

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 and catalysis to explain the nature of adsorption, the role of weakly-held 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. These examples include CO adsorption on Pd single crystals and catalysts and implications for CO oxidation, and extreme examples of the precursor effect, where adsorbate molecules can appear to ‘seek out’ active sites which are in very low concentration on the surface. The decomposition and oxidation of formic acid is just such an example. Such reactivity patterns then also lead to concepts such as the ‘collection zone’ or ‘diffusion circle’ describing how much of an area of surface is ‘swept’ by incoming weakly-held molecules during their brief sojourn there.

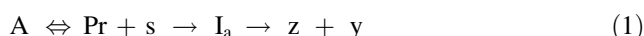
Keywords Precursor states · Physisorbed states · Adsorption kinetics · Sticking probabilities · CO adsorption · CO oxidation · Formic acid

1 Introduction

The purpose of this paper is to consider the role of relatively short-lived, intermediate states, often called ‘precursor’ states, in the kinetics of adsorption and surface reactions. 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 or between molecules/atoms. The surface mediates this process by forming the adsorbed state and the kinetics of these transformations can often be rate-determining in catalysis. Hence it is important to consider the role of physisorbed species in these processes.

2 Precursor States’, ‘Transients’, ‘Intermediates’, Some Definitions

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. Thus we can consider adsorption to occur as follows:



where A is the adsorbing molecule, s is a surface site, I_a is some intermediate species on the surface and z and y are, in this case, gas phase break-down products of A, and we use the symbol Pr to represent the physisorbed state, though we may more generally refer to it, as many others before have, as the ‘precursor’ state.

At this stage let us make a very simple definition of the ‘precursor state’, It is a species which has thermally

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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 Ia. The precursor can exist over both empty and filled 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 1 (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, that is, the experiment is carried out below it's decomposition/desorption temperature.

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 [1]), whereas the precursor does not occupy chemisorption sites.

It was found very early in the era of adsorption measurements that the sticking probability (and hence adsorption rate) did not follow the sharp decrease with increasing coverage which might have been expected from the original Langmuir considerations. For example, in the work of Becker and Hartman [2] for a nitrogen adsorption on a W film, together with results from King et al. for planar W(100) [3] and a stepped surfaces, W(320) [4] the sticking probability stays high, 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 considered in 1933 by Taylor and Langmuir [5] 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 two seminal papers in 1957 Kisliuk, working at Bell Labs presented an analytical approach to understanding such high adsorption rates [6, 7]. He quantified the importance of diffusion in the physisorbed (as he considered it to be) 'precursor' state and in two elegant papers, he outlined the mathematical application of such an idea, which is pictorially outlined in Fig. 1. Here it is considered that there are two types of precursor which have mobility in this weakly held state—'extrinsic' (that over a filled site) and 'intrinsic' (that over an empty chemisorption site) [8]. 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

$$S = S_0 \{1 + (Kp\theta / (1 - \theta))\}^{-1} \tag{2}$$

The resulting dependence of sticking upon coverage is given in Fig. 2, for a variety of values of Kp . Here it can be

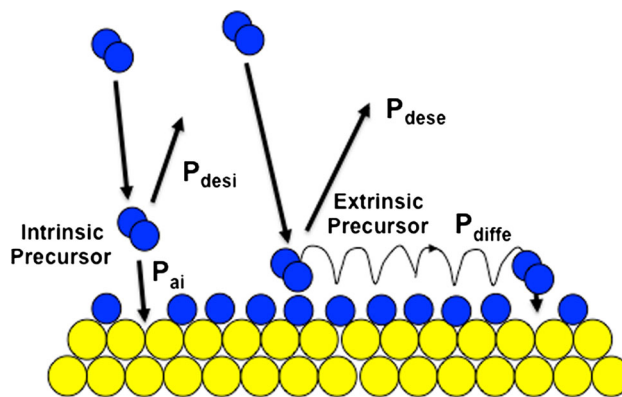


Fig. 1 Showing adsorption into the precursor state over filled (extrinsic) sites and empty (intrinsic) sites. The intrinsic state can adsorb (P_{ai}), or desorb (P_{desi}), or diffuse to another site (not shown) from adsorption over an empty site at the surface. In contrast, the extrinsic precursor adsorbs on parts of the surface with filled chemisorption sites. It can then either desorb (P_{dese}) or diffuse to an adjacent site (P_{diffe}) before eventually adsorbing at an empty site

seen that the equation reduces to the simple Langmuir form when $Kp = 1$ (that is, no role of the precursor), whereas when Kp is very small there is a very large precursor effect and S stays high to very high coverage. The so-called precursor state parameter Kp is given by basic probabilities as follows

$$Kp = S_0 P_{de} / P_{ai} \tag{3}$$

where the probabilities are defined as shown in Fig. 1.

We can express the number of 'hops', N_h , that a molecule makes on the surface from the ratio of the Frenkel

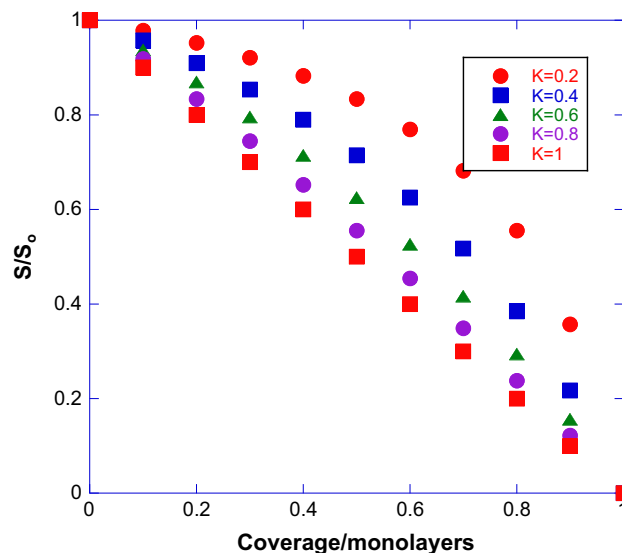


Fig. 2 The effect of the precursor parameter on the adsorption curve, $K = 1$ corresponds to no precursor effect and Langmuirian kinetics

lifetime on the surface before desorption (τ_{des}) to the lifetime for the hopping process (τ_{diff}):

$$N_h = \tau_{des}/\tau_{diff} = k_{diff}/k_{des} = (A_{diff}/A_{des})\exp\{(E_{des} - E_{diff})/RT\} \tag{4}$$

Here we have also expressed the lifetimes in terms of inverse rate constants and their Arrhenius expansion. Further, if we assume $A_{des} \sim A_{diff}$, and that the diffusion activation energy is 1/3rd 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 38 kJ mol^{-1}). Though the lifetime of such a state at ambient temperature is very low, less than one microsecond, nonetheless it can diffuse over many sites, $\sim 30,000$ of them! We can re-interpret this in terms of a lateral extent of diffusion by using the concept of the ‘diffusion circle’ [9–12]. Here we simply consider the hops as distributed in a circle around the landing site on the surface (Fig. 3), and so we can describe the extent of the diffusion by the radius of this circle, that is,

$$r \sim (N_h/\pi)^{1/2} \tag{5}$$

This is, of course, 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 Fig. 3, but is a distribution related to Fickian diffusion, that is,

$$\langle x^2 \rangle = Dt \tag{6}$$

And so the range of diffusion from the landing site is

Table 1 The dependence of physisorbed species lifetime and diffusivity upon surface temperature

T/K	Nh	τ_{des}/s	r/sites
200	4×10^6	8×10^{-4}	12000
300	3×10^4	4×10^{-7}	90
500	450	10^{-9}	12

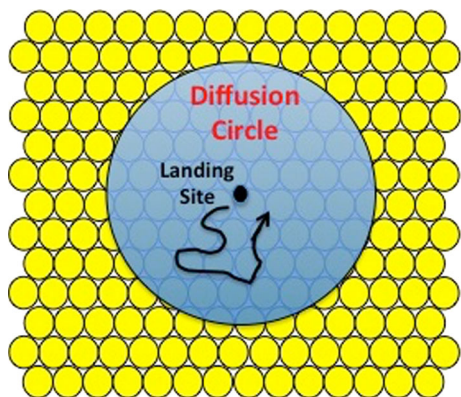


Fig. 3 The diffusion circle concept, indicating an area of the surface visited by the diffusing precursor state

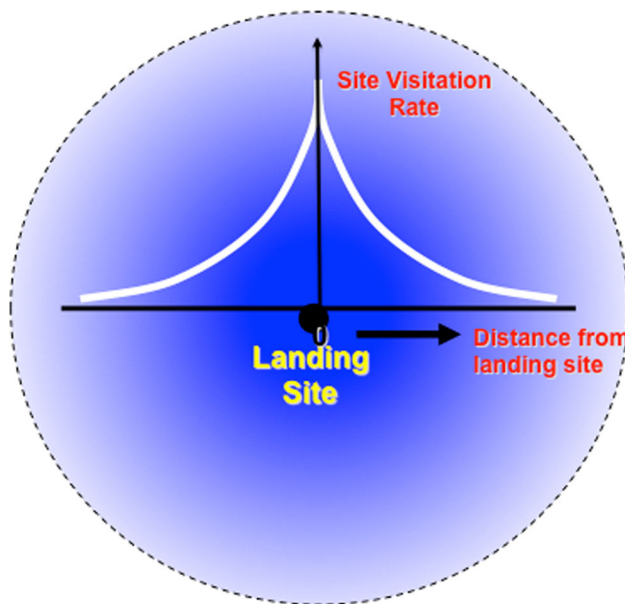


Fig. 4 The radial probability of diffusing different distances from the landing site

related to the square root of the time of residence at the surface.

$$x_{rms} = (Dt)^{1/2} \tag{7}$$

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

$$dx_{rms}/dt = ct^{-1/2} = d/x_{rms} \tag{8}$$

where c and d are constants. This gives the type of distribution shown in Fig. 4, with a big decrease in probability of finding the diffusing molecule away from the landing site. These diffusion concepts will be exemplified in the following sections.

3 Practical Examples of Precursor States in Adsorption and Catalysis

Various examples of the effect of precursor states follow, mainly from the work in our own laboratory. These 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 CO Adsorption on Transition Metals and the CO Oxidation Reaction

Figure 5 shows a sticking probability curve for the adsorption of CO on Pd(110) [13]. There is no doubt that CO adsorbs molecularly, and it desorbs again in TPD with a peak at $\sim 450 \text{ K}$. However, it is clear that the behaviour

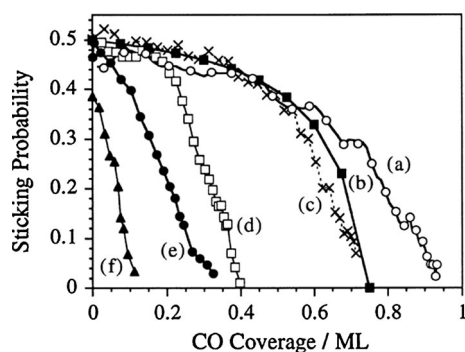


Fig. 5 The sticking of CO on Pd (110) as a function of coverage for a variety of surface temperatures: (a) 210 K, (c) 327 K, (d) 377 K, (e) 423 K, (f) 470 K, while curve (b) is the fit to the 327 K data using Eq. 2 with a precursor state parameter of 0.13

is non-Langmuirian and that the sticking stays high as the coverage increases, only decreasing significantly at high coverages. Applying Eq. 2 above gives a value for K of 0.13, indicating a significant effect and hence the large curvature of the sticking plot.

As mentioned in Sect. 2 above, 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 Fig. 5f 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 Fig. 5 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) [14], Cu(110) [15, 16], Ir(110) [17] and W(320) [18] for instance.

Because of its importance in adsorption the precursor state 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 [19].

3.2 Mobile Precursors Result in Increased Surface Reaction Rates: Oxygenates on Cu(110)

The examples given above were for relatively simple adsorption processes, but we will now consider situations in which the precursor state interacts with another species with which it reacts—such as acid–base reactions. First of all let us consider the reaction between pre-adsorbed oxygen atoms (the base) and gas phase formic acid. The

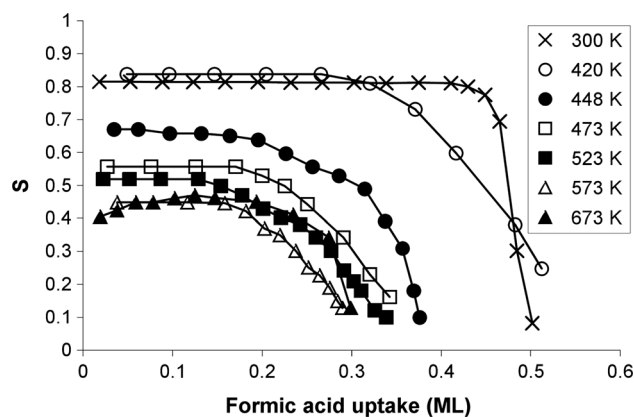
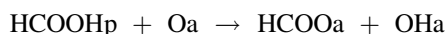
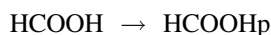


Fig. 6 Formic acid sticking probability dependence of uptake on Cu(110), for 0.25 monolayers of preadsorbed atomic oxygen, at a variety of crystal temperatures [20, 23]. Note the independence of S upon uptake at 300 K up to $\sim 90\%$ of the maximum uptake

sticking probability of formic acid is low, at ~ 0.1 [20, 21], but upon pre-adsorption of oxygen atoms the reaction probability is very high at 0.82 (see Fig. 6) [20, 22]. This is because it is more 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:



As Fig. 6 shows the initial sticking probability is very high, and remains constant during most of the reaction, until almost all the oxygen is used up. This is due to the high mobility of formic acid in the precursor state which enables it to ‘seek out’ remaining oxygen atoms, even as their coverage becomes very low on the surface. This is even more obvious if only a very small amount of oxygen is dosed onto the surface. Even with only 0.03 monolayers of pre-adsorbed oxygen, S_0 is still 0.82. Once again, this is due to the precursor molecules diffusing around the surface and finding the oxygen atoms with high efficiency.

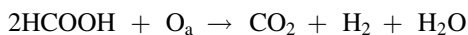
We were able to examine this effect in even more detail for propan-2-ol, where we could measure the adsorption at pre-coverages of oxygen atoms as low as 0.008 monolayers [9]. The net sticking probability is close to zero on the clean copper surface, but is increased to 0.75 with this very low pre-coverage of oxygen atoms, and demonstrates the extreme mobility of the alcohol molecules in the weakly held layer.

This reaction of formic was modelled in some detail for the case where a quarter of a monolayer of oxygen was pre-adsorbed; it was essential for the modelling to include the precursor state influence on the adsorption, since this was required to fit the flat plateau of the sticking versus time

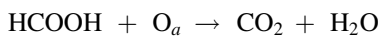
shown in Fig. 6 [23]. This is a difficult system to model over a range of adsorption temperatures because gas phase reaction products are also evolved during the reaction (CO_2 , H_2 and H_2O), and also the stoichiometry of the reaction varies with temperature. Further, the active sites are located at the oxygen atomic sites, so that the reaction rate modelling has to include oxygen coverage, in the following way:

$$R_1 = A_1 \times \exp(-E_1/RT) \times (1 + (K \times [1 - \theta_0]/\theta_0))^{-1}$$

A very good fit to the data is obtained by this approach (Fig. 7); the stoichiometry change with temperature, and the change in product ratios from the formate reaction with oxygen could be fitted by taking into account the formate stability and the importance of precursor state adsorption which has been obtained from surface science investigations from several groups [21–26]. The product evolution depends upon temperature in the following way. At intermediate temperatures where the formate can decompose (up to ~ 400 K) the reaction is:



Whereas at higher temperatures the reaction shifts to,



the reaction proceeds exclusively this manner at 680 K. The reason for this is that at the lower temperatures the formate decomposes only slowly at that temperature. Thus a second formic acid molecule can react with the OH formed from the primary reaction, before a hydrogen atom is liberated from the formate by decomposition. However, at the higher temperatures, in contrast, the formate

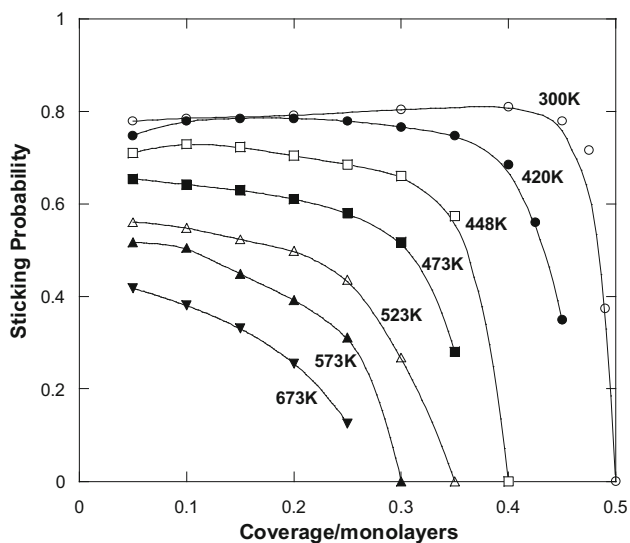


Fig. 7 Theoretical modelling of formic acid uptake curves at a variety of adsorption temperatures upon a Cu(110) surface with 0.25 monolayers of oxygen preadsorbed [23]

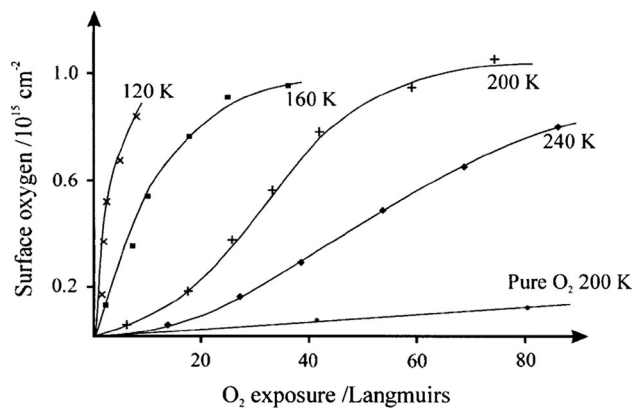


Fig. 8 XPS measurements of the uptake of oxygen onto Zn(0001) from the work of Roberts et al. [27]. It shows the large sticking increase when ammonia is incorporated into a gas feed compared with the pure O_2 case

decomposition is fast and so H atoms from it react with OH before another formic acid molecule does [20, 23].

Roberts et al. [1, 27–29] have reported surface reactions which are of an inverse type, that is, oxygen adsorption itself is enhanced via the precursor state. In these experiments oxygen was not pre-adsorbed, but precursors are pivotal for 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, Fig. 8 [1, 27]. It was proposed that this was due to a mobile, precursor molecular oxygen “ $\text{O}_2^{\delta-}$ ” species, interacting with ammonia in the weakly-held state. This enabled facile O_2 dissociation, and hence a higher net sticking probability for oxygen into a long-lived state.

3.3 Precursor States Can “Seek and Find” the Active Site on Model Catalysts and High Area Catalysts

Some time ago Boudart et al. reported some unusual findings for the adsorption of hydrogen on glass and also for the oxidation of carbon monoxide on Pt catalysts supported on sapphire [30, 31]. They discovered that the rate of CO oxidation was considerably higher than expected on the basis of the measured areal coverage of Pt nanoparticles on the catalyst surface. Boudart’s explained this in terms of reverse spillover of CO to the metal from the support, proposing the ‘collection zone’ concept, which is discussed below.

In more recent times surface science has advanced in the complexity of materials which can be fabricated and analysed in situ. This includes the production of model materials, for instance, nanoparticles have been deposited

on well-defined support surfaces, either in the form of single crystal oxides [32, 33] or as thin film oxides on top of metals [34, 35]. As a result some surface studies have returned to study the collection zone idea, though it has also been expressed in different terms as the ‘diffusion circle’ described above, as a shorthand way of describing the extent of diffusion of a precursor state on the surface [36]. Matolin et al. performed a series of elegant experiments by and found a significant enhancement of the sticking of CO on model supported Pd catalysts, using a number of different types of support material [37–40]. They incorporated this idea of CO mobility into a formulation for the sticking. This essentially consists of two parts—that arising from those molecules adsorbed weakly in the capture zone and that due to a fraction directly adsorbing on the Pd particles. For the situation in which metal nanoparticles are well-separated and capture zones do not overlap:

$$S_m = \{S_{su}Z_d(2r + Z_d) + S_{Pd}r^2\}\pi n$$

where S_m is the measured sticking probability, S_{su} 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, etc.), they nonetheless could model the process with good success.

Henry et al. [32, 41, 42] also developed these kinds of ideas and have experimented with molecular beams, going beyond adsorption to catalytic reaction. They stress the importance of accounting for the extent of the capture zone effect when interpreting the effects on catalytic reactivity of particle size, an example being the CO/NO reaction on Pd/MgO model catalysts [42]. The capture zone can result in higher reaction rates than might be otherwise expected by the Pd coverage on the support MgO, but the magnitude depends on the number density of the particles on the surface. Several theoretical descriptions have evolved [43–45], and Zhdanov and Kasemo [45] have applied Monte-Carlo modeling to the effect of the diffusion around nanoparticles on the bi-stability profiles (rate versus pressure variation) of bimolecular surface reactions. There can be significant shifts of the maximum to lower reactant pressure due to such effects

We have measured the adsorption of carbon monoxide on Pd nanoparticles (of ~ 4 nm diameter) [36] and have found a gain of the sticking probability of CO of a factor of ~ 5 over what would be anticipated from the areal coverage of the surface by Pd nanoparticles. This arises from the influence of the precursor state, and this effect is shown in Fig. 9, and schematically illustrated in Fig. 10. The adsorption is of two main types as described above—direct

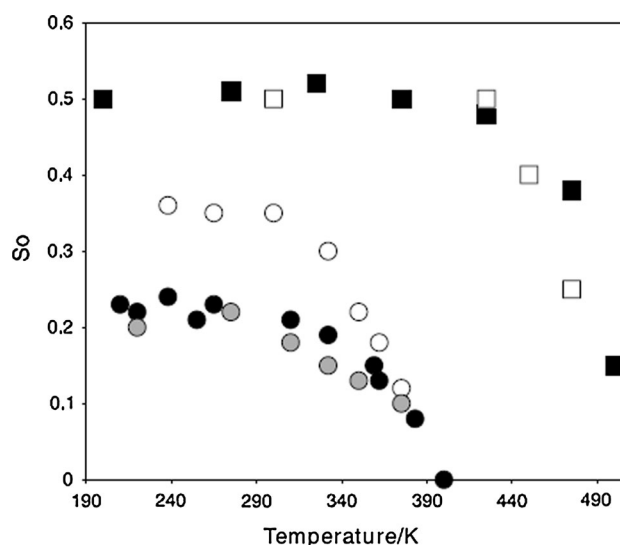


Fig. 9 The dependence of initial (low coverage) sticking probability upon temperature for Pd(110) (filled squares) Pd(111) (open squares) and for three different loadings of the TiO₂(110) surface with Pd (open circles, 35 %; filled circles, 12 %; grey circles, 8 %) [36]

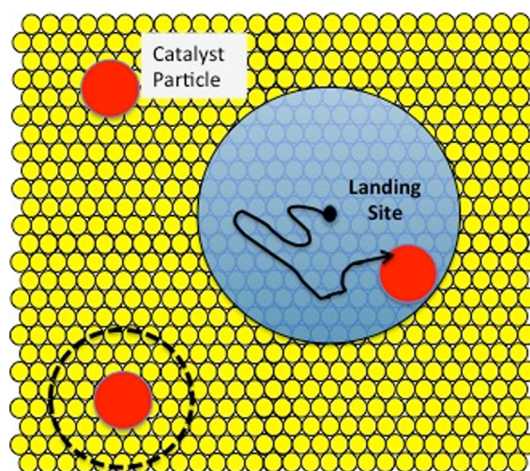


Fig. 10 Illustrating a surface with a dilute distribution of metallic nanoparticles present (red circles), and a molecule landing remotely from them. Because the diffusion circle is large enough the molecule nevertheless has a high probability of finding a particle within its zone of diffusion where it then becomes trapped into a long-lived, chemisorbed state. Also shown is the ‘collection zone’ concept of Boudart (dashed circle) [30, 31] (Color figure online)

adsorption on the nanoparticles, plus that from a diffusing flux of CO via the precursor state on the support. The adsorption of CO on oxidic surfaces is generally weak, usually ~ 20 – 50 kJ mol⁻¹, and so the lifetime at 300 K is very short. The best fit to the data was obtained with 38 kJ mol⁻¹ binding energy; the lifetime is $\sim 10^{-7}$ s at 300 K, and so the radius of the ‘diffusion circle’ on the support would be about 2 nm. Thus the particle (of approximate cross-sectional area 12 nm²) would capture CO molecules from an area on the support of about four

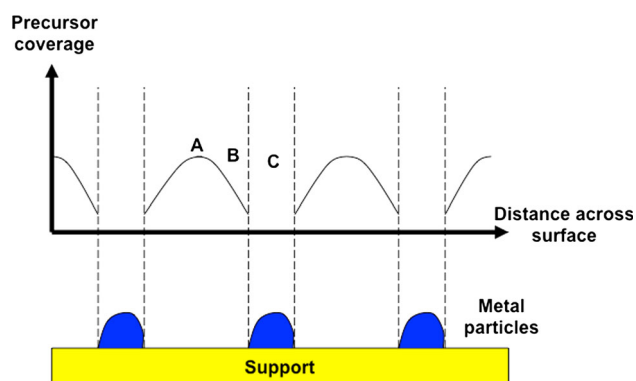
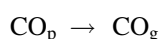
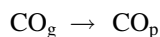


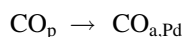
Fig. 11 Schematic diagram of the distribution of precursor state coverage as a function of position on the surface (*upper panel*) of an array of supported metal nanoparticles supported (*lower panel*). The metal particle is in region C, while A is the point of maximised precursor coverage at the bisect of adjacent particles. B is a region of depleted precursor coverage, due to loss of molecules to the metal by non-equilibrium diffusion onto them and loss from the precursor layer

times it's own area, and so there is the significant enhancement of the CO sticking seen in these kinds of measurements. In Fig. 10 the Boudart proposal of the collection zone is shown too, which reflects the higher cross-section for adsorption on to the particles, and the diffusion circle is just another way of expressing this idea.

Besides the considerations above it must be remembered 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. [41]. As shown in Fig. 11 there will be loss of the CO near the nanoparticles since, on the support, the coverage will be determined by the equilibrium with the gas phase, as follows



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



This results in the depletion of precursor state illustrated schematically in Fig. 11. What this shows is a concentration reduction around the particles from that far from the particle. Of course, the adsorption situation is not at equilibrium and is dominated by the kinetics of the chemisorption onto the metal nanoparticles, and so the situation illustrated in Fig. 11 would change as the metal becomes saturated with adsorbate and the precursor concentration around the particle would then become isotropic. If we consider a reacting system, CO oxidation for instance, there will be a continuous loss of precursor from the support in the way shown in Fig. 11.

4 The Significance of Precursor States in Industrial Heterogeneous Catalysis

Clearly, then, precursor states have a major role to play in adsorption, on both single crystals and on nanoparticulate catalysts, and can strongly affect reaction kinetics, as in the example of formic acid oxidation above. However, will they be of any significance in industrial scale catalysis? The answer is yes, but it depends very much on which types of reaction are involved. If the reaction is carried out at relatively low temperature, using large molecules, such as hydrocarbon dehydrogenation reactions, which often take place ~ 400 K, then the precursor, physisorbed form of the hydrocarbon will be important and will affect the kinetics. On the other hand it will be much less significant for high temperature reactions using small molecules, for example, methane steam reforming on Ni catalysts, taking place at ~ 1000 K, and for which the lifetime of the low molecular weight precursor will be very short. In many cases in catalysis, the 'active site' may have very small coverage on the surface. For instance, in naphtha reforming on Pt/SiO₂ catalysts the Pt loading is only ~ 0.3 %; in oxide catalysts sometimes the active site is a defect centre which may be sparsely distributed on the surface [46]. As described above 'light-off' in automobile catalysts is affected by the diffusivity of CO across the supported metal surface. From all these considerations it can be concluded that the properties of such weakly-held states affect the kinetics in some major industrial processes too.

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