The Production of Heavy Water

HYDROGEN-WATER DEUTERIUM EXCHANGE OVER PLATINUM METALS ON CARBON SUPPORTS

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Catalysts using suitably supported platinum show promise for the commercial production of heavy water. Carbons are potential primary supports for the platinum and metal-support interactions have been observed in this system. These interactions lower the chemical activation energy and increase the rate of reaction under conditions where it seems likely that the support donates electrons to the metal.

The Canadian nuclear power system, the so-called CANDU system, is based on the use of natural uranium oxide fuel. To use this fuel, a very efficient moderator is required, and the only practical moderator is heavy water, D_2O. The present generation of heavy water-moderated, pressurised, heavy water-cooled reactors use about 1 Mg of D_2O per MW (electrical). Thus, at current prices, the heavy water in a 400 MW(e) unit costs £1.3×10^7, so there is considerable incentive to produce it more cheaply.

The current commercial process for making heavy water uses a dual temperature exchange between the deuterium in water and hydrogen sulphide, H_2S. The process is highly developed but suffers from a number of shortcomings including the inability to extract more than 20 per cent of the deuterium from water of natural deuterium abundance, and the necessity of dealing with Mg quantities of H_2S at pressures of 2 MPa. An alternative process is the dual temperature exchange between hydrogen and water. However, this exchange reaction requires an efficient catalyst. Supported platinum and chromia-promoted nickel are good catalysts in the vapour phase but lose their activity rapidly in the liquid phase. Fortunately, Stevens (2, 3) recently demonstrated that supported platinum catalysts would retain their activity in the presence of liquid water if they were protected from wetting by a permeable hydrophobic film. The exchange reaction then takes place in the vapour state in the interior of the catalyst, which is surrounded by liquid water. This process is much more likely to be economic.

Various charcoals have often been used as primary supports for the platinum, and vapour phase rates over carbon-supported catalysts have often been higher than over alumina- or silica-supported platinum (1). However, it is only recently that methods have been developed for measuring metal surface areas in the presence of a support (4). Therefore it is not clear from the earlier work whether there is a true metal support interaction with the carbon supports or whether the platinum is merely better dispersed on these supports. It seemed desirable to learn whether the specific rates (rates per unit metal surface area) were, in fact, higher with the carbon supports. Also, since the electronic properties of carbon are easily altered by heat treating (5), it might be possible to find optimum electronic properties for the support and at the same time to learn something about the mechanism of the exchange reaction.

Fig. 1 Research workers at Atomic Energy of Canada Limited have found that the mass spectrometer is an indispensable tool for the study of isotopic exchange reactions. This instrument monitors the deuterium content of hydrogen from the catalytic reactor

Support Effects

Rates for the H_2-HDO exchange were measured in the vapour phase using platinum black and platinum on carbon catalysts (6). The carbon was graphitised at various heat treatment temperatures before the platinum was deposited on it. The results are shown in Fig. 2, where the specific rate, r_s, is the number of moles of HD that would be initially produced if static experiments could be done using pure HDO and H_2. In actual fact, rates were measured in a flow system using H_2 with its natural abundance of deuterium and water containing about 4 per cent deuterium (8 per cent HDO). Rates are given in terms of the platinum surface area. Obviously, graphitising the support lowers the apparent activation energy (makes it more negative) and increases the rate at lower temperatures. Since the rates are calculated from plots of the logarithm of the conversion against reciprocal flow, we do

not think that external diffusion is important. Since varying the particle size did not change the rates, neither do we think that pore diffusion is causing these effects.

Over a relatively small range of pressures, the rate of a catalytic reaction may often be adequately represented by a power law

$$r = k_o \, p_{H_2O}^a \, p_{H_2}^b \qquad (1)$$

Under these conditions, and with surface exchange rate controlling (7), the true activation energy for the surface exchange (8) is given by:

$$E_o = E_{app} + a \, \lambda_{H_2O} + b \, \lambda_{H_2} \qquad (2)$$

where E_{app} is the apparent activation energy, and the λ's are the heats of desorption of water and hydrogen. Since a and b can be obtained experimentally and values of λ are available, then E_0 can be calculated, and E_0 values are shown in the Table overleaf. Clearly, graphitisation of the support leads to
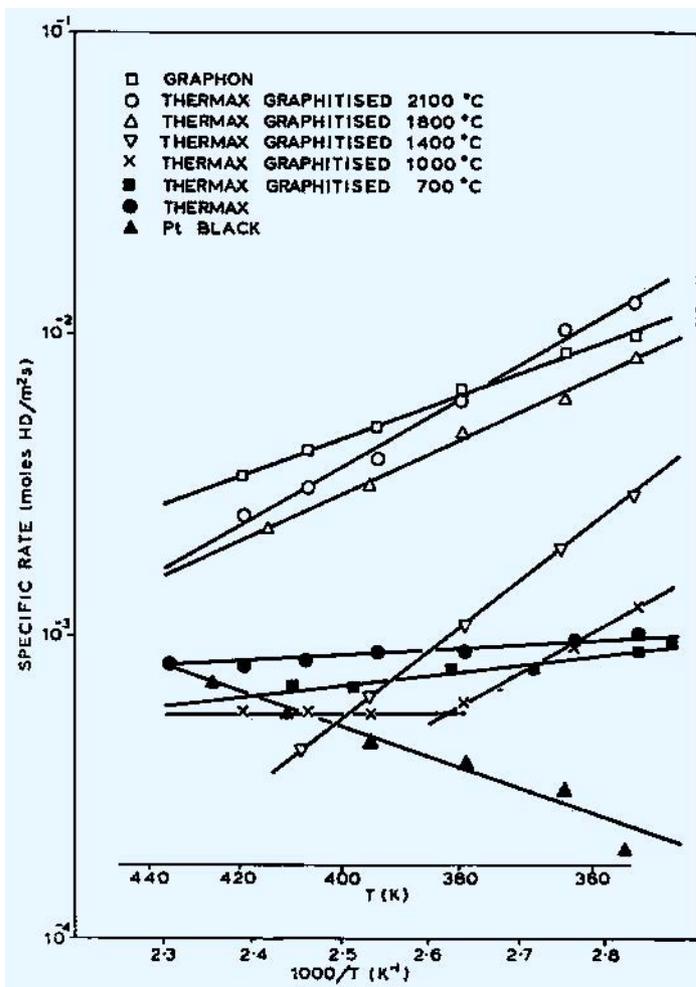
Fig. 2 Specific rates for H₂-HDO exchange over carbon-supported platinum catalysts when carbon is heat treated at the indicated temperature. $p_{H_2O} = 23.7$ *kPa and* $p_{H_2} = 78.0$ *kPa*

a considerable lowering of E_0. Since the work function of well graphitised carbon is less than that of platinum, it was suggested that electron transfer to the platinum might be responsible for this effect.

Noble Metals on Graphon

In the above section, we suggest that electron transfer from the graphitised carbon might be responsible for the lowering of E_0 as the graphitising temperature of the support is changed. Since all the Group VIII noble metals catalyse the hydrogen-water exchange, we measured specific rates, orders and apparent activation energies over all six platinum group metals, supported on Graphon (8). For comparison, data were obtained over unsupported metal powders (10). The work

Activation Energies for Hydrogen-Water Deuterium Exchange over Platinum Catalysts			
Support	E_{app}	E_o	Reference
Al_2O_3	6.5	~16.5	8
SiO_2	7.5	17.5	9
None	4.0	14.0	7
Thermax	−1.0	9.0	7
Graphon	−5.1	4.9	7
Thermax (2100)	−7.9	2.1	7

Fig. 3 Ratio of chemical activation energies over powders to those over Graphon-supported catalysts (Fig. 3a); ratio of frequency factors over powders to those over Graphon-supported catalysts (Fig. 3b); in both cases plotted against thermionic work function in eV
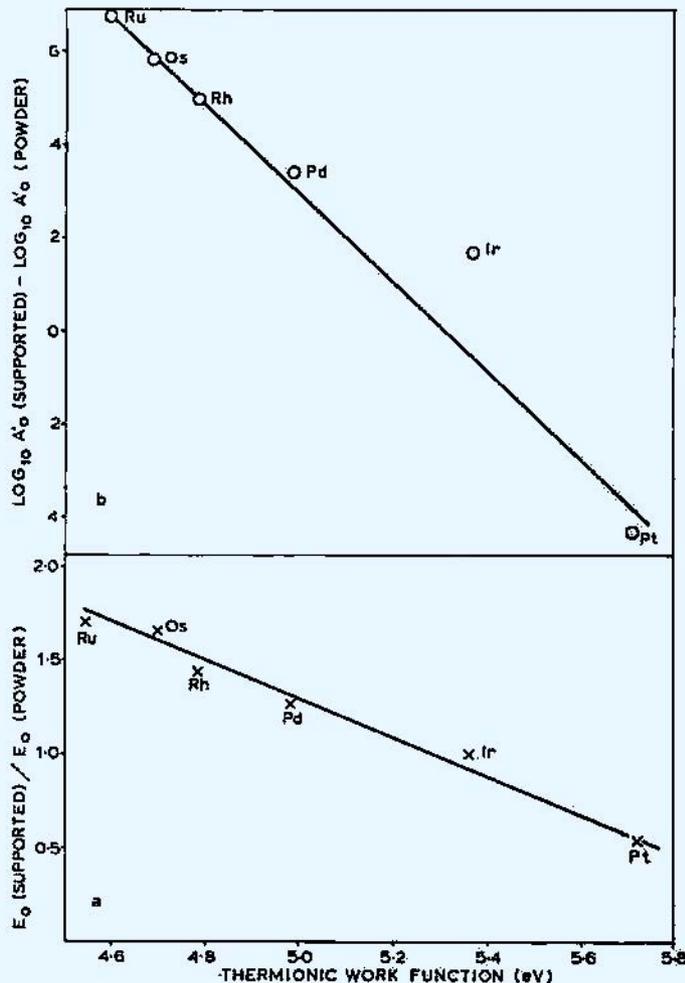
functions of these metals cover the range 4.5 to 5.7 eV whereas the work function for Graphon is probably somewhere above that for well crystallised graphite (4.4 eV). Therefore we would expect electron transfer effects to be minimal with metals of lower work function and to become more pronounced as the work function of the metal increases.

Over the unsupported powders, the true activation energies (E_0) were within the range 61 ± 6 kJ/mol for all six metals. However, when the same metals were supported on Graphon, the E_0 values varied from 103 kJ/mol for Ru to 36 kJ/mol for platinum.

Figure 3 shows the ratio of E_0 over supported catalysts to E_0 over unsupported powders, plotted as a function of the thermionic work functions selected by Bouwman and Sachtler (11). A good correlation was obtained and the slope suggests that for each kJ/mol that the work function is raised, E_0 is lowered by 0.67 kJ/mol. The quantitative aspect of the correlation may be somewhat suspect, as the reported values of work functions vary considerably. However, we did use a consistent set measured recently.

The observed orders of reaction were best explained by a mechanism involving exchange between chemisorbed hydrogen atoms

and physically adsorbed water (6, 7). Since hydrogen chemisorption is not hindered by the presence of water vapour (12), it is thought that hydrogen and water are adsorbed on separate types of sites and do not interfere with each other. This leads to a rate expression of the form

$$r = k_1 \, \theta_{H_2O} \, \theta_H \qquad (3)$$

If a Freundlich isotherm is assumed, k_1 can be identified with the k_0 of equation (1). Thus, writing k_0 in its Arrhenius form,

$$r = C_H \, C_{H_2O} \, A_0 \, ^{-E_0/RT} \qquad (4)$$

where C_H and C_{H_2O} are the surface concentrations in mol/m^2 which can be calculated from the reaction orders. Relative frequency factors for supported and unsupported catalysts are shown in Fig. 3b. There seems to be some compensation between the frequency factor and the activation energy, but fortunately this compensation is not complete and the actual specific rates at 433K are always increased by supporting the metal on Graphon.

If our proposed mechanism holds, the observed lowering of E_0 is associated with a lowering of the activation energy for the exchange step where a deuterium atom is exchanged between physically adsorbed water and a chemisorbed hydrogen atom. Since the water is weakly bonded, it is most reasonable to assume that the major way in which the activation energy can be lowered is by a change in the Pt-H bonding.

With platinum on Graphon, electron donation from the Graphon to the metal occurs because of the difference in work function. Because both phases are conductors, complete equilibrium should be achieved. Now at room temperature and above, the polarisation of the platinum-hydrogen bond is $Pt^{\delta+}-H^{\delta-}$ (13). Thus, charging the platinum negatively will weaken the platinum-hydrogen bonds. Indeed, in hydride-platinum complexes, it has been shown that adding ligands which withdraw electrons from the platinum strengthens the platinum-hydrogen bond (14). Adding electrons to the platinum should therefore weaken this bond. Weakening the platinum-hydrogen bond should lead to a lower activation energy. In the case of metals with lower work functions, the bonding seems to be changed in the opposite direction, leading to higher E_0 values. Figure 3 suggests that the effective work function of Graphon is about 5.2 eV.

We think that the donation of electrons to the metal affects the platinum-hydrogen bond but other explanations are possible. Levy and Boudart (15) suggested recently that the following equilibrium may exist on the platinum surface in the presence of hydrogen and water

$$PtH + H_2O \rightleftharpoons Pt^- + H_3O^+ \qquad (5)$$
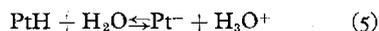
This reaction provides a mechanism for exchange between chemisorbed hydrogen and physically adsorbed water. The work function of the metal would be involved directly in the thermochemistry of this exchange.

The frequency factor for supported platinum divided by the frequency factor for platinum black is less than unity. This suggests that there are relatively fewer active sites produced by electron transfer to the metal than were present in its absence. Similarly, the ratios of frequency factors for the other metals are greater than unity, suggesting that more of the metal surface participates in the reaction.

In summary, we have noted a metal support interaction in the hydrogen-water deuterium exchange. The evidence suggests that the activation energy for surface exchange is lowered when the work functions of the metal and the support are such as to allow electrons to be donated to the metal. This evidence may be summarised as follows:

(i) Graphitising the carbon support lowers the chemical activation energy for hydrogen-water exchange.

(ii) When different noble metals are used on graphitised carbon supports, a

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 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 Pd^+ at TiO_2 has been studied as an initial step towards a photographic process with 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 Pd^+ ions on TiO_2 is, of course, accompanied by a corresponding oxidation process at the TiO_2.

Simultaneous studies of the photocatalytic reduction of Pd^+ and of the electrochemical properties of 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 TiO_2 films on conducting substrates (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 TiO_2 was interpreted on the basis of the photovoltaic effect of the semiconducting 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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