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Synergism in the Hydrogenation of *p*-Nitrophenol on Platinised WO_3

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Summary WO_3 has been shown to exhibit a synergistic effect with Pt for the hydrogenation of *p*-nitrophenol in acid solution at 80 °C.

HOBBS and Tseung[1,2,3] have shown the existence of synergism in the electrochemical oxidation of hydrogen on platinised WO_3 electrodes. Their conclusions have been challenged by Vertes and Horanyi[4] who also claim that WO_3 is an inactive support for the hydrogenation of *p*-nitrophenol on Pt.[5,6] Hydrogenation catalysed by Pt can be shown as in equations (1) and (2).

$$Pt + H_2 \rightarrow Pt(2H)_{ads} \qquad (1)$$

$$6Pt(H)_{ads} + p\text{-}NO_2C_6H_4OH \rightarrow 6Pt + p\text{-}NH_2C_6H_4OH + 2H_2O \qquad (2)$$

In the presence of H atoms a hydrogen tungsten bronze (H_xWO_3, $0<x<1$) is formed from WO_3[1] which could subsequently react with an organic compound as shown in equations (3) and (4). If the rates of reactions (3) and (4)

$$xPt(H)_{ads} + WO_3 \rightarrow xPt + H_xWO_3 \qquad (3)$$

$$\frac{6}{x}H_xWO_3 + p\text{-}NO_2C_6H_4OH \rightarrow 6WO_3 + p\text{-}NH_2C_6H_4OH + 2H_2O \qquad (4)$$

are comparable with that of (2) then a synergistic effect will be seen.

In designing experiments to test the effect of WO_3 as an active catalyst support, Hobbs and Tseung[4] stress the need for a constant Pt crystallite size and the necessity of ensuring that the reaction is not limited by hydrogen diffusion. We have repeated the experiments of Vertes and Horanyi taking into account these factors, which were not controlled in their earlier work.

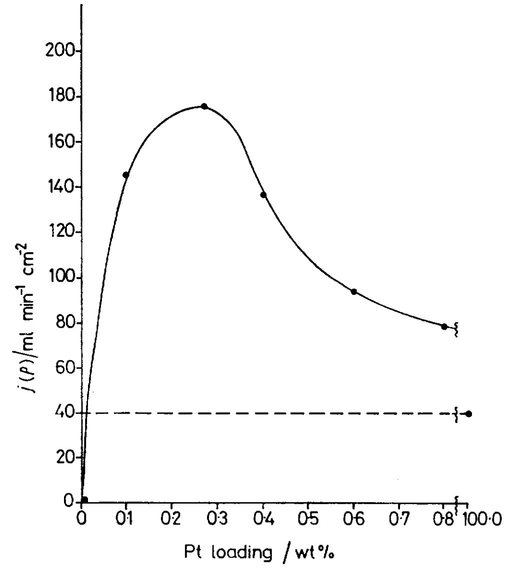

FIGURE. The variation of specific activity, *j*(*P*) with Pt loading for the hydrogenation of *p*-nitrophenol at 80 °C. ---- is theoretical line for an inactive support based on the platinum black result. Total weight catalyst, 50 mg; *p*-nitrophenol, 100 mg; volume of 2N H_2SO_4, 38 cm^3.

The uptake of H_2 was measured at constant pressure in an apparatus similar to that used by Vertes and Horanyi.[6] A 1 wt% Pt on WO_3 catalyst was prepared by freeze-drying.[7] A superior dispersion of Pt on the support is obtained by this technique leading to an increase in the rate of H atom 'spillover' from the Pt to WO_3. In order to maintain constant Pt particle size this catalyst was mechanically mixed with more WO_3 to produce lower Pt loadings (0·8 to 0·1 wt%). We consider this to be of great importance to the validity of the experimental approach. Pt dispersed on WO_3 by freeze-drying has a specific surface area of 35 $m^2 g^{-1}$,[1] which may be compared to a surface area for platinum black of 20 $m^2 g^{-1}$.[1] In all experiments on supported platinum a constant weight of 50 mg of catalyst was used. The weight of Pt black used was 1 mg. The catalyst was equilibrated with hydrogen in the apparatus before addition of a solution of the organic compound. Experiments were performed to determine the optimum volume of sulphuric acid and to ensure that diffusion of hydrogen to the catalyst was not a controlling factor. Pure WO_3 does not react with H_2[1] and, in agreement with Vertes and Horanyi,[6] we found no activity towards hydrogenation of *p*-nitrophenol. The rate of hydrogenation on Pt black was also measured.

In comparison with the electrochemical studies[2] we define specific activity, $j(P)$, as shown in equation (5), where

$$j(P) = r_0/W(P) \qquad (5)$$

r_0 is the initial rate of uptake of hydrogen expressed in $cm^2 H_2 min^{-1}$ and $W(P)$ is the platinum loading expressed as the surface area of platinum (m^2).

The Figure shows a plot of $j(P)$ against Pt loading. The absence of a synergistic effect would be revealed by a constant $j(P)$. The results obtained, $j(P)$ increasing with decreasing loading, may be interpreted as the effect of an active support. The appearance of a maximum or plateau in the curve near 0·2 wt% platinum may indicate that the diffusion of H atoms across particles of WO_3 is rate-limiting, thus allowing no further increase in activity. The result on Pt black is difficult to interpret owing to the different method of preparation, but the low specific activity is in accord with the trend shown by the Pt on WO_3 catalysts.

We conclude that platinised WO_3 shows a synergistic effect for the hydrogenation of *p*-nitrophenol in sulphuric acid at 80 °C. This agrees with previous results on the electrochemical oxidation of H_2 by Pt–WO_3.

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