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## Oxygen Dissociative Adsorption on Platinum Surfaces

The chemical and physical processes occurring between gases and solids during surface catalysis are under continuous investigation and revision. Since platinum metals find wide use as catalysts, and readily chemisorb molecules and dissociate bonds, the interaction between platinum and oxygen was selected for detailed study. Surface kinetics of a heterogeneous reaction are usually described by the Langmuir model, which assumes that free adsorption sites on a surface are randomly occupied.

Now, however, scientists at the Fritz-Haber-Institut der Max-Planck-Gesellschaft in Berlin have observed that oxygen dissociation is affected by nearby chemisorbed species (T. Zambelli, J. V. Barth, J. Wintterlin and G. Ertl, *Nature*, 1997, **390**, (6659), 495–497). Using a platinum(111) surface, the distribution of chemisorbed oxygen was recorded by scanning tunnelling microscopy, at intervals from 160 down to 50 K, after exposure to  $10^{-6}$  torr s oxygen. At 160 K the O atom coverage first formed randomly distributed adatom pairs, then as tem-

peratures were lowered, the pairs formed clusters, which grew into quasi-one dimensional chains, 10 to 50 Å long, with branches at  $120^\circ$  angles. The chains formed an irregular network, followed by the appearance of triangular O clusters at the points where three chains met. The clusters had inhomogeneous distribution alongside large areas of bare platinum. Finally, triangular islands protruded from the surface.

It is assumed that there is a mobile adsorbed molecular precursor state, which is trapped and dissociated by already adsorbed O atoms – the active sites. At lower temperatures the precursor lifetime and its mean free path increase, giving it a higher probability of reaching an O atom. It is suggested that dissociation of the precursors is highest at the ends of the chains.

This apparent increased local reactivity and modification of the electronic properties near chemisorbed particles is an important finding for the general description of catalytic reaction kinetics, and has relevance for most high temperature and pressure industrial heterogeneous catalyses.