the profiles illustrated in figure 21 would evolve as the metal becomes saturated with adsorbate and the precursor concentration around the particle would become isotropic. However, if we consider the situation of a reacting system, CO oxidation for instance, there will be a continuous drain of precursor from the support of the type shown in figure 21.

4. Are precursor states important in industrial heterogeneous catalysis?

From all we have said above it is clear that precursor states have a very significant role to play in adsorption, on both single crystals and on nanoparticulate catalysts, and can strongly affect reaction kinetics, as in the case of formic acid decomposition described above. However, will they be of significance in industrial scale catalysis? Well, the answer is yes, but it depends very much on the reaction concerned. Thus, if the reaction is a relatively low temperature one, using large molecules, like, for instance, hydrocarbon dehydrogenation reactions, which often take place at \( \sim 400 \) K in temperature, then the precursor of the hydrocarbon will be important and will affect the kinetics. On the other hand, it will be insignificant for very high temperature reactions using small molecules, for instance, the steam reforming of methane on Ni catalysts, which take place at \( \sim 1000 \) K, and for which the lifetime of the low molecular weight precursor will be very low. In many cases in catalysis, the ‘active site’ may have minority areal coverage on the surface. Examples would be naphtha reforming on Pt/SlO\(_2\) catalysts where the Pt loading is only \( \sim 0.3\%\); in oxide catalysts sometimes the active site is a defect centre which may be sparse on the surface. As mentioned above ‘light-off’ in automobile catalysts is affected by the diffusivity of CO across the supported metal surface. Thus it is a factor of practical interest in industrial processes too.

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