Pd nanoparticle enhanced re-oxidation of non-stoichiometric TiO_2: STM imaging of spillover and a new form of SMSI

R.A. Bennett, P. Stone and M. Bowker *

Catalysis Research Centre, Department of Chemistry, University of Reading, Reading, RG6 6AD, UK
E-mail: M.Bowker@reading.ac.uk

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We have used STM imaging *in situ* to demonstrate two fundamental steps in catalytic processes on model catalysts at elevated temperature. We show that Pd nanoparticles on sub-stoichiometric $TiO_2(110)$ dissociatively adsorb O_2 at 673 K which "spills over" onto the support where further reaction takes place. The spillover oxygen re-oxidises the surface by removing Ti^{n+} interstitial ions trapped in the crystal lattice, preferentially re-growing TiO_2 around and over the particles. The identification of the metal enhanced re-oxidation mechanism may have important and general consequences for the understanding of catalysis and gas sensing.

Keywords: Pd nanoparticles, $TiO_2(110)$, O_2 adsorption, O_2 spillover, re-oxidation

Nanoscale particles supported on surfaces show physical and chemical properties which can differ markedly from those of the bulk material due to their low-dimensionality [1,2]. Such effects are used in heterogeneous catalysis and gas sensing, where metal particles are spatially separated on a support material, to enhance selectivity and sensitivity. The interaction between support and particle can give rise to new chemistry as new sites are formed at the support/particle interface [3]. For example, the decoration of metal particles by TiO_x ($x < 2$) species strongly influences catalysis and the various effects resulting from this have been collectively termed as the strong metal support interaction (SMSI) [4].

TiO_2 is commonly used as a support or modifier in photocatalysis and in catalysis, or as a sensing agent in gas sensors [5]. In common with other d^0 transition metal oxides (e.g., V_2O_5, MoO_3 and WO_3) TiO_2 can exist as sub-stoichiometric (reduced) phases which have marked effects upon electrical conductivity, chemical reactivity and structure. On reduction in vacuum by sputtering and/or annealing TiO_2 forms oxygen vacancies and Ti^{n+} interstitial ions dissolved in the bulk, which accommodate the reduction to form TiO_{2-x} (where $x < 10^{-3}$), while maintaining the rutile structure. Higher levels of reduction lead to crystallographic shear (CS) plane formation where slabs of rutile slip with respect to one another to form planar defects with locally higher Ti stoichiometry [6]. These have recently been imaged by STM at the surface of (110) oriented crystals [7,8]. In catalysis, metal particles can catalyse the reduction of the TiO_2 support by reaction in a reducing environment, even to the extent that CS planes are formed [9]. The characteristic physical properties of non-stoichiometric titania at elevated temperature have recently been reviewed [10].

For SMSI effects to take place in catalysts it has been widely reported that the TiO_2 support must first be reduced. We have modelled this by vacuum annealing a single $TiO_2(110)$ crystal at 1173 K to produce a clean surface with a (1×2) termination [11,12]. By deposition of Pd from high-purity wire wrapped around a tungsten filament onto the surface maintained at 673 K and subsequent annealing at 773 K we produce well dispersed particles approximately 60 Å in diameter and 20 Å high. The deposition and high-temperature annealing procedure has been shown to lead to the encapsulation of Pd (and similarly Fe, Ni, Rh, Ir and Pt) particles on TiO_2 by a thin layer of TiO_x, $x < 2$ [13]. The supported particles prepared in this way are comparable to real supported metal catalysts which also show decoration effects in reducing environments. While there have been numerous studies of metal deposition on TiO_2 surfaces [13,14] to our knowledge there are no high-temperature STM studies of nanoscale particles supported on metal oxides or of reactions taking place on these model catalyst systems.

Figure 1 shows a large-area scan of the surface after deposition and shows a low surface density of Pd nanoparticles distributed across the surface, with some preference for decoration of step edges. The (1×2) reconstruction of the reduced surface is imaged between the particles. Figure 2 shows the surface after exposure to ∼900 L O_2 over a period of several thousand seconds. The region bounded by the white box indicates the same area as in figure 1. The surface morphology has significantly changed with the formation of raised islands on the originally flat terraces. These islands correspond to areas of the surface that were covered by Pd particles which themselves have been signif-

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* To whom correspondence should be addressed.

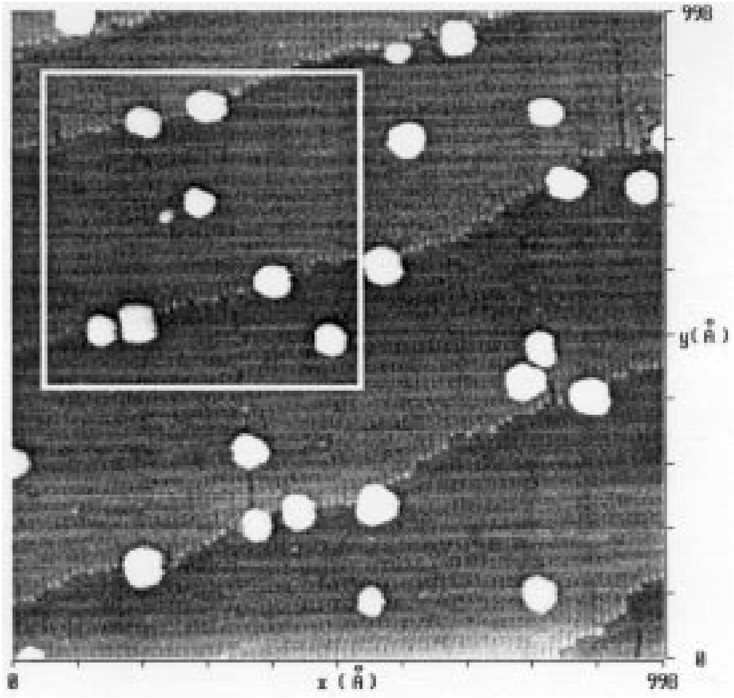

Figure 1. 1000 Å square scan of Pd nanoparticles on sub-stoichiometric TiO_2 displaying a cross-linked (1 × 2) reconstruction taken at 673 K. The white box denotes the same area as in figure 2 and the sequence shown in figure 4 (A)–(I).

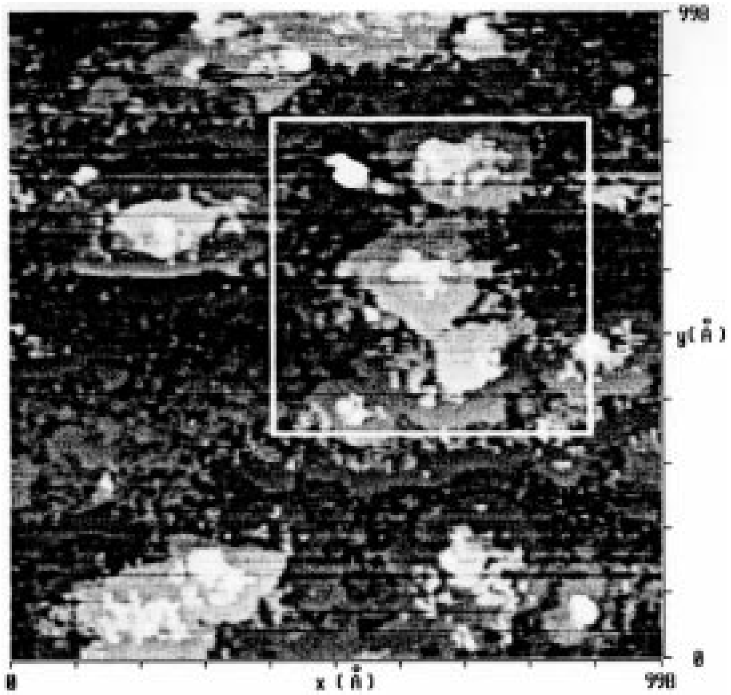

Figure 2. Shows the same area of surface as figure 1 after exposure to 1×10^{-7} mbar O_2 for 9,300 s at 673 K. The white box denotes the same area as in figure 1 and the sequence shown in figure 4 (A)–(I).

icantly diminished in apparent size and height by reaction. There are several plausible mechanisms by which these particles may be removed from the surface. The first is by disruption and dispersion of the particles by the oxygen. A second possibility is that the particles have simply spread and wetted the surface. The third is that the particles have been incorporated into the crystal and are therefore removed from the surface region probed by STM. In a recent paper

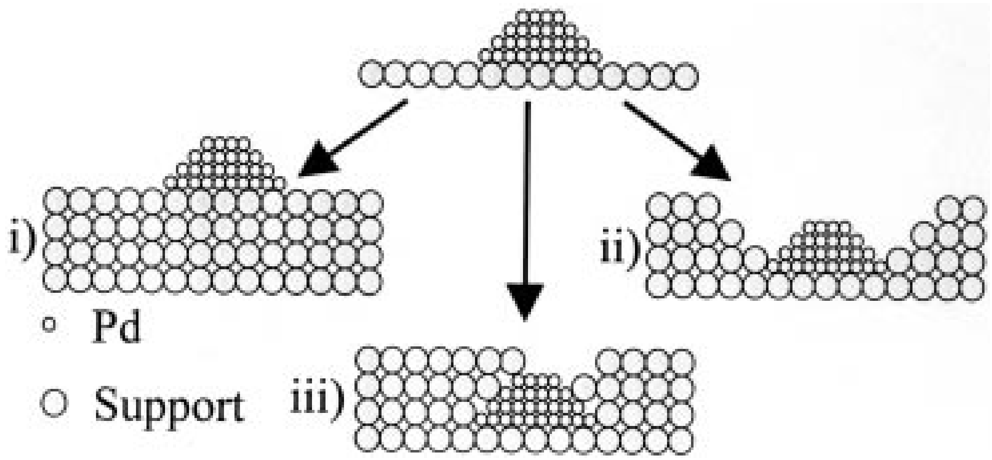

Figure 3. Three possible outcomes of support material growing around a supported nanoparticle. (i) The particle floats on the growing surface, (ii) the particle prevents growth near the particle and so appears in a pit and (iii) the support grows up and over the particle.

we have shown that the clean (1 × 2) surface re-oxidises slowly under these reaction conditions [15] by re-growth of TiO_2 on top of the original surface. Specifically Ti^{n+} interstitials are removed from the sub-surface region of the crystal by the oxygen ambient leading to nucleation and growth of (1 × 1) islands within the (1 × 2) and then to the formation of a new layer of (1 × 2) on top of the newly formed (1 × 1) islands. On the basis of this scheme one may expect that nanoparticles on such a reacting surface may (i) be buried or (ii) form pits if the TiO_2 grows around them or (iii) float on the new surface if the TiO_2 grows beneath them. These three possible outcomes are indicated schematically in figure 3.

Figure 4 shows nine images taken in a sequence between those of figures 1 and 2 during the exposure of the surface to 1×10^{-7} mbar O_2 at 673 K. In figure 4(A) seven particles can be seen on the surface, five on step edges and two in the centre of the (1 × 2) terminated terrace. In figure 4(B) small (1 × 1) islands have begun to nucleate *within the (1 × 2) terrace* and (1 × 1) regions at the lower step edges have extended into the (1 × 2) terrace, as is observed for the reaction without Pd present [15]. In figure 4(C) a second layer has begun to nucleate as points and short rows *on top of the newly formed (1 × 1)* areas. In areas far from the particles the second layer appears as a disordered array of points which grow preferentially in the ⟨001⟩ direction to form another layer of (1 × 2) terminated surface which then ultimately transforms to (1 × 1). This behaviour is characteristic of the re-oxidation of the clean surface. The initial stage of this reaction is therefore cyclic with alternate terminations of (1 × 2) then (1 × 1) within a single layer. There also appears to be no preferential growth around the particles at this stage. However, there is a change in the reaction by figure 4(D) as islands of (1 × 1) grow directly *on top of the (1 × 1) terrace* and preferentially around the nanoparticles. These raised terraces of (1 × 1) grow rapidly outwards from the Pd particles and merge together. In contrast, regions far from the particles still show a relatively slow growth following the alternating (1 × 2) and (1 × 1) sequence. Upon reaching a size of ∼150 Å the (1 × 1) terraces around the particles begin to grow another layer which again forms as a (1 × 1) terrace extending out from the particle, figure 4(E). This process is repeated as layers of (1×1) TiO_2 grow outwards from the Pd particles which are now embedded in the surface. By figure 4(H) the Pd particle is covered by TiO_2 and the rapid growth around the particle reverts to the slower alternating sequence (which the surface far from the particles has been following), with aggregates of bright points nucleating on (1 × 1) terraces. Figure 4(I) shows that the surface over the buried particles and far from the particles show similar structures characteristic of the re-oxidation of a clean TiO_2 surface, i.e., bright points and rows poorly ordered on top of a (1 × 1) terrace.

Oxygen adsorbs dissociatively on Pd surfaces in this temperature regime and so the Pd particles become a source of O atoms with which the surface can re-oxidise and grow. Thus with oxygen “spilling over” from particle to support, the TiO_2 grows out from the particles in its stoichiometric (1 × 1) termination as it is locally rich in oxygen atoms. The spillover oxygen species appear quite mobile on the (1 × 1) terraces as they tend to grow to ∼150 Å diameter before a new (1 × 1) terrace is grown from the particle. The proposed mechanism of growth is shown schematically in figure 5, where a Pd particle is supported on the reduced TiO_2 support. There are three sources of reactants, Ti^{n+} interstitials diffusing from the bulk, gas-phase oxygen and spillover oxygen. The flux of gas-phase oxygen is constant across the surface as is the flux of interstitials from the bulk The enhanced rate of growth around the particles is due to an increased oxygen coverage around the particles arising from the spillover oxygen.

Large aggregates of bright points or (1 × 2) type rows are not seen around the Pd nanoparticle periphery during the enhanced (spillover) phase of growth. In contrast, on the clean surface the reaction sequence moves from (1 × 1) growing within the (1 × 2) and (1 × 2) growing on top of the (1 × 1) leading to an alternating termination [12,15].

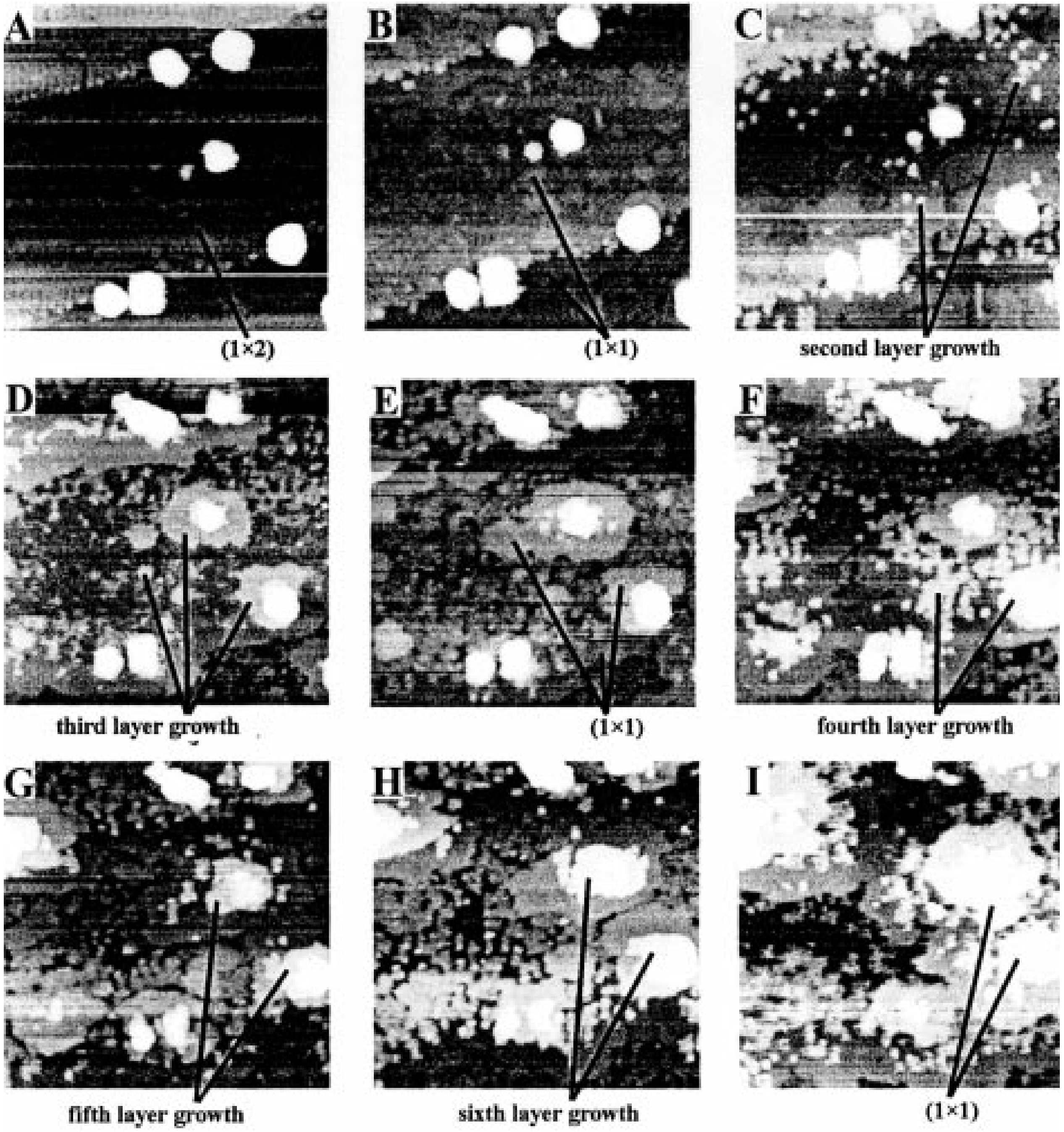

Figure 4. Nine 500 Å square images taken at 673 K during the exposure of the surface to oxygen, as described in figure 2, and corresponding to the region bounded by the white box in figures 1 and 2. These nine selected frames are taken from a sequence of over 40. (A)–(C) The (1 × 2) surface reacts with the oxygen gas to form small islands of (1 × 1) termination which merge to form a terrace. Bright features form on the terrace as the second layer begins to grow, as is observed for the surface without particles present. (D)–(G) (1 × 1) terraces form and grow outwards from the nanoparticles while regions far from the particles react slower and do not directly form (1 × 1) islands. (H)–(I) the particles are covered and the reaction reverts to the slow growth mode observed far from the particles.

Furthermore the Pd particles are always surrounded by the (1 × 1) terminated terraces during reaction and thus have modified their local environment. The rate at which the Pd particle covered surface re-oxidises is ∼16 times faster than for clean sub-stoichiometric TiO_2 under similar reaction conditions [15]. To detail the oxidation mechanism, figure 6 shows close up images of the TiO_2 particle situated in the centre of the terrace in figure 1 during the reaction along with line profiles taken horizontally over the particle (in the fast scan direction of the STM). The first panel, figure 6(A), shows the particle on the (1 × 2) surface with an apparent height of ∼15 Å and width of ∼50 Å. The second panel shows the particle as it begins to grow (1 × 1) terminated TiO_2 preferentially around itself. The line profile shows the corrugation of the (1 × 1) terrace, the step down to the lower surface and the growth of a new layer of

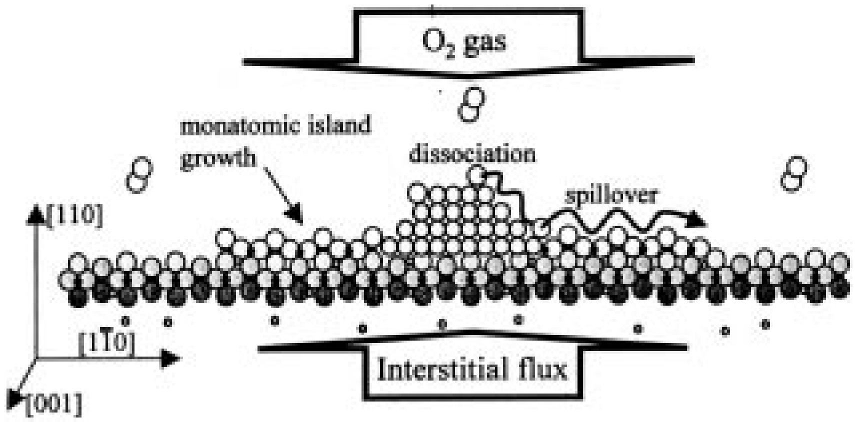

Figure 5. Schematic showing the mechanism of re-oxidation. Ti^{n+} interstitials constantly diffuse into and out of the surface region from the bulk of the crystal. Oxygen adsorbs onto the Pd nanoparticle and spills over onto the TiO_2 support, where it captures Ti^{n+} and adds to the (1 × 1) island periphery.

TiO_2 to the left of the particle. At this stage the particle has narrowed in width and shrunk in apparent height by ∼2 Å. We believe that this change in size may be associated with de-encapsulation of the Pd particles in which the reduced TiO_x covering layer is removed by re-oxidation with the oxygen [9]. The exposed Pd metal surface is then free to dissociate and spill over more oxygen atoms onto the support. These atoms rapidly combine with Ti^{n+} interstitials to extend the (1 × 1) island and also to nucleate the growth of new layers. The time taken to activate the particle under these reaction conditions is ∼25 min. This is a direct observation by STM of spillover and de-encapsulation which removes the SMSI (TiO_x covered) state which is generally catalytically inactive.

In panel (C) the particle has become buried in the TiO_2 and a new layer has begun to grow over the particle leading to the formation of a small (1 × 1) island in the centre of the (1 × 1) terrace. The (1 × 1) rows of the surface can also be seen in the line profile. In (D) the terrace contains a the bright feature appearing ∼3 Å above the terrace. This bright feature is similar to the new layers growing far from the particles in figure 4 (C)–(I) and has the correct apparent height for the disordered growth of a new layer of TiO_2 on the (1 × 1). In total, six complete monolayers of TiO_2 have been re-grown on the surface around the particle which is sufficient to completely cover the particle.

The complete burial of nanoparticles has no reported analogue in catalysis as the support material is itself generally a nanoscale material with a high surface area to volume ratio. Such support particles cannot contain enough Ti^{n+} interstitials in the bulk, even in the most reduced state (Ti_4O_7), to grow several TiO_2 monolayers over the entire surface when re-oxidised. However, as we have demonstrated the local growth of TiO_2 at the particle periphery, it may be possible that small metal particles would experience dramatic changes in local environment on re-oxidation of the support. Such changes would be effective in changing chemical pathways on the surface and constitute a new form of strong metal support interaction. Furthermore, the larger the particles of the support material, the greater the potential for partial coverage or burial of the supported metal particles. This may provide a mechanism for the selective modification of catalysts by support size and throws some light on the often cited high-temperature reduction, calcination and low-temperature reduction cycles employed to activate and stabilise real TiO_2 supported catalysts. Additionally thin and thick film gas sensors which employ nanoscale metals on reducible oxide supports may also behave similarly to the single-crystal example shown here [5].

The conditions under which spillover of oxygen to the support is evident may be expected to be strong functions of gas pressure, level of crystal reduction and temperature. We shall explore some of this parameter space in future to quantify the various steps in the mechanism shown here.

In summary, we have shown, by the application of STM, the mechanism by which metal particles enhance the re-oxidation of reducible support materials by adsorbing oxygen which spills over onto the surface of the support. Interstitial ions are removed from the bulk and react with the oxygen to form a new surface layer. The nanoparticle enhanced removal of Ti^{n+} from the bulk by this mechanism is ∼16 times as fast as on the clean surface. The re-oxidation and growth of TiO_2 enhanced locally by Pd particles is a new form of the SMSI. We have also observed de-encapsulation of TiO_{2-x} decorated Pd particles induced by oxygen adsorption and the activation of the particle allowing the spillover of oxygen atoms. Many layers of TiO_2 may grow during re-oxidation such that the metal particles become buried. This has possibilities for engineering the surface properties, but may also limit the application of single-crystal reducible metal oxides as supports for model catalysts in oxidising environments.

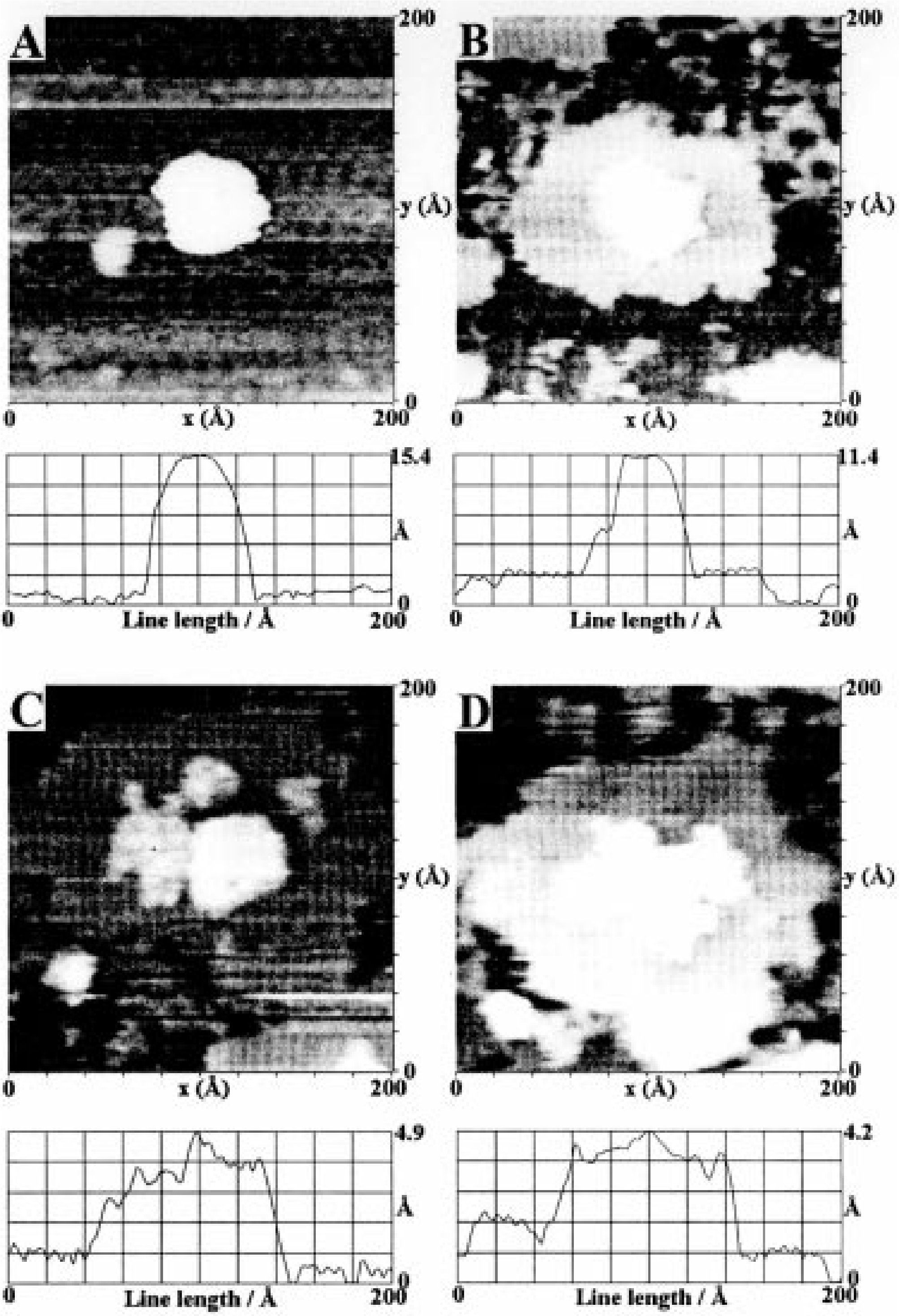

Figure 6. Close up images of the nanoparticle during the four stages of reaction. (A) An unreacted Pd particle on the (1 × 2) reconstructed surface. (B) A reactive particle spilling oxygen onto the support where it is re-oxidised to form a (1 × 1) island. (C) A buried particle which no longer has active facets to supply oxygen to the surface. (D) Surface over a buried particle behaving as the clean surface does with the bright feature the same as that observed far from the particles. The line profiles show the changes in apparent particle size *as the support grows up around the particle,* thus the 0 on the z scale does not represent an absolute zero but the level of the surface at that time. In (A) the particle rests on the (1 × 2) surface and has an initial height of ∼15 Å. In (B) the surface has grown two layers around the particle so its apparent height is reduced. The particle has noticeably narrowed and the (1 × 1) corrugation is visible. In (C) the surface has started to grow the sixth layer which displays a (1 × 1) termination in the centre of the island over the particle. The particle is completely buried. In (D) a seventh layer has started to form.

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