

correlation is obtained between the chemical activation energies and the work functions of the metals. Metals with lower work functions have the highest chemical activation energies.

- (iii) When these noble metals are not supported, the chemical activation energies are constant, which means that the correlation observed in (ii) is not a property of the metals themselves.

This type of chemical, or electronic, promotion may well be of more importance than is generally realised. It has already been noted in the alkali metal promotion of supported ruthenium catalysts for the synthesis of ammonia (16).

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## Photocatalytic Properties of Materials

### THE PHOTOREDUCTION OF PALLADIUM IONS ON TITANIUM DIOXIDE

The predominant position occupied by the metal silver in photographic processes often obscures the fact that other metals and materials possess photographic properties. Both scientific and economic reasons have prompted recent studies of these alternatives with varying degrees of success.

It has been known since 1920 that titanium dioxide  $\text{TiO}_2$  exhibits photocatalytic properties, since it is darkened by ultra-violet radiation. Both electrons and holes produced by light excitation may be involved. More recently, the photoreduction of palladium ions  $\text{Pd}^+$  at  $\text{TiO}_2$  has been studied as an initial step towards a photographic process with  $\text{TiO}_2$ . Photoreduction of a few metal ions forms the initial image in a photographic process and this image has subsequently to be developed during a second stage to make it visible and to retain it. Any photocatalytic reduction of  $\text{Pd}^+$  ions on  $\text{TiO}_2$  is, of course, accompanied by a corresponding oxidation process at the  $\text{TiO}_2$ .

Simultaneous studies of the photocatalytic reduction of  $\text{Pd}^+$  and of the electrochemical

properties of  $\text{TiO}_2$  have now been reported by F. Möllers, H. J. Tolle and R. Memming of Philips Forschungslaboratorium Hamburg G.m.b.H. (*J. Electrochem. Soc.*, 1974, **121**, (9), 1160-1167). They carried out electrochemical and photocurrent measurements on vapour-deposited  $\text{TiO}_2$  films on conducting substrates ( $\text{SnO}_2$  on glass, or titanium sheet).

It was shown that the primary step in this process is the generation of an anodic photocurrent, i.e. evolution of oxygen, which catalyses the cathodic deposition (reduction) of palladium under open-circuit conditions.

The nature of the photocatalytic deposition of palladium on  $\text{TiO}_2$  was interpreted on the basis of the photovoltaic effect of the semiconducting  $\text{TiO}_2$ . Further studies included an examination of the various parameters affecting the phenomenon, e.g. space charge effects, film thickness and doping. The results are clearly illustrated by a series of graphs depicting the various electrochemical data and the whole is presented as a useful and stimulating paper.

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