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ON THE NEED FOR HIGHER GAS PRESSURES TO OBTAIN
SURFACE STRUCTURES IN LOW ENERGY ELECTRON DIFFRACTION STUDIES

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Low energy electron diffraction (LEED) experiments have shown\(^{(1,2)}\) that ordered structures result from the chemisorption of gases on the surfaces of most solids studied so far. These structures are attributable either to an ordered arrangement of the adsorbed species or to a rearrangement of the substrate atoms during chemisorption\(^{(2)}\). In these experiments, the pressure of the gas, whose chemisorption is a necessary condition for producing the surface structure, is usually in the range of \(10^{-9} \text{ - } 10^{-5}\) torr. If a lengthy exposure of the surface to the adsorbing gas molecules is required [on account of low sticking probabilities or other chemical considerations] the time of exposure is usually varied rather than increasing the gas pressure. There are several reasons for restricting chemical reaction studies to low pressures in LEED experiments; 1) steady state gas flow conditions can be easily established and maintained by continuous pumping only at low gas fluxes, 2) the purity of the ambient can be better maintained since at higher
pressures there is a substantial backstreaming of unwanted gases from the ion-pump and contamination and subsequent deterioration of the electron gun optics can be minimized.

Oxygen on the (0001) face of $\alpha$-$\text{Al}_2\text{O}_3$

The structure of the hexagonal (0001) face of aluminum oxide has been studied in several laboratories. After heating in vacuum (by electron bombardment or by radiation) at temperatures $\geq 1250^\circ \text{C}$, the surface exhibits a complex structure which indicates a mesh with a unit cell larger by $\sqrt{3}a$ and rotated $9^\circ$ with respect to the projection of the bulk unit cell to the (0001) surface $[\text{Al}_2\text{O}_3 \text{(0001)} - (\sqrt{3}\text{a} \times \sqrt{3}\text{a})R \pm 9^\circ]$. The structure may also be indexed by the transformation matrices for the two equivalent orientations of the unit mesh: $(11/2 \quad \sqrt{3}/2), \quad (11/2 \quad -\sqrt{3}/2)$. It has been reported that oxygen at pressures $\leq 10^{-5}$ torr has no effect on this surface and produces no new surface structures in the temperature range $25^\circ - 1800^\circ \text{C}$. We have found that heating the rotated $\text{Al}_2\text{O}_3 \text{(0001)} - (\sqrt{3}\text{a} \times \sqrt{3}\text{a})$ surface structure in an ambient of $2 \times 10^{-4}$ torr oxygen at $1000^\circ \text{C} - 1200^\circ \text{C}$ generates the (1x1) structure, which is the stable low temperature structure in vacuum. The transformation $\text{Al}_2\text{O}_3 \text{(0001)} - (1\times 1) \longrightarrow (\sqrt{3}\text{a} \times \sqrt{3}\text{a})R \pm 9^\circ$ is completely reversible. The complex surface structure is stable at high temperatures and can always be produced by heat treatment in vacuum, while the (1x1) surface structure can be regenerated at will in oxygen as long as the oxygen partial pressure is $\geq 2 \times 10^{-4}$ torr.
**Hydrogen on the (100) Face of Platinum**

The (100) face of platinum exhibits a stable (5x1) surface structure. (8) Hydrogen, at gas pressures in the range of $10^{-9} - 10^{-6}$ torr, does not appear to affect the Pt(100) - (5x1) surface in any detectable way over a wide temperature range (25$^\circ$ - 1400$^\circ$C). (9) However, if the crystal is heated between 500$^\circ$ - 1000$^\circ$C in a hydrogen partial pressure greater than $10^{-5}$ torr, the (5x1) structure is removed and a (2x2) surface structure formed (9) [Pt(100) - (2x2) - H]. Heating the sample to these temperatures prevents the adsorption of ambient carbon monoxide which would compete with hydrogen for the adsorption sites. The (2x2) surface structure is stable in vacuum. Heating the platinum crystal at 1200$^\circ$C in vacuo (for a few minutes) is necessary to remove this structure and to restore the (5x1) surface structure. However, heating the crystal at only 500$^\circ$C in $2 \times 10^{-8}$ torr of oxygen is sufficient to remove the (2x2) surface structure.

It is apparent that high gas pressures are often necessary to form surface structures of different kinds for several reasons;

a) frequently there is a competition between two adsorbing gases for surface sites and changes in the partial pressures can markedly affect the relative adsorption rates and therefore the subsequent formation of ordered surface structures. For example, carbon monoxide has a great affinity for platinum surfaces and the adsorption of most gases on platinum takes place in competition with the carbon monoxide always present in the ambient of an ultra-high vacuum system. (8,9)

b) The dissociation of a diatomic molecule ($\text{H}_2$, $\text{O}_2$, $\text{N}_2$, etc.) on the solid surface may well be the rate-limiting step in the formation of ordered surface structures.
Increased gas pressures should certainly increase the rate of dissociation.

c) There is evidence that gases dissolved in the bulk of the crystal may play an important role in surface reactions. The formation of certain surface structures (especially during oxidation) may require the presence of gas atoms which have diffused below the surface. Both the solubility and diffusion rate of gases in solids increase with increasing ambient gas pressures.

The question often arises as to how applicable the results of low pressure LEED studies are to industrially important surface reactions which take place at higher pressures. It is apparent that the application of higher pressures in LEED experiments may lead to the formation of new surface structures. Therefore higher pressure LEED experiments should be carried out in order to utilize the obtained structural information in the analysis of the mechanisms of high pressure surface reactions.

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