EXPERIMENTAL VALIDATION OF A THEORETICAL ANALYSIS OF THE RANGE OF OPERATION OF CATALYST POISONS

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A formula to calculate the *minimum* quantity of material necessary to poison or promote a supported metal catalyst, based on theoretical criteria of poisoning range, has recently been proposed (R.W. Joyner and J.B. Pendry, Catal. Lett. 1 (1988) 1). This paper reports experimental tests of this formula for chlorine, sulphur and iodine poisoning of a Pd/C catalyst for the hydrogenation of cyclohexene. For chlorine and sulphur a significant excess of poison is required compared to the estimate, while the results for iodine are in excellent agreement with the calculation. The theory is also compared with a number of literature studies of sulphur poisoning and appears to have wide validity.

1. Introduction

The extent to which an adsorbate influences the properties of a surrounding surface is a topic of considerable current interest. A number of theoretical studies have indicated that, on metal surfaces, adsorbates exert only a short range influence, which does normally not exceed 5 Å, (0.5 nm), (ref. [1]). We have recently published a theoretical study where the range of poisoning is derived from consideration of the local density of electronic states, giving a reasonable account of the suppression of CO chemisorption on Ni(100) by a number of poisons, [2].

It is clearly of interest, and possibly of technological importance, to relate these theoretical studies to practical problems of poisoning and promotion in heterogeneous catalysis. In a recent paper, [3], we have shown how this may be done, using a very simple equation. For a supported metal catalyst, the minimum quantity of poison or promoter required is given by:-

$$\text{Concentration/ppm} = L \cdot A \cdot D \cdot P \cdot W_p/(W_m \cdot R^2) \quad (1)$$

where L is the metal loading, in weight %;
A is the area of surface occupied per metal atom, in Å^2;

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D is the % dispersion of the catalyst;
P is the percentage loss of catalytic activity;
R is the range of operation of the poison or promoter, in Å;
and W_m and W_p are respectively the molecular weights of the metal and the poison/promoter species.

L, D, P, W_p and W_m are readily available and values of A and R are given in [3], so that the concentration of poison or promoter can easily be calculated. In deriving eq. (1), it is assumed that all of the promoter or poison is located at the surface of the active metal and not on the catalyst support. The result is therefore an estimate of the *minimum* quantity of material which is required, since poison or promoter on the support will not influence the activity of the metal, [4]. We refer to eq. (1) as the JP equation.

This paper describes experimental tests of the JP equation for a number of poisons on a commercially available palladium/carbon catalyst, employing a very simple test reaction, the hydrogenation of cyclohexene:

$$C_6H_{10} + H_2 \rightarrow C_6H_{12} \quad (2)$$

Since sulphur poisoning is most commonly studied, [5], we also discuss the application of eq. (1) to published results for a number of sulphur compounds.

2. Experimental

The catalyst used for all of the experiments described here was a 5% by weight palladium on activated carbon formulation, supplied by Ventron, Karlsruhe, FRG. The palladium dispersion, determined by carbon monoxide chemisorption at room temperature, was 17%. Sulphur was impregnated onto samples of the catalyst from a solution of thiophene in cyclohexane. Chlorine was introduced both from adsorption from an aqueous solution of ammonium chloride and by impregnation from a similar solution to achieve higher concentrations of poison. Iodine was added to the catalyst by adsorption from a solution of methyl iodide in methanol. Analysis of the iodine content of the solution before and after exposure to the catalyst, by standard thiosulphate titration techniques, showed that the iodide was irreversibly adsorbed by the catalysts at 298 K. All of the poisons used were BDH reagent grade.

The hydrogenation of analytical reagent grade cyclohexene was studied in the liquid phase. The catalyst samples were pre-reduced at 470 K in flowing hydrogen for ten hours prior to use and transferred to a multi-neck flask containing 75 ml of cyclohexene, which was held in a water bath at 333 ± 1 K. Hydrogen from a cylinder, (BOC), was bubbled through the liquid at ca 60 ml mn^{-1}. Samples were withdrawn from the liquid using a syringe, and aliquots, (0.2 micro litre) were analysed by gas chromatography, (Pye-Unicam 104), with a 3 m column containing 15%CW-20M on Emeacel, (100–120 mesh), at 353 K and flame ionisation detector, at 432 K.

3. Results

The activity of the unpoisoned catalyst for cyclohexene hydrogenation was studied first. The reaction is slow at 333 K and percentage conversion per hour was therefore used as a measure of catalytic activity. The mean of several runs was $5.8 \pm 0.3\%\ h^{-1}$. The activities of a number of poisoned catalysts were

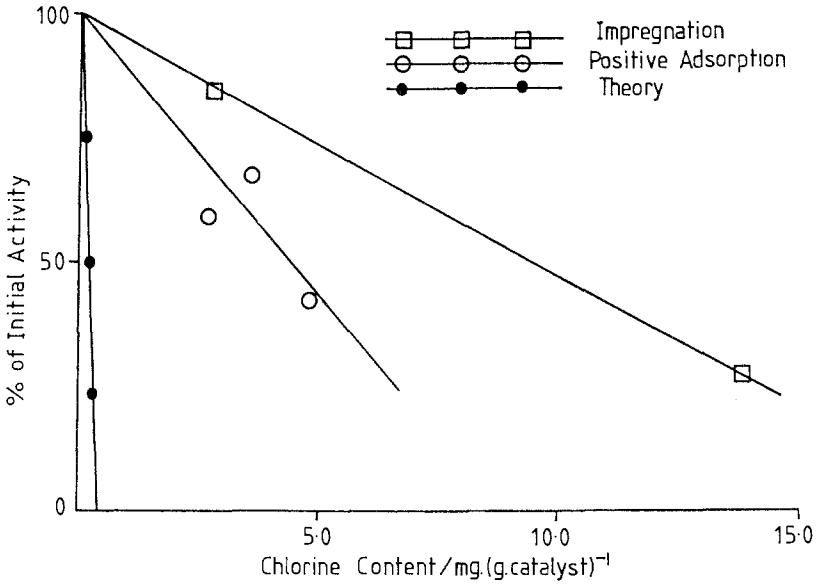

Fig. 1. Poisoning of cyclohexene hydrogenation activity by chlorine.

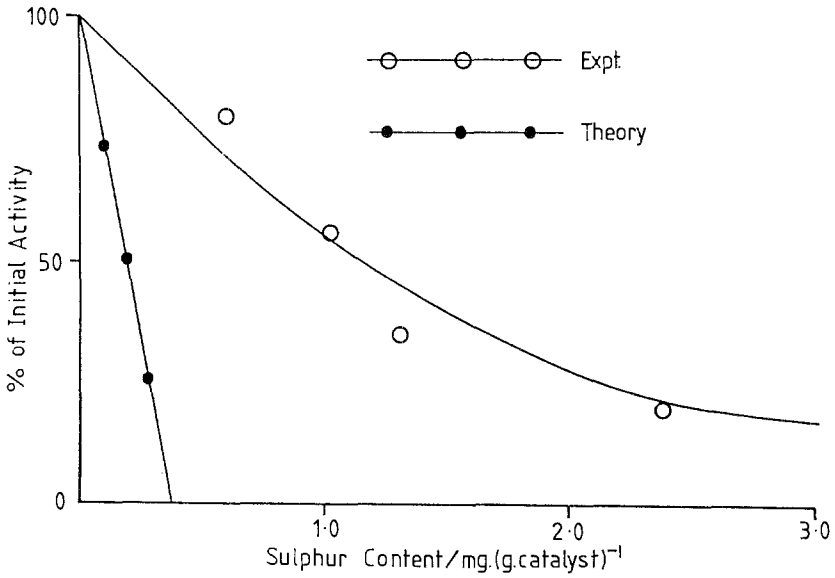

Fig. 2. Poisoning of cyclohexene hydrogenation activity by sulphur.

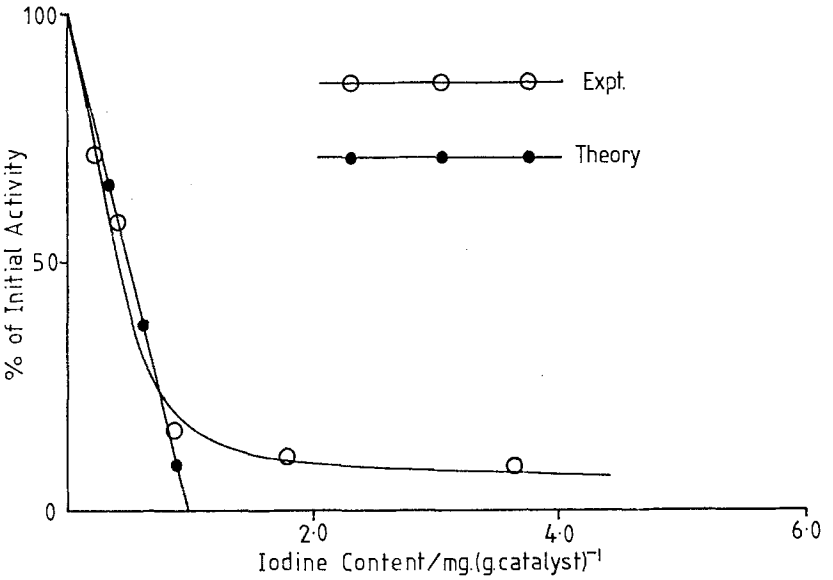

Fig. 3. Poisoning of cyclohexene hydrogenation activity by iodine.

measured and expressed in the same way and the results for the three poisons studied are shown in figs. 1–3, respectively for chlorine, sulphur and iodine.

4. Discussion

4.1. PRESENT RESULTS

Figures 1–3 show, as well as the experimental results, estimates of the minimum necessary quantity of poison calculated from eq. (1). The dispersion of the catalyst is 17% and other required quantities are taken from [2]. In all cases, we have used the 'preferred poisoning range' from this reference and it can readily be seen that quantity of poison required is more than the minimum calculated. For chlorine, poisoning is about an order of magnitude less effective than suggested by the JP equation and, in the spirit of our earlier analysis, this must imply that much of the poison is located on the carbon support rather than at the surface of the palladium. It is of interest to note that, for chlorine, adsorption and impregnation of the poison have different degrees of effectiveness. As might be expected, adsorption is the more effective, suggesting some selectivity for the metal rather than the support. Sulphur is also a less effective poison than implied by the JP equation, although the discrepancy is now only a factor of five.

The results of most interest are for iodine and are shown in fig. 3. Here it has been possible to introduce all of the poison by adsorption from solution and it noteworthy that there is excellent agreement between theory and experiment up

to ca 85% deactivation. We take this to mean that, in these circumstances virtually all of the poison is adsorbed on the palladium surface, and that the JP equation is well obeyed. Above 85% deactivation, poisoning is less effective than predicted by the JP equation. Again we note that, since the JP treatment predicts only minimum levels of poison, the theory is not violated. It is interesting to ask, however, why adding poison has little significant influence on reactivity above a loading of ca 1 mg g^{-1} catalyst, and we note that Goodman et al have observed a similar situation in sulphur poisoning of the menthantation reaction, [6]. It is possible that 15% of the metal surface is unpoisoned, due to imperfect packing of relatively large poison atoms; alternatively it may be that the poisoned surface retains a low level of residual activity for cyclohexene hydrogenation. Further work is needed to address this point.

4.2. OTHER POISONING STUDIES

Since the JP equation gives a reasonable account of the poisoning experiments reported above, it is clearly of interest to see how successful it is in accounting for other studies in the literature. Figure 4 shows a number of results taken from a recent study of Smith et al., [7] on the poisoning by carbon disulphide of the hydrogenation of (+)-apopinene, using a number of palladium and platinum catalysts supported on silica. Smith et al express the relative rate of hydrogenation as a function of adsorbed poison molecules per exposed metal atom. This can readily be related to eq. (1), and fig. 4 also shows our theoretical result, calculated from the JP equation. It has been assumed that the adsorption of

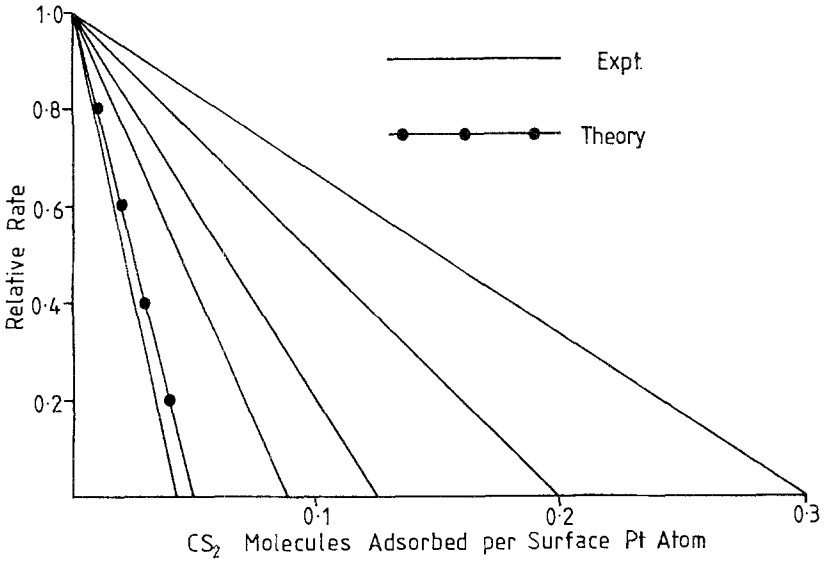

Fig. 4. Comparison of the results of Smith et al., [7], for hydrogenation poisoning by CS_2, with the prediction of the Joyner-Pendry equation.

Table 1

Poison	Quantity required for 90% deactivation / molecules. (g catalyst)$^{-1}$	
	Observed	Calculated
CS_2	1.5×10^{18}	1.1×10^{17}
COS	1.5×10^{18}	1.2×10^{17}
C_4H_4S *	5.4×10^{18}	2.2×10^{17}
H_2S	6×10^{18}	2.2×10^{17}

* Values for 50% deactivation.

carbon disulphide as dissociative, as has been demonstrated by Saleh, [8]. Again it can be seen that the result from the JP equation is in excellent agreement with the observed minimum effective amount of CS_2 poison.

This success of the JP equation casts doubt on the explanation of the results offered by Smith et al., namely that both CS_2 adsorption and hydrogen dissociation occur at edge sites of the precious metal particles. It seems more probable that the whole metal surface is active in hydrogenation, and that carbon disulphide is a much more effective poison than these workers realised.

Tejuca and Turkevich, [9], have also studied carbon disulphide as a poison for hydrogenation reactions, and also examined a number of sulphur containing poisons. The activity of a Pt/Al_2O_3 catalyst for ethene hydrogenation decayed linearly with increasing quantities of adsorbed CS_2, COS and H_2S. The quantities of poison required for 90% deactivation are given in table 1, where they are compared with the results of calculations based on the JP equation. In each case, at least a ten-fold excess of poison, over and above that given by the JP equation, seems to be required.

The effectiveness of sulphur poisoning for the methanation reaction has been extensively studied on supported nickel catalysts by Bartholomew et al., [10], and by Katzer et al., [11]. In these experiments sulphur has been introduced to the catalyst as hydrogen sulphide in the feed gas. This method has the disadvantage that only an upper limit of the poison present may be deduced, since not all of the H_2S need be adsorbed by the catalyst. Katzer et al. report the deactivation of a Ni/Al_2O_3 catalyst when the H_2S concentration in the synthesis gas feed is 13×10^{-9} parts, (13 ppb, American units) and show that, during the early stages of reaction, all of the sulphur is adsorbed by the catalyst. The methane synthesis rate appears to decrease by an order of magnitude, (ie 90% loss in activity) in about 200 minutes on stream. The nickel area of the catalyst studied was ca 30 cm^2, so that, from the Joyner-Pendry criteria, the number of sulphur atoms required for 90% deactivation is 3.4×10^{15}. This compares very well with the number of H_2S molecules fed to the catalyst in this time, which we calculate to be 6.4×10^{15}. In each of the cases discussed the JP equation appears to underestimate slightly the quantity of sulphur poison required. Perhaps a more accurate estimate of sulphur poisoning range would be 3.5 Å, rather than the figure of 5 Å

given in ref. [3], and this would still accord well with our earlier theoretical studies [2].

5. Conclusions

The previously proposed Joyner-Pendry equation, which allows calculation of the minimum quantity of material required to poison a supported metal catalyst has been tested for a number of poisons deliberately added to a supported palladium catalyst. Sulphur and chlorine are significantly less easily poisoned than calculated from the JP equation, while good agreement was obtained for iodine. The JP equation has also been applied to a number of literature studies of sulphur poisoning and has been shown to have excellent general validity.

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