

Complex pathways in dissociative adsorption of oxygen on platinum

T. Zambelli, J. V. Barth*, J. Wintterlin & G. Ertl

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6,
D-14195 Berlin, Germany

Gas adsorption on solid surfaces is the basis of heterogeneous catalysis. Gas–surface interactions may be complex and in many cases the fundamental mechanisms of the chemisorption process are hard to discern. The macroscopic kinetics of a heterogeneous catalytic reaction are usually modelled within the Langmuir model¹, which assumes that free adsorption sites are occupied at random. The adsorption of oxygen on a platinum (111) surface has been studied extensively as a model system for surface chemical processes generally^{2–15}, owing to its significance in platinum catalysed oxidation reactions such as that of CO and NO. Here we show that even for this well studied system the chemisorption process may be much more complicated than the Langmuir model implies. Our observations with the scanning tunnelling microscope show that the dissociation probability for an oxygen molecule becomes affected by chemisorbed species in the vicinity that have dissociated already. This introduces a dynamic heterogeneity in the adsorption mechanism which leads to kinetically limited ordering of the adsorbate. This effect is likely to be quite general and to affect the bulk kinetics of catalytic reactions conducted at the high temperatures and pressures of most industrial heterogeneous catalysis.

It is believed that, in the regime of low incident kinetic energy, the dissociative adsorption of oxygen on Pt(111) proceeds by sequential population of precursor states^{10–12}—that is, a physisorbed and a chemisorbed molecular oxygen species, which can be stabilized on the surface if the crystal temperature is reduced to values below 30 K and 160 K, respectively. We have used the scanning tunnelling microscope (STM) to study the initial distributions of chemisorbed oxygen on Pt(111) resulting from interaction with O₂ between 50 K and 160 K. The experiments were done in an ultrahigh-vacuum chamber (base pressure 3×10^{-11} torr) with a home-built STM cooled by liquid helium. Sample preparation and characterization followed procedures described previously¹⁴. The STM data were obtained in the constant-current mode with typical tunnelling currents of 0.1–1 nA and voltages of 30–500 mV (the possible effect of tip-induced dissociation of molecules reported recently¹⁶ was carefully investigated and can be excluded). Samples were exposed to oxygen by backfilling the chamber. In agreement with electron energy-loss spectroscopy⁵ and recent STM observations¹⁶, we find that for small coverages oxygen adsorbs dissociatively down to about 95 K. At even lower temperatures adsorbed O₂ molecules may accumulate on the surface.

Thermally activated surface diffusion of chemisorbed O atoms is suppressed on the timescale of the experiments at temperatures below about 160 K (ref. 14) and hence the STM images reproduced in Fig. 1, recorded after exposing the Pt(111) surface to 1 L O₂ (1 L = 10^{-6} torr s) at sample temperatures between 50 and 160 K, reflect the distributions of adsorbed particles just after thermal accommodation following equilibration. At the highest temperature, $T = 160$ K, the O-atom coverage corresponds to only about 0.016 monolayers, from which an initial dissociative sticking coefficient (the probability that an impinging oxygen gas molecule is

dissociatively chemisorbed on the clean Pt surface) of $S_0 = 0.03$ is derived (1 monolayer corresponds to 1 O atom per Pt substrate atom), in agreement with earlier observations¹². The adatoms always appear as pairs (imaged as dark spots) which are randomly distributed across the surface. In agreement with previous findings, atoms in these pairs have, on the average, a separation of twice the lattice constant of the Pt surface, $2a = 5.6$ Å (ref. 14). There is no preferential adsorption on surface defects, such as atomic steps. On lowering the substrate temperature to 115 K, we find that cluster formation of the oxygen pairs is predominant, where most (~70%) of the atoms are assembled in small islands, corresponding to a marked increase of the total coverage to 0.022 monolayers O. At $T = 110$ K, these clusters grow quasi-one-dimensionally with lengths between 10 Å and 50 Å. Atomic resolution data reveal that they grow preferentially along the close-packed directions of the surface; accordingly branched clusters form mostly 120° angles reflecting the three-fold symmetry of the substrate. At 105 K the atoms are almost exclusively arranged in such chains, which are partly interconnected forming an irregular network. A change in the island morphology occurs on reducing the temperature below 100 K: triangular oxygen clusters preferentially evolve at the points where three differently oriented chains come together. With further temperature reduction the island distribution becomes more inhomogeneous with the coexistence of wide patches

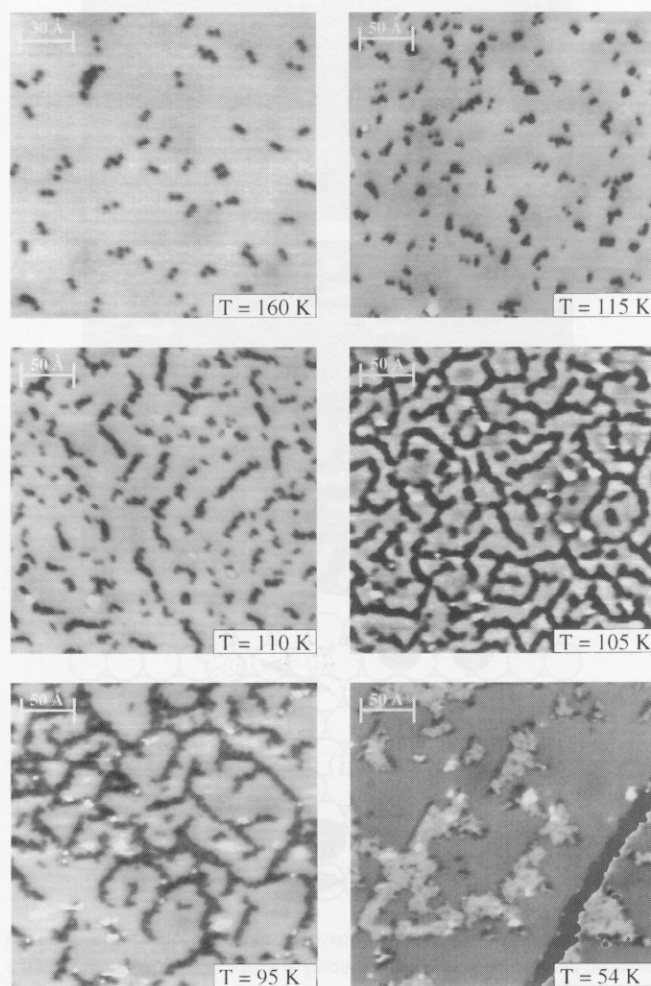


Figure 1 Temperature dependence of oxygen adsorption on Pt. These STM images of Pt(111) were recorded after adsorption of 1 L of O₂ at the indicated temperatures, and reveal the temperature-dependent sticking and anisotropic growth of oxygen islands on the surface. Scale bar in top left image, 30 Å; scale bar in all other images, 50 Å.

* Permanent address: Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland.

of uncovered Pt and oxygen clusters, and the chains are continuously replaced by the more compact triangular islands. Finally, for temperatures below 80 K formation of one-dimensional structure ceases and exclusively compact triangular islands exist. In contrast to the atom islands formed at higher temperatures they are always imaged as protrusions on the Pt substrate. They are thus associated with molecularly adsorbed oxygen, in agreement with recent other STM observations¹⁶.

At first sight, one is tempted to attribute the formation of adsorbed oxygen (O_{ad}) chains to a locally increased dissociative sticking coefficient for gas molecules that impinge near already chemisorbed species, as was suggested to explain the increasing sticking coefficient with increasing coverage at low temperatures^{5,12}. This idea can be rejected if one analyses STM data for very small coverages in the earliest stages of oxygen uptake. Such data reveal that the fraction of clusters composed of four or more oxygen atoms far exceeds the maximum value to be expected from this effect. Furthermore, the strong temperature dependence of both the

sticking coefficient and the shape of the oxygen agglomerates formed cannot be explained this way. The observations, however, can be entirely rationalized by the assumption of a mobile adsorbed molecular precursor state. The mechanism of island formation is attributed to the action of already chemisorbed O atoms as active sites for trapping and dissociation of this precursor.

The temperature dependence of the sticking is thus understood as the result of the competition between precursor mobility, allowing it to reach the active sites for equilibration, its spontaneous dissociation on the clean surface and thermal desorption of the molecules from their weakly bound precursor state. With decreasing temperature the lifetime τ of the precursor at the surface increases. But as the activation energy for surface diffusion is generally only a fraction of the adsorption energy, this causes an increase in the mean free path of the precursor molecule on the surface (this is just the opposite behaviour to non-evaporating particles, where diffusion lengths increase with the temperature). The resulting higher probability of reaching an active site (an O atom) accounts for the marked increase of the dissociative sticking coefficient below 120 K reported previously¹² and also observed here. An estimate of the mobility and adsorption energy criteria required for agglomeration, using the known energy of the physisorption potential (~ 100 meV; ref. 15), indicates that the mobility in the physisorbed molecular state is the essential parameter for this behaviour.

Our data suggest interactions between chemisorbed O atoms and precursor molecules whereby the dissociation probability of the latter is locally increased. This mechanism is substantiated with the help of the atomic-resolution STM data reproduced in Fig. 2. Whereas at 160 K essentially isolated pairs of O atoms are formed, at 140 K small agglomerates are generally found (Fig. 2a), whose average size increases as the temperature is lowered further. The atomic-resolution image at 105 K (Fig. 2b) in addition resolves the growth of chain-like configurations of O_{ad} -pairs, preferentially following the close-packed directions of the substrate. This quasi-one-dimensional growth indicates that the effect of the O_{ad} -atoms on the precursors has an anisotropic nature, which presumably results from the local arrangement of the oxygen atoms within the agglomerates. We suggest that the dissociation probability of the O_2 -precursors is higher at the protruding chain ends than near the adatoms within a chain which are more highly coordinated with neighbouring atoms and consequently have a different electronic environment. The resulting anisotropic growth is sketched in the model in Fig. 2. A simple hit-and-stick mechanism would cause the formation of fractal islands, as found for example in two-dimensional simulations of diffusion-limited aggregation¹⁷, in contrast to the present observations. On oxygen adsorption at even lower temperatures (below ~ 100 K) the transition to compact island formation sets in until for $T < 80$ K exclusively compact molecular islands of the type shown in Fig. 1 (for $T = 54$ K) evolve. For their formation, the precursors must be sufficiently mobile along the island edges to ensure the observed triangular shapes rather than ramified growth. These observations signal that the interactions between the precursors and adsorbed molecules or atoms are attractive.

Our data demonstrate the complexity of an apparently simple surface reaction, the precursor-mediated dissociative adsorption of a molecule on a metal surface, resulting from the precursor mobility and local reactivity of chemisorbed particles, and the interaction anisotropy between the adsorbed species and the precursor. This effect is essentially kinetic in nature and may lead to metastable configurations of the adsorbed particles. It cannot be treated theoretically simply by including interaction energies between adsorbed particles in statistical concepts leading to equilibrium properties. Any catalytic reaction is governed by the same kinds of elementary processes, even if these become faster at the higher pressures and temperatures of 'real' conditions. The effects are

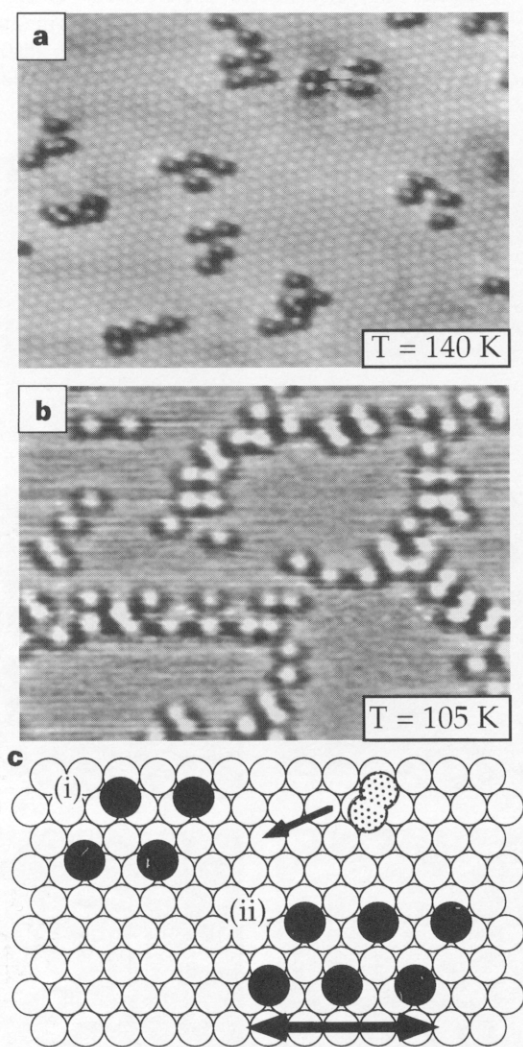


Figure 2 Atomic-resolution images of oxygen islands. The images illustrate the enhanced precursor dissociation probability at adsorbed oxygen atoms and the resulting quasi-one-dimensional growth for (a) $T = 140$ K (3 L dose, image $100 \times 60 \text{ \AA}^2$), (b) $T = 105$ K with chain-like islands corresponding to strings of oxygen pairs (1 L dose, image $70 \times 40 \text{ \AA}^2$). c, Model illustrating the directional growth of O_{ad} (black spheres) chains on Pt(111): (i) an oxygen precursor molecule (shaded) approaches an atom island; (ii) on its dissociation a chain segment evolves.

essentially induced by local modifications of the electronic properties of a surface near chemisorbed particles and hence, we believe, are of general importance for chemical processes at surfaces whenever the diffusion lengths of adsorbing species reach critical values compared with their lateral distribution.

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Correspondence should be addressed to J.V.B. (e-mail: johannes.barth@ipe.dp.epfl.ch).

Chemisorption of molecular oxygen on Pt(111) at low temperatures is characterized by a high sticking probability and a chemisorbed precursor state. We have used scanning tunneling microscopy to study the initial distribution of chemisorbed oxygen molecules resulting from interaction with O₂ between 30 K and 160 K. Our experiments were done in an ultrahigh-vacuum chamber (base pressure 3×10^{-10} torr) with a home-built STM (model 900A, Digital Instruments). Sample preparation and characterization followed standard procedures^{1,2}. The STM data were obtained in the constant-current mode with typical tunneling currents of 0.1–1 nA and voltages of 50–300 mV (the possible effect of the voltage on dissociation of molecules reported recently³ was carefully investigated and can be excluded). Samples were exposed to oxygen by backfilling the chamber. In agreement with electron energy loss spectroscopy⁴ and atomic STM observations⁵, we find that for small coverages oxygen adsorbs on Pt(111) at room temperature and even lower temperatures. At low coverages, oxygen may adsorb on the surface.

Thermal annealing and diffusion of chemisorbed O₂ leads to suppression of the precursor state of the experiment at temperatures below about 100 K and a new precursor STM image is produced (Fig. 1, extended after exposing the Pt(111) surface to 1 L O₂ ($1 \text{ L} = 10^{-6}$ torr s)) at sample temperatures between 30 and 160 K, reflect the distributions of adsorbed particles just after thermal accommodation following equilibration. At the highest temperature, $T = 160$ K, the O-atom coverage corresponds to only about 0.018 monolayers, from which an initial dissociative sticking coefficient (the probability that an incoming oxygen gas molecule is

dissociatively chemisorbed on the clean Pt surface) of 2.5×10^{-2} is derived (1 monolayer corresponds to 10^{19} atoms per Pt substrate atom), in agreement with earlier observations⁴. The adsorbed oxygen appears as pairs (Fig. 1a) or as dark spots which are randomly distributed across the surface. In agreement with previous findings, atoms in these pairs have an average separation of about the lattice constant of the Pt surface, $a_{\text{Pt}} = 3.8$ Å (ref. 14). There is no preferential adsorption on surface defects, such as atomic steps. On lowering the substrate temperature to 115 K, we find that cluster formation of the oxygen pairs is predominant, where most ($\sim 70\%$) of the atoms are assembled in small islands, corresponding to a marked increase of the total coverage to 0.022 monolayers O. At $T = 110$ K, these clusters grow quasi-one-dimensionally with lengths between 10 Å and 50 Å. Atomic-resolution data reveal that they grow preferentially along the close-packed direction of the surface, accordingly branched clusters form nearly 135° angles reflecting the three-fold symmetry of the substrate. At 105 K the atoms are almost exclusively arranged in such chains, which are partly interconnected forming an irregular network. A change in the island morphology occurs on reducing the temperature below 100 K: triangular oxygen clusters preferentially evolve at the points where three differently oriented chains come together. With further temperature reduction the island distribution becomes more inhomogeneous with the coexistence of wide patches

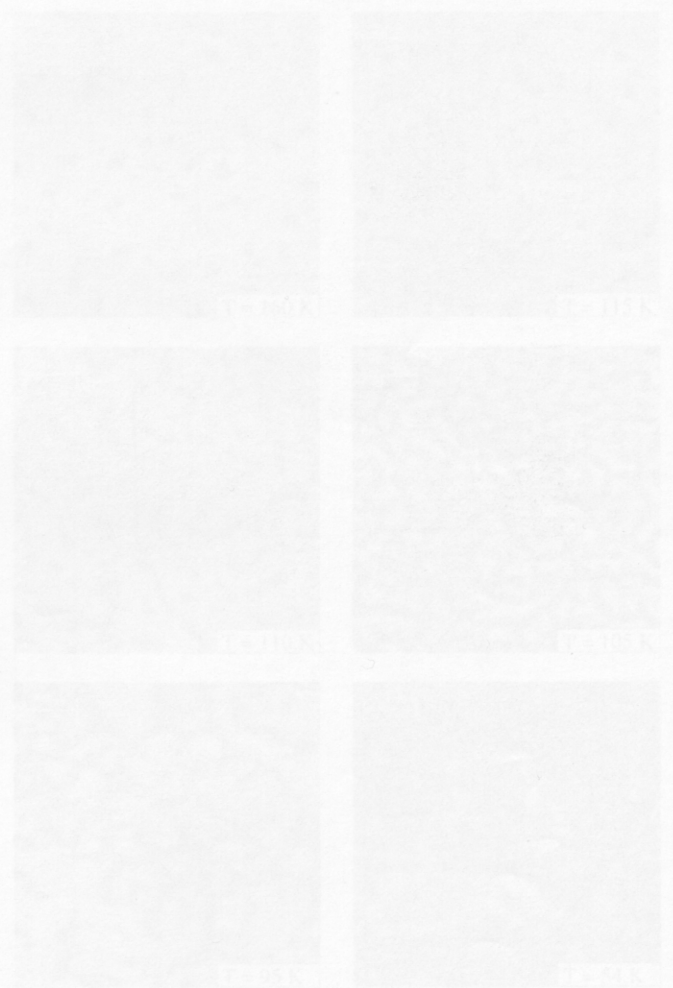


Figure 1 Temperature dependence of oxygen adsorption on Pt. These STM images of Pt(111) were recorded after adsorption of 1 L of O₂ on the cleaned and annealed surface. The temperature-dependent sticking and subsequent growth of O₂ on Pt(111) at low coverages have been discussed in the left column. 30 Å scale bar in color legend, STM.

¹ Zenzinger, J. et al. *Surf. Sci.* **342**, 119–133 (1995). ² Wurth, W. et al. *Phys. Rev. Lett.* **65**, 2426–2429 (1990). ³ Stipe, B. C. et al. *Phys. Rev. Lett.* **78**, 4410–4413 (1997). ⁴ Artsykhovich, A. N., Ukrainsev, V. A. & Harrison, I. *Surf. Sci.* **347**, 303–318 (1996).