Catalysis at the metal-support interface: exemplified by the photocatalytic reforming of methanol on Pd/TiO$_2$

Michael Bowker,[*,1] David James, Peter Stone,[1] Roger Bennett, Neil Perkins, Lucy Millard, Jane Greaves, and Amanda Dickinson

Centre for Surface Science and Catalysis, Department of Chemistry, University of Reading, Whiteknights Park, Reading RG6 6AD, UK

Received 22 November 2002; revised 14 February 2003; accepted 17 February 2003

Abstract

Some types of catalytic reaction may take place at the boundary between a metal and a support. In this paper we describe the mathematical relationships between observed reaction rates and the loading of the supported phase. The reaction rate shows a sharp maximum with increasing loading, and at high loadings the rate is reduced to zero, due to the lack of active sites (the support is completely covered). We report a study of a particular reaction where the kinetic data indicate rather clearly that the active site is at the boundary between such phases. The particular reaction is the photocatalytic degradation of methanol on a Pd/TiO$_2$ catalyst under anaerobic conditions. The reaction produces CO$_2$ and hydrogen and only proceeds at steady state when light is introduced to the system. We propose that this is due to blockage of the Pd by adsorbed CO, and the role of light is to produce a reactive form of oxygen on the support, which cleans off CO from the Pd at the boundary, thus allowing a catalytic cycle to be completed. The larger the extent of this boundary, the higher the reaction rate. A general mathematical model of such reactions is given and applied to these data.
© 2003 Elsevier Science (USA). All rights reserved.

1. Introduction

Reactions at the interface between a metal particle and the support material could be of great significance for a number of reactions. Phenomena which have been highlighted are spillover to/from an active phase to a support [1] and SMSI, the so-called strong metal-support interaction [2]. In many cases the support itself is not thought to be the location of the active site, though it may act as a channel of faster supply of reactants in adsorbed form to the active site. However, in some cases the support may play a direct role in the catalysis, which will not take place in the absence of a particular support- metal/oxide combination. In particular it may be the case that some reactions have the active site located at the interface between support and metal. An example of this is the careful work of Boffa et al. [3] who showed that the methanation of CO$_2$ on oxide-decorated Pt single crystals took place at the metal-oxide interface. However, it is rare for direct evidence of this phenomenon to be found from kinetic measurements. In this letter we show such direct evidence for the particular case of the anaerobic photocatalytic reforming of methanol (Section 3), though it is the more general phenomenon of two-dimensional interface reactions which is the focus (Section 2). We derive the relationship between the reaction rate and the loading of the metal on the support. We describe how the particular photocatalytic data presented in Section 3 can be explained by assuming that the rate-limiting step in the reaction occurs at the boundary between the Pd particles and the support titania; thus, the rate is proportional to the length of that boundary. In this case both the support and the metal are essential components of the reaction, the titania being responsible for energy storage by light absorption.

2. The relationship between activity and loading for reactions at the metal-support interface

We can attempt to formulate a general description for reactions of this type, where the active site (and therefore the rate-determining step) is at the boundary between two solid

---

* Corresponding author.
  E-mail address: m.bowker@rdg.ac.uk (M. Bowker).
[1] Current address: Department of Chemistry, Cardiff University, Cardiff CF10 3TB, UK.
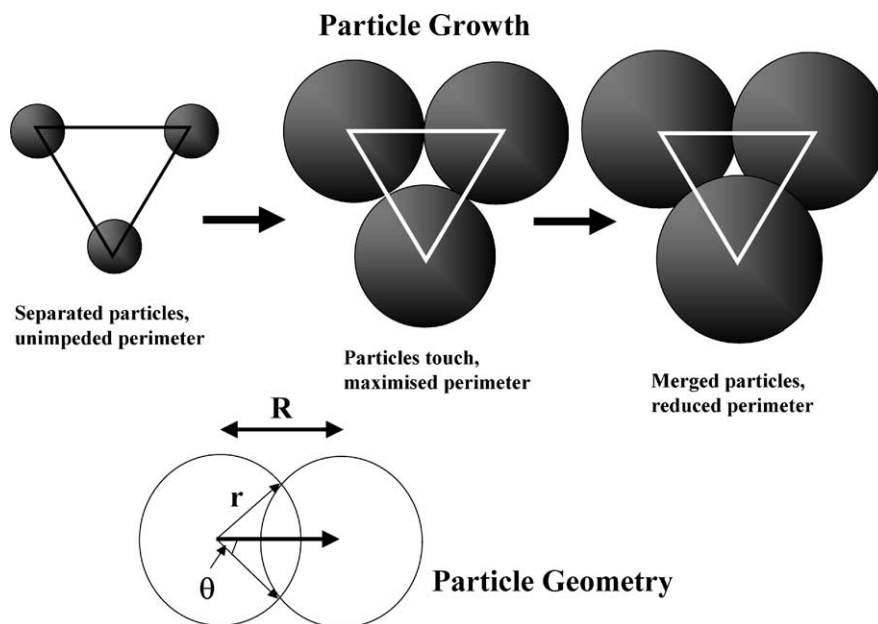
Particle Growth

Fig. 1. An idealized schematic model of the growth of islands on a surface, showing small islands arranged in an ordered hexagonal way, which grow to merge at a particular loading; at that point the peripheral length is at a maximum. With further growth the perimeter length reduces as coalescence increases. The lower panel shows the geometrical considerations for the mathematical model of catalysis at the perimeter of particles.

phases, and assuming that changes in the size of the particles of the second, added phase do not significantly alter the inherent activity of the active site. In mathematical terms, the loading dependence can then be described in the following idealized way, and with reference to Fig. 1. At low Pd loadings there are separate particles on the support, and then, as the loading increases, they merge and the total perimeter begins to shrink. At some point there is no perimeter left when the support is completely covered with metal. If we assume a homogeneous array of hemispherical shape for the small Pd particles, the radius of each particle, r, is related to the volume per particle, V, as follows,

$$r = (3V/2\pi)^{1/3} \tag{1}$$

and similarly, the perimeter of each particle, P, is given by

$$P = (12\pi^2 V)^{1/3}. \tag{2}$$

These terms need to be expressed in the form of the directly measurable quantity, that is, the total volume loading, V_T (equal to the measured weight loading divided by the metal density),

$$P_T = N^{2/3}(12\pi^2 V_T)^{1/3}, \tag{3}$$

where N is the total number of particles in the sample, and P_T is the total perimeter. Of course the perimeter is also given by the following in the growth phase before particle touching,

$$P_T = 2\pi r N. \tag{4}$$

More specifically, $P_T' = 2\pi r/R^2$ for a square array of particles, where P_T' is the perimeter per unit area of the support. The situation is a little more complicated after touching and

relates to Fig. 1. The hemisector angle θ in the figure is given by

$$\cos\theta = R/2r. \tag{5}$$

The perimeter lost per particle by overlap is

$$P_L = 2\pi r(2n\theta/360), \tag{6}$$

where n is a geometric factor related to the packing of the hemispheres on the surface; it is 4 for a square array of particles and 6 for a hexagonal array. Replacing the angular term in Eq. (6) by substitution from Eq. (5), we have the total perimeter lost as the following,

$$P_L N = 2\pi r N(n\cos^{-1}(R/2r)/180). \tag{7}$$

Relating this to Eqs. (3) and (4) we obtain, for the perimeter dependence on loading

$$P_T = N^{2/3}(12\pi^2 V_T)^{1/3}$$
$$\times \{1 - (n\cos^{-1}[R/(12V_T/N\pi)^{1/3}]/180)\}. \tag{8}$$

If we consider the number of active sites per unit area, then we can replace N with R^{-2} in this equation, and so this becomes, for a hexagonal array,

$$P_T' = (4/3R^4)^{1/3}(12\pi^2 V_T)^{1/3}$$
$$\times \{1 - (\cos^{-1}[1/(6.3^{1/2}V_T R/\pi)^{1/3}])/30\}. \tag{9}$$

Here we consider that the rate-determining step is the reaction at the boundary, which in turn is proportional to the
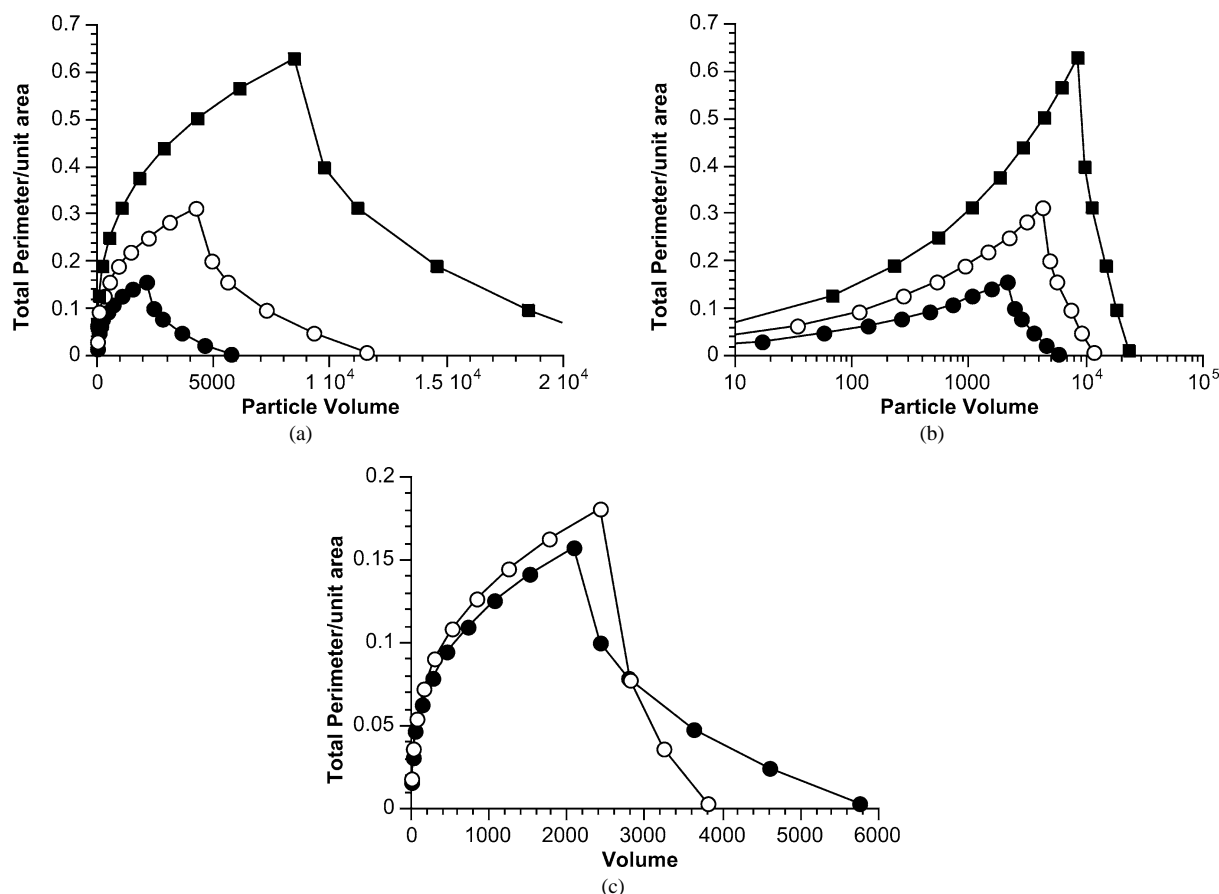
Fig. 2. (a) A plot of the dependence of the amount of perimeter per unit area of surface and its dependence upon the radius of the particles, expressed in volume terms (the radius at any point on the x axis is $(1.5\ V)^{1/3}$, where V is the particle volume). The axes are unitless. Thus the particle radius is 20 units at approximately 1.7×10^4 cubic units volume. The parameter for the three curves is the cell size (R) for the square array of particles. (b) The plot of (a) now in logarithmic form to clearly show the dependence at very low loading. (c) A comparison of the dependence of perimeter on loading for hexagonal (open circles) and square (filled circles) arrangements of particles on the surface.

surface concentration of active sites, P'_T. The relationship between rate and this perimeter is then

$$\text{Rate} = k P'_T, \qquad (10)$$

where k is the rate constant for the RDS.

Eqs. (8) and (9) are really in two parts. The first is a cube root dependence on loading which dominates at low loadings, while at high loadings, with particle coalescence, there is an inverse cosine dependence on the reciprocal of loading. This is based on the model of Fig. 1, but, assuming uniform particles in a square arrangement ($n = 4$) on the support. The results of such a model are shown in Fig. 2, on both a normal plot and a log plot, the latter to make the low loading dependence more apparent. The figure shows the cube root relationship at low loadings with a sharp transition, at particle touching, to the $\cos^{-1}$ dependence at higher loadings. The rate at very low loadings is high compared with the maximum (e.g., the rate drops only 4-fold from the maximum for a 40-fold drop in loading). We have also shown a comparison of the variation of the loading dependence with the

interparticle separation, R. As R increases, so the loading for any particular particle radius decreases. The maximum in perimeter occurs at higher loading as the interparticle separation decreases due to the higher particle number density on the support. In Fig. 2c we have also compared the shape for hexagonal versus a square arrangement of particles. The curves are similar, but the most notable effects are that the hexagonal packing maximum occurs at slightly higher loading, and that the drop off with loading above this point is faster than for the square array. This is because the hexagonal loading allows closer packing before coalescence, but after this there is a faster decline because of a 6-fold contribution to the particle expansion process.

Of course, the reality in most cases is that the catalyst will contain a distribution of particle sizes, arranged nearly randomly on the support. Both of these effects will tend to broaden the maximum which is shown in Fig. 2, but the general shape of the curve should still be observed. In what follows we will apply these ideas to a particular case where we think that a reaction at the interface determines the rate of reaction.

3. The model applied and modified: photocatalytic methanol reforming on Pd/TiO$_2$

Photocatalysts were prepared by incipient wetness impregnation of titania (Degussa P25) with an acidified aqueous solution of PdCl$_2$. The catalyst so produced was then dried at 110 °C for 2 h before calcining in air at 500 °C for a further 2 h. The resulting material was sieved through a stainless-steel mesh (to < 53 µm) and was placed in 100 ml of deionized water containing 110 µl of methanol (Fisher Scientific 99.99%) in a Pyrex flask. The mixture was purged for 30 min with Ar to remove dissolved gases and the reactor was finally sealed under Ar before switching on the light source (400 W Xe arc, Oriel Model 66084). The product hydrogen was measured on line by GC while analysis for other products (such as formaldehyde, formic acid, CO, and CO$_2$) was carried out off line. The only measurable other product was CO$_2$, produced in a 1:3 (±0.3) ratio with hydrogen, although the exact ratio may be time dependent in the early part of the reaction as reported by Kawai and Sakata [4] and Sakata and Kawai [5]. This confirms that the reaction was water reforming of methanol with the following overall reaction stoichiometry,

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2.$$
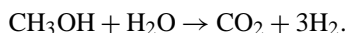
Some work on this system has been carried out by others, mainly by measuring reaction rates for precious metal-titania catalysts [4–7]. The water involvement in the reaction was previously proposed by Kawai and Sakata [4], and this is supported by the work here where nearly 3 mol of hydrogen was produced for each mole of methanol used in the reaction taken to completion. In this paper we will concentrate on the dependence of the reaction rate upon the metal loading in the catalyst, since it gives a clear insight into the nature of the active site for the reaction, and since this dependence has not been reported in any detail before.
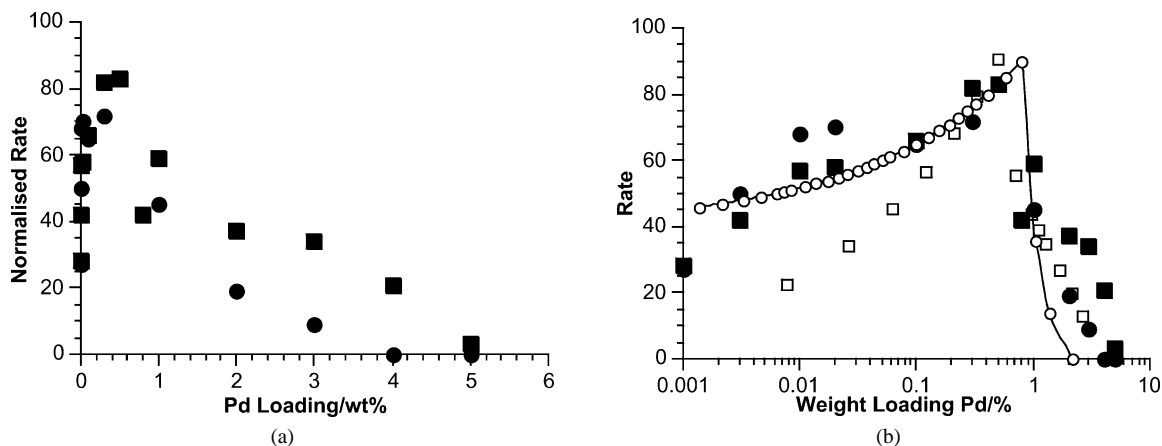
Fig. 3 shows this dependence. Because of the wide range of loadings used, the graph is also plotted with a logarithmic abscissa so the dependence at low loadings is clear. This shows a marked maximum in the rate of methanol reforming at a loading of around 0.5 wt% Pd. There is a sharp drop in rate with increased loading such that by 2 wt% the initial rate of reaction is essentially zero. If the loading is decreased from that at the rate maximum, there is only a very slow drop-off in reaction rate; thus decreasing the loading by a factor of 100 only decreases the rate by a factor of 5 or so.

Such surprising observations of a sharp maximum with loading have been seen before by Bamwenda et al. for the related reaction of ethanol photodecomposition on Pt and Au/TiO$_2$ catalysts [8], though the range of loading was not as great as reported here. They propose that at higher loadings the Pt blocks the TiO$_2$ to light sensitization. However, the loading at which total cessation of rate occurs is much too low for complete blockage of the surface by metal, so a detailed consideration of this effect is required, as follows. A possible explanation for these effects can be given in relation to the theme of this paper, that is, by a mechanism involving reactions at the metal-support interface, as described schematically in Fig. 4. It is important to first consider what happens when methanol reacts with the individual components of the catalyst, beginning with the more catalytically active material, Pd. The reaction between methanol and Pd has been measured in vacuum on a single crystal surface [9]. This pure Pd decomposes methanol efficiently at first during adsorption at 300 K, liberating hydrogen into the gas phase, but the reaction stops very quickly after approximately one monolayer of methanol has adsorbed. This is because a product of the reaction is CO, which is strongly adsorbed, remains on the surface, and poisons the reaction when it reaches high coverage. Although the situation here is somewhat different (aqueous solution), we believe that this is likely to also be the state of the surface in our reaction, that is, with a high coverage of CO completely poisoning

Fig. 3. (a) The dependence of the rate of hydrogen evolution on weight loading of Pd on the TiO$_2$ support, showing the extreme dependence of the rate at low Pd loadings, for two sets of catalysts. (b) The same data as in a plotted on a logarithmic abscissa to more clearly illustrate the dependence (solid data points). Also shown is the mathematical form of the rate dependence upon loading from the two treatments described in the text; the simple model (open squares) and the extended perimeter model (fitted line and open circles). For the simple model the loading for the maximum rate has been arbitrarily fitted (see text), but not so for the extended model.
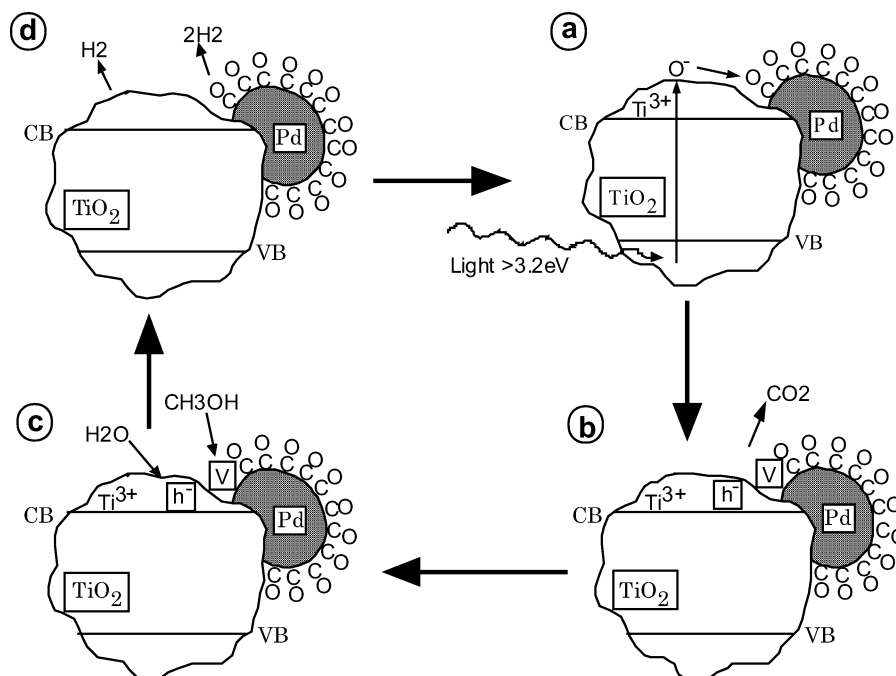
Fig. 4. The proposed catalytic cycle for photocatalytic methanol degradation under anaerobic conditions, described fully in the text.

the reaction. Without light there is no steady-state hydrogen evolution due to an inactive, CO-poisoned Pd surface on the catalyst (Fig. 4a). When light is introduced CO_2 is produced and H_2 evolves with it at a near steady-state rate (measured over many hours). The data in Fig. 3 are initial rates (i.e., measured over the first 2 h after the light is switch on), with methanol conversion below 5%. Note that this is short of the maximum reaction rate we can obtain with more sophisticated catalysts, but is of a similar value to that reported by others [4–7]. Thus, the introduction of light to the system has enabled the steady-state reaction to take place. We have determined the wavelength threshold to be approximately 340 nm [10].

We propose that this unusual loading dependence occurs because of a reaction between lattice oxygen at the surface of the TiO_2 and CO adsorbed on the metal at the interface between the two. The oxygen is likely to be highly reactive O^-, produced by band-gap excitation of electrons from the essentially $O(2p)$ valence band into the mainly Ti^{3+} conduction band, which is normally empty, since Ti^{4+} is the predominant cationic species (Fig. 4a). However, it is also possible that the active species is a hydroxyl of some kind. The threshold for the reaction quoted above is very close to the accepted band gap in titania (3.2 eV or 370 nm). This leaves an anion vacancy in the titania, and a CO vacancy on the Pd (Fig. 4b). The vacancy on the Pd is filled by methanol, thus liberating 2 mol of hydrogen and leaving adsorbed CO again (Figs. 4c and d), as described in the earlier publication [9]. The hole in the titania lattice is filled by water dissociation, liberating a mole of H_2 and fulfilling the stoichiometry above (Figs. 4c and d).

Some justification for the assumption of hemispherical particles can be found in the STM image of Fig. 5, which shows the Pd to be present in such a form on a flat $TiO_2(110)$ support [11], with an average particle diameter of around 3 nm. In the present case TEM was used to identify particles on the support before reaction, but the particles were so small for the optimum loading (0.5%) that they could not
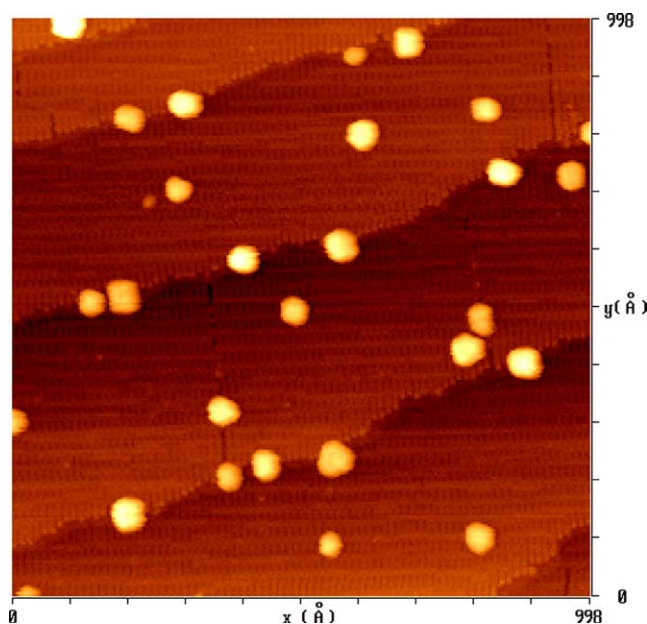

Fig. 5. An STM image of a $TiO_2(110)$ surface (showing the (1×2) structure) with Pd deposited by MVD at room temperature, then annealed to 773 K, and here imaged at 673 K. This shows a fairly homogeneous array of rounded Pd particles. Image size 99.8×99.8 nm.

be clearly observed. Particles could be seen for higher loading, for instance for the 5 wt% catalysts the particles were generally very small ($\sim$ 4 nm diameter after reaction), approximately hemispherical, and spaced apart by about 15 nm on average.

The fit of the model described in Section 2 to the real data for the reaction is shown in Fig. 3 as the solid curve. Here it can be seen that the fit is quite good, indeed surprisingly good for such a simple model. The important point we wish to stress here is not the absolute values, but the lineshape, which is reasonably well described by the model, within the experimental reproducibility, that is, it shows a high rate at low loading, a sharp maximum, and a marked decrease in rate as the loading goes above 1%. However, it is clear that the model appears to underestimate the rate at low loading, and, most importantly, *the model is fitted to the maximum in the experimental curve*. Within the hemispherical particle model it is not possible to have particle overlap at a loading of only 0.5%. In fact, even if we assume complete coverage of the TiO$_2$ by only a monolayer of Pd (TiO$_2$ surface area 50 m^2 g-1), then the loading would still be high at approximately 14 wt%. For a homogeneous distribution of touching circles this loading is little reduced to around 13%. Thus, there appears to be a quantitative inadequacy in the model, which can be rectified by considering that the loss of active perimeter occurs earlier than expected in loading. Fig. 3 also shows the results of a refined model in which the active sites are actually located at a perimeter which is somewhat remote from the particles on the TiO$_2$ surface. This requires a modification to the basic model as follows. The perimeter of the particles in the growth phase is simply given by

$$P_T = N2\pi r_z, \tag{11}$$

where r_z is the radius of the extended zone. This equation can be expanded since $r_z = r + d$, where d is the width of this extended zone. Thus

$$P_T = 2\pi N(3V/2\pi)^{1/3} + 2\pi Nd. \tag{12}$$

If we extend this to higher loadings where coalescence is included, then Eq. 12 is modified to become

$$P_T = 2\pi Nr_z\{1 - [\cos^{-1}(R/2r_z)]/30\}. \tag{13}$$

Application of this model to the particular case here results in the curve shown in Fig. 3. Clearly the fit is now better, and the rate maximum actually occurs at 0.5% loading in the model, assuming that the perimeter exists at 15 nm from the edge of the metal particles, and that particle touching occurs when the particles are about 2 nm diameter with a particle density of 4×10^{11} cm^{-2}. The model has many assumptions within it, as described above, but gives a reasonable description of the data. It may seem farfetched that such a remote perimeter could exist or play a role in the reaction. However, as shown in Fig. 6, STM reveals that, under certain circumstances, perimeters of changed structure can be formed at a distance somewhat remote from the catalyst particle on the TiO$_2$ support [12]. In this case the perimeter is formed during high temperature oxidation of a Pd/TiO$_2$ model catalyst and the perimeter consists of newly grown TiO$_2$ layers formed by extraction of Ti^{3+} from the bulk to the surface in the presence of gas-phase oxygen. Oxidation occurs preferentially next to the Pd because oxygen is preferentially dissociated there and spills over onto the support local to the particle. Other possible sources of this "remote perimeter" are electronic depletion zones around the particles or regions of adsorbate spillover from the nanoparticles.

Although this is only one particular reaction, a broadly similar experimental dependence has been observed in our laboratory for the photocatalytic degradation of glucose, and for the water-splitting reaction carried out in a quartz vessel [13].
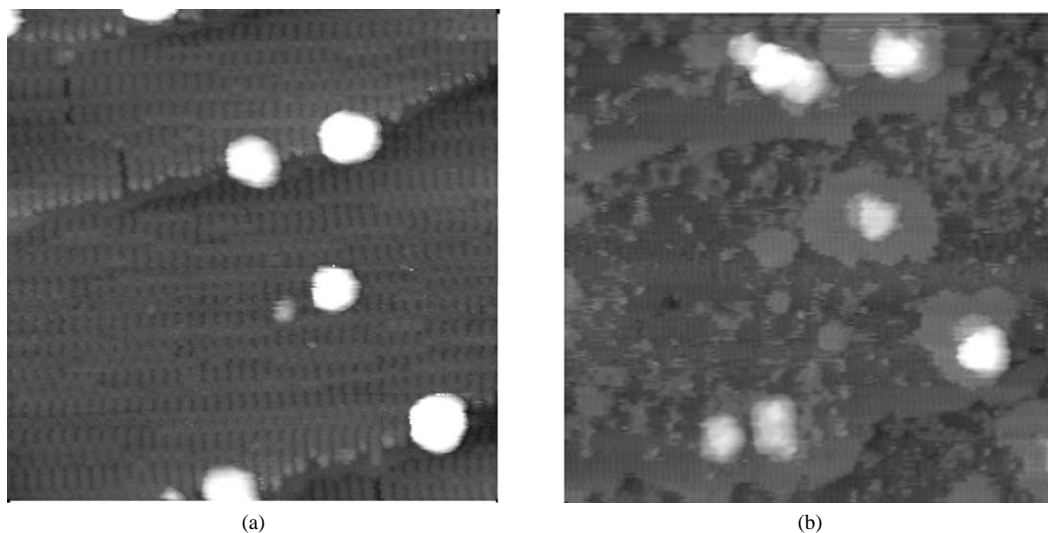

(a)

(b)

Fig. 6. STM images of Pd nanoparticles on a TiO$_2$ surface; the particles are about 5 nm in diameter. The left panel shows the surface before treatment in oxygen at 723 K, while the right hand panel is the same area after treatment and shows an area of oxygen spillover with new layers of TiO$_2$ grown around the Pd particles. This produces an extended boundary with possible new properties. Image size is 49.7 × 49.7 nm.

We believe that this kind of dependence will generally be seen for reactions of this type where the interface sites are the "active centres" for the reaction, and where both the support and the metal play an active part in the reaction. An example of this may well be the low temperature, high activity catalysts for CO oxidation described by Haruta, Au/TiO_2 and Au/Fe_2O_3, for instance, where it is proposed that interface sites are important [14]. It would be very interesting to see if a careful study of the loading dependence of that reaction conformed to the mathematical description above. In one paper there is a report of a broadly similar dependence (maximum rate of CO oxidation at 3 nm average diameter), though with only 5 loadings of Au [15], and Goodman and co-workers have reported a similar maximum [16]. A problem with that system is, however, the extreme sensitivity of the reactions to the Au particle size (that is, there may be a rate constant dependence on the particle size), which might distort the overall shape of such a curve. In the present case the reaction seems to be described well simply by the variation of the number of active sites at the perimeter. Boffa et al. [3] showed a maximum in CO_2 methanation for TiO_x films of Pt, but the effective loading of Pt (and therefore the relative interface area) was much higher than that in the present work. STM studies could prove very useful as a check on the model proposed in Fig. 2. Several groups have imaged small Pd particles (and other metals) on TiO_2 single crystals [11,12,17,18]. If experiments were carried out with CO adsorption, and then with UV irradiation, we predict that anion vacancies should appear in the region adjacent to the metal particles (providing their bulk or surface diffusion is slow) as CO_2 is lost into the gas phase. This kind of catalytic phenomenon would represent an excellent meeting ground for catalytic and surface scientists.

Acknowledgments

References

[1] J. Sinfelt, P. Lucchesi, J. Am. Chem. Soc. 85 (1963) 3365.

[2] S.J. Tauster, Acc. Chem. Res. 20 (1987) 389.

[3] A. Boffa, C. Lin, A.T. Bell, G.A. Somorjai, J. Catal. 149 (1994) 149.

[4] T. Kawai, T. Sakata, J. Chem. Soc. Chem. Commun. (1980) 694.

[5] T. Sakata, T. Kawai, Chem. Phys. Lett. 80 (1981) 341.

[6] S. Naito, J. Chem. Soc. Chem. Commun. (1985) 1211.

[7] P. Pichat, J.-M. Herrman, J. Disdier, H. Courbon, M.-N. Mozzagena, Nouv. J. Chem. 5 (1981) 627.

[8] R. Bamwenda, S. Tsubota, T. Nakamura, M. Haruta, J. Photochem. Photobiol. 89 (1995) 177.

[9] M. Bowker, R. Holroyd, R. Sharpe, J. Corneille, S. Francis, D.W. Goodman, Surface Sci. 370 (1997) 113.

[10] D. James, MSc thesis, University of Reading, 1998.

[11] P. Stone, S. Poulston, R. Bennett, M. Bowker, Chem. Commun. (1998) 1369.

[12] R.A. Bennett, P. Stone, M. Bowker, Catal. Lett. 59 (1999) 99.

[13] A. Dickinson, PhD thesis, University of Reading, 1997.

[14] See, for instance, M. Haruta, Catal. Today 36 (1997) 153, and references therein.

[15] M. Haruta, A. Ueda, S. Tsubota, R. Torres Sanchez, Catal. Today 29 (1996) 443.

[16] M. Valden, X. Lai, D.W. Goodman, Science 281 (1998) 1647.

[17] C. Henry, Surf. Sci. Rep. 7/8 (1998) 231.

[18] C.T. Campbell, Surf. Sci. Rep. 27 (1997) 1.