821. *The Reversibility of the Adsorption of Catalyst Poisons. Part I. The Revival of Poisoned Catalysts by Simple Washing.*

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The desorption of thiophen, methyl sulphide, and mercury and zinc ions from a platinum catalyst has been examined by treating poisoned catalysts with various changes of a washing liquid, and it has been found possible completely to remove the poison. Similar results were obtained for the desorption of thiophen from a nickel surface, complete removal being, however, reached with somewhat greater difficulty than with platinum. With cadmium ions on nickel, although a considerable recovery in the activity of the poisoned catalyst was observed, complete re-activation was not reached in the present work. This washing method constitutes an alternative to the revival of a poisoned catalyst by changing the state of an adsorbed poison into a shielded form, as studied in previous work, and is of interest both from the standpoint of its simplicity and since metallic poisons cannot be dealt with by chemical detoxication.

If a dilute solution of a catalyst poison is allowed to remain in contact with a limited amount of a catalyst, a partition of the poison between the adsorbed and the free phase occurs in such a way as to suggest an adsorption–desorption equilibrium even with strong poisons. Little is known, however, as to the rate at which this equilibrium state can be approached from the desorption side with, for instance, poisons such as sulphur compounds or toxic metal ions on platinum or nickel hydrogenation catalysts: indeed, the adsorption of these and other types of strong poisons is sometimes considered to constitute cases of catalyst poisoning which are in practice substantially irreversible, at any rate at room temperature.

As an approach to measurements of the order of the length of the mean adsorbed lives of typical poisons, it was considered of interest to examine the ease with which these can be removed from platinum or nickel surfaces by repeated dilution of the liquid phase, namely, by simple washing of the poisoned surface with a suitable solvent. This is of some practical importance since, if desorption can be obtained easily and rapidly, it should be possible in this way to revive a poisoned catalyst; and this simple washing method should form a useful alternative to the revivification of a poisoned catalyst by chemical detoxication, *i.e.*, by changing the state of the adsorbed poison from a so-called non-shielded to a shielded state (Maxted *et al.*, *J.*, 1940, 252; 1945, 204, 763, 766; 1946, 23; 1947, 624; 1948, 1091, 1093, 1916; *J. Soc. Chem. Ind.*, 1948, **67**, 93; *Chem. and Ind.*, 1951, 242). The desorption method, moreover, is applicable for the removal of metallic poisons, which cannot be detoxicated by chemical treatment.

Experimental

The platinum catalyst used was made from chloroplatinic acid by alkaline formate reduction, the final stages in the washing being carried out by vigorously shaking the stock of catalyst with repeated changes of water until the activity had become constant. For the work with nickel, a stock of Raney nickel was prepared by Covert and Adkins's method (*J. Amer. Chem. Soc.*, 1932, **54**, 4116), modified by the use of water saturated with hydrogen for the washing in order to minimise any oxidation.

The hydrogenation tests, by means of which the restoration of the activity of poisoned

catalysts as a result of the revivification treatment was studied, were carried out in a hydrogenation shaker operated under standardised conditions in a thermostat at 30°. *cyclo*Hexene, in acetic acid solution, was used as a standard unsaturated substance in the hydrogenation runs with platinum. This was also employed, in alcoholic solution, in the tests on the degree of revivification of nickel poisoned with thiophen. In the corresponding tests of the poisoning of nickel with cadmium ions, crotonic acid in aqueous alcohol was taken.

Revivification of Platinum Poisoned by Sulphur Compounds.—(i) *Desorption of thiophen.* The revival of platinum poisoned with thiophen is shown in Fig. 1, in which the hydrogen absorbed is plotted against the time. Curve I relates to a blank run, with an unpoisoned catalyst, the system hydrogenated consisting of 0·025 g. of stock platinum black and 1 c.c. of *cyclo*hexene, dissolved in 9 c.c. of acetic acid. Curve II shows the corresponding hydrogenation of a similar system containing 10^{-5} g.-mol. of thiophen. For the hydrogenation test shown in Curve III, 0·025 g. of platinum was first poisoned with the same amount of thiophen as in Curve II, in 10 c.c. of acetic acid, and shaken for 15 minutes in a closed pipette (in the absence of

FIG. 1. *Removal of thiophen from platinum.*

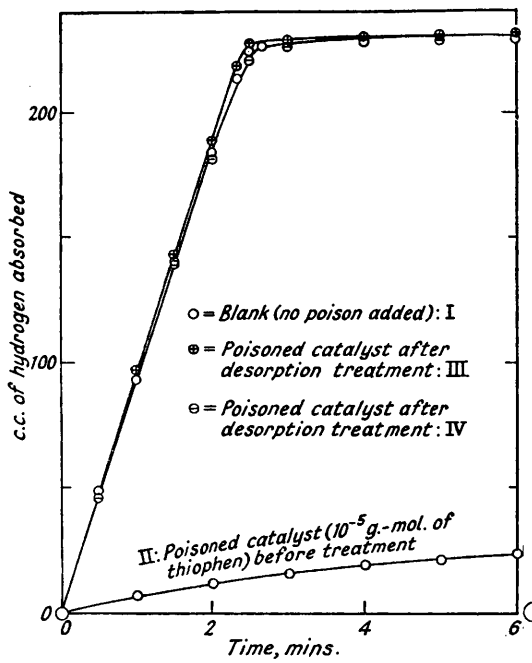
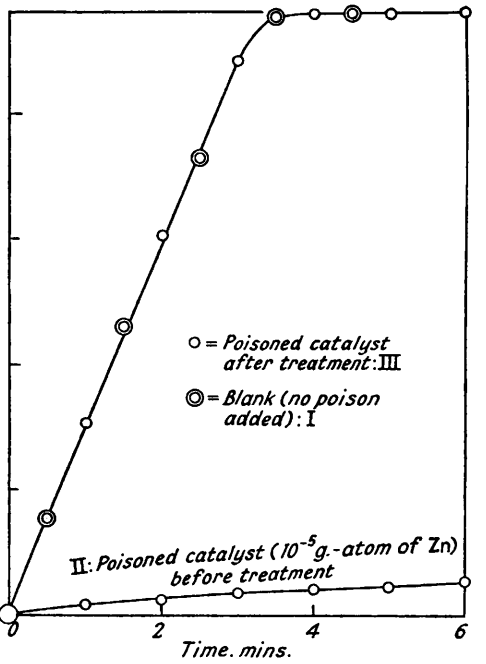


FIG. 2. *Removal of zinc ions from platinum.*

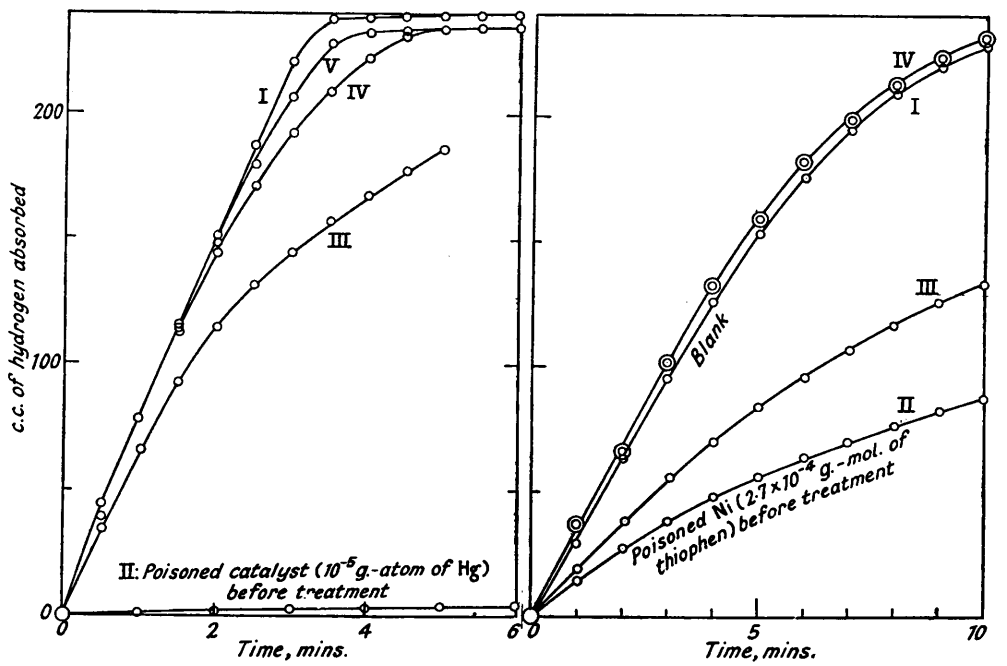


hydrogen) to allow the adsorption of the poison. The solvent was then removed from the poisoned catalyst by centrifuging and decanting, after which the catalyst was washed at room temperature by shaking for 15 minutes with a fresh charge of 10 c.c. of acetic acid in order to try to remove poison from the adsorbed state into the free liquid phase. The supernatant liquid was again removed by centrifuging and decantation as before, and, finally, a charge of 10 c.c. of acetic acid containing 1 c.c. of *cyclo*hexene was added (when presumably more of the poison would move from the adsorbed into the liquid phase) and the activity of the platinum was tested by hydrogenation. The liquid over the poisoned catalyst had thus been changed twice, namely first from the original poisoning solution to a fresh charge of acetic acid and, secondly, from this to the hydrogenation charge. Curve IV shows a similar run, in which only one change of liquid (from the poisoning solution to the hydrogenation charge) was applied. It will be seen from the figure that both of these runs are substantially identical with the blank run; indeed, the thiophen has been almost completely desorbed from the catalyst by one wash. However, the degree of dilution after each centrifuging, namely, the dilution of the small amount of residual liquid still adhering to the 0·025 g. of platinum black to the normal volume of 10 c.c., is of course rather great even for a single change of liquid. This relatively easy removal of thiophen by a single wash should be compared with the desorption of mercury ions (Fig. 3) which are only partly

desorbed by one change of liquid and seem to be bound more strongly to platinum than thiophen and to have a longer adsorbed life.

A further point was also examined with regard to thiophen. Since, in the above treatment, the system had been shaken either once or twice in the absence of hydrogen, it was necessary to make sure that the disappearance of poisoning was not due to the rather unlikely oxidation of the poison on platinum by traces of air during the shaking. To this end, a poisoned charge as in Curve II was shaken in air for two periods of 15 minutes, with centrifuging between and after the two treatments with air but without at any time changing the liquid, *i.e.*, without extraction of the poison, after which the activity of the catalyst was tested by hydrogenation. The hydrogenation curve was still substantially identical with Curve II, indicating that no poison had been removed by oxidation.

FIG. 3. *Removal of mercury ions from platinum.* FIG. 4. *Removal of thiophen from nickel.*



(ii) *Desorption of methyl sulphide.* A set of runs, similar to those of Fig. 1, was carried out with 0·025 g. of platinum poisoned with 4×10^{-6} g.-mol. of methyl sulphide in place of thiophen. Complete re-activation of the catalyst was obtained by changing the liquid above the poisoned platinum twice, with shaking and centrifuging as already described; indeed, as for thiophen, a nearly complete desorption of the poison was reached even after only one change. In the case of methyl sulphide, a little detoxication by oxidation in the presence of the platinum could be detected after shaking the poisoned system with air, but without any change of liquid up to and including the final hydrogenation. In this respect, methyl sulphide differs from thiophen, which cannot be oxidised directly by air at room temperature.

Revivification of Platinum Poisoned by Toxic Metals.—(i) *Desorption of zinc ions.* The hydrogenation system used in this series of tests contained 0·025 g. of stock platinum catalyst, as before, together with a 10-c.c. charge of liquid containing 1 c.c. of *cyclo*hexene, 8·5 c.c. of acetic acid, and 10^{-5} g.-mol. of zinc acetate dissolved in 0·5 c.c. of water. This amount of poison was sufficient to reduce the activity of the platinum to a low value (Curve II of Fig. 2) relative to that given in the blank run (Curve I), in which the poison was omitted. In the hydrogenation test shown in Curve III, the poisoned catalyst, after having been used for Curve II, was separated by centrifuging and washed for 15 minutes at room temperature with 10 c.c. of water, which was then removed by centrifuging, following which a fresh hydrogenation charge of 8·5 c.c. of acetic acid, 0·5 c.c. of water, and 1 c.c. of *cyclo*hexene was added for the hydrogenation test. It will be seen that the original activity of the previously poisoned catalyst has been completely

restored, although this catalyst had already been used for Curve II; indeed, in a further test with another specimen of a similarly poisoned catalyst, an almost complete extraction of the poison was reached even with one change of supernatant liquid. With this poison there is, of course, no question of detoxication by oxidation.

(ii) *Desorption of mercury ions.* The system used was identical with that employed for zinc, save that the catalyst was poisoned with 10^{-5} g.-atom of mercury, applied as the acetate. Curves I and II of Fig. 3 refer, as before, respectively to a blank run and to a poisoned run before any washing treatment. It will be seen from the very low hydrogenation rate of Curve II that mercury ions are more toxic to platinum than the same amount of zinc (cf. Curve II of Fig. 2). The progressive revival of the catalyst by desorption of the mercury ions, as a result of one, two, and three replacements of the supernatant liquid as previously described, is shown respectively in Curves III, IV, and V of Fig. 3, water being used as the washing liquid. The slower desorption rate of this poison, *i.e.*, the longer adsorbed life on the platinum compared with that of thiophen or zinc, was indicated by a lesser degree of response to a single change in the solvent over the poisoned catalyst. The slowness of the removal of the last traces of the poison was further confirmed by two parallel runs, in the second of which the time of shaking with two changes of solvent was increased from the normal period of 15 minutes to 30 minutes for each wash. The slight but consistent benefit in employing a longer washing time is shown in the two hydrogenation runs given in Table 1, which refers in each case to 0·025 g. of platinum poisoned with 10^{-5} g.-atom of mercury.

TABLE 1.

	Hydrogen adsorption (c.c.) with 0·025 g. of poisoned platinum	
Time (mins.)	After 2 washes of 15 mins. each	After 2 washes of 30 mins. each
1	77·0	78·4
2	144·2	148·8
3	191·7	205·3
4	221·3	231·4
5	232·7 (satd.)	232·3 (satd.)

Revivification of Poisoned Nickel.—Work with nickel is less accurate than with platinum, since charges of the catalyst cannot be weighed out as required on account of the oxidisability of the finely-divided metal in a dry state. Approximately uniform amounts were, however, measured out from a paste of Raney nickel stored under alcohol, by means of a small glass bucket attached to a glass dipping rod and having a capacity of about 0·5 g. of nickel for each test. The individual charges of nickel, after being poisoned, were protected from oxidation during the subsequent treatment for the desorption of the poison by using a closed extraction and centrifuging vessel provided with a tap through which the vessel could be evacuated and the air replaced by hydrogen, the unsaturated substance being added only immediately before the hydrogenation run. It was shown, by testing, that the activity of the nickel was not appreciably affected by this shaking and centrifuging unless the liquid was changed to remove adsorbed poison.

(i) *Desorption of thiophen from nickel.* The hydrogenation charge in this series consisted of 0·5 g. of nickel, poisoned by $2·7 \times 10^{-4}$ g.-mol. of thiophen in 11 c.c. of alcohol, 1 c.c. of *cyclo*hexene as before being used as the unsaturated substance. Curves I and II of Fig. 4 show, respectively, a blank hydrogenation run in which the poison had been omitted and a poisoned run in the presence of the above amount of thiophen. In any subsequent treatment of poisoned catalysts, 12 c.c. of water, which had previously been saturated with hydrogen to avoid oxidation of the nickel, were used as the washing liquid. Curve III was given by a catalyst which, after having been poisoned with $2·7 \times 10^{-4}$ g.-mol. of thiophen, had been subjected to two washes of one hour each, with centrifuging as before between each change of liquid. Since the poison was obviously being desorbed from the nickel with greater difficulty than from platinum (cf. Fig. 1), a fresh charge of nickel was first poisoned with thiophen as in Run II of Fig. 4 and then given a more extended washing treatment consisting of four successive washes of 1, 14, 1, and 1 hour respectively. It will be seen from Curve IV that this treatment completely removed the poison. Actually, the activity of the washed catalyst was a little above that in the blank run, but this was probably due to the above-mentioned slight uncertainty in measuring out precisely the same amount of nickel for each hydrogenation run.

(ii) *Desorption of cadmium ions from nickel.* It had been found in previous work that cadmium ions were poisonous towards nickel, sulphate ions being non-toxic, and this metal was accordingly applied as the sulphate. The 12-c.c. hydrogenation charge used in this series con-

sisted of 7 c.c. of water containing 5×10^{-4} g.-mol. of cadmium sulphate, 5 c.c. of alcohol containing 0·01 mole (0·86 g.) of purified crotonic acid, and 0·5 g. of the Raney nickel. Water, previously freed from dissolved air, was used as the washing liquid for the subsequent desorption of the adsorbed cadmium ions from the catalyst. In order to examine the response of the poisoned catalyst to the washing treatment, the usual succession of hydrogenation tests was carried out, namely, first a blank run in the absence of the poison, secondly, a poisoned run in the presence of the above amount of cadmium and, finally, a series of tests with catalysts which, after having been poisoned, had been subjected to various degrees of washing with successive 12-c.c. charges of water. The results of these hydrogenation tests are summarised in Table 2, in which the volume of hydrogen absorbed during an initial 5 minutes period in each test is given as an approximate indication of the activity.

TABLE 2.

State of catalyst	C.c. of hydrogen absorbed (5 min.)
Unpoisoned catalyst (blank run)	116
Catalyst poisoned with 5×10^{-4} g.-atom of Cd^{2+}	32
Poisoned catalyst after 2 washes of 1 hr. each	64
Poisoned catalyst after 3 washes of 2 hrs. each	72
Poisoned catalyst after 4 washes of 1, 14, 1, and 1 hr. each, respectively	76

It will be seen that, although a progressive improvement in the activity of the poisoned catalyst was obtained as the number and length of the washes was increased, a complete restoration to the original activity was not reached for cadmium on nickel. This may, however, have been due to some slight oxidation of the Raney nickel during the prolonged washing treatment.

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