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The Inhibition of Hydrocarbon Oxidation over Supported Precious Metal Catalysts

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Supported palladium and platinum catalysts suffer a decrease in their activity with respect to hydrocarbon oxidation when they are exposed to halogenated hydrocarbons or to organosiloxanes. With halogen compounds, the deactivating effect depends markedly on temperature. However, in the range 625–730 K, the resulting loss in activity increases with the number of chlorine atoms in the molecule; moreover, bromine is a more effective inhibitor than chlorine. Platinum catalysts are more resistant to poisoning than palladium catalysts. The extents of deactivation and of subsequent recovery of catalytic activity are more pronounced at high temperatures and when there is strong interaction between the precious metal and the support. Generally similar behavior is observed when hexamethyldisiloxane is passed over powdered catalysts at a temperature of 650 K. However, this compound causes total and almost irreversible poisoning of catalytic beads for methane oxidation but has a much smaller effect on the activity with respect to butane oxidation. Physicochemical studies of the poisoned catalysts suggest that the halogenated hydrocarbons act as inhibitors as a result of their preferential adsorption on sites normally required for the activation and adsorption of oxygen, whereas the organosilicon compound functions by virtue of the penetration of silicon atoms into the precious metal and the consequent physical blocking of active sites on the catalyst surface.

INTRODUCTION

Supported palladium and platinum catalysts are used for the total oxidation of hydrocarbons in atmospheric scrubbers, automobile exhausts, and flammable gas detectors. A major limitation imposed on the reliable operation and useful lifetime of such catalysts is their susceptibility to poisoning by a number of types of compound, including in particular halogenated hydrocarbons and organosiloxanes, which cannot readily be removed from the gas stream.

Cullis *et al.* (*1*) found that chloromethanes poisoned a palladium sponge catalyst for methane oxidation. The loss in catalytic activity was attributed to the ability of the adsorbed halogen compounds to form dipoles with the negative charge facing outwards, so that the surface coverage by oxygen ions is decreased. Barnes *et al.* (*2*) studied the effects of some chlorinated and brominated hydrocarbons on palladium and platinum catalysts and found that these compounds were dissociatively adsorbed; the loss in catalytic activity caused by these additives was generally only transient. A similar conclusion was reached by Otto and Montreuil (*3*), who explained the inhibiting effect of two haloethanes in terms of their competitive adsorption on the active catalyst sites.

There is little published work on the influence of organosiloxanes on precious metal oxidation catalysts. Gentry and Jones (*4*) showed, however, that the degree of deactivation caused by an organosiloxane depended on the type of site involved. High-energy sites, such as those required for the oxidation of methane, were rapidly poisoned, while those of low energy, which would bring about the oxidation of hydrogen at low temperatures, were almost unaffected. The chemical fate of the organosiloxanes was not determined.

No study of the poisoning of supported

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precious metal catalysts can be complete if the work is confined to the metal on its own. The complex interactions that occur between the precious metal and its support profoundly affect the reactions taking place on the surface of the catalyst as well as the extent to which such reactions are poisoned. The geometric and electronic structures, the accessibility of the reactants, and the stability and degree of dispersion of the metal are to some extent controlled by the support (*5*). In addition the poison may be adsorbed on the support as well as on the catalyst surface (*6*). In such a case, the catalyst is in an environment different from that which would be expected if the support took no part in the poisoning reaction.

A previous paper (*7*) described a detailed study of the oxidation of methane over palladium and platinum catalysts supported on various refractory metal oxides and special attention was paid to the effects of the supports on the activity of the catalysts. It was shown that, with palladium, the support influenced the ability of the metal to adsorb oxygen and hence to oxidize methane. The rate of oxidation of the hydrocarbon was increased by the use of high surface area supports. The present work involves a study of the deactivation of similar catalysts, with particular reference to the contribution which the support makes towards both the initial loss and the subsequent recovery of catalytic activity.

EXPERIMENTAL

The sources of the precious metal compounds and catalyst supports have already been described (*7*). The surface areas of the supports were γ-aluminium(III) oxide, 45 $m^2\ g^{-1}$, tin(IV) oxide, 12.5 $m^2\ g^{-1}$, titanium(IV) oxide, 6.8 $m^2\ g^{-1}$, thorium(IV) oxide, 2.5 $m^2\ g^{-1}$. Details have already been given of the methods of preparation of the supported catalysts for use in the pulse-flow microreactor system (*7*).

The catalysts were also prepared in the form of microcalorimetric beads using the procedure recommended by Baker and Firth (*8*), the alumina beads were coated with thoria and palladium was deposited on the outer surface, the final Pd:Th weight ratio being approximately 1:20.

Details have also been given elsewhere of the sources and methods of purification of methane, oxygen, nitrogen, and helium (*7*), butane was supplied by Air Products Limited and was condensed and distilled before use. Tetrachloromethane and trichloromethane ("Aristar" grade), dichloromethane ("AnalaR" grade), 1,2-dichloroethane, and dibromomethane were supplied by B.D.H. Limited and were carefully degassed before use. Hexamethyldisiloxane, obtained from Dow Corning Limited, was distilled at low pressure and only the middle fraction was retained.

The apparatus and the gas-handling techniques used have already been fully described (*7*), as have most of the analytical procedures. Auger spectroscopic studies were carried out using a JEOL JAMP-10 Scanning Auger Electron Microscope (*9*, *10*), the very low electron currents used (10^{-10} A) minimized surface damage to the samples. As with X-ray photoelectron spectroscopy, samples were pressed into indium foil before examination.

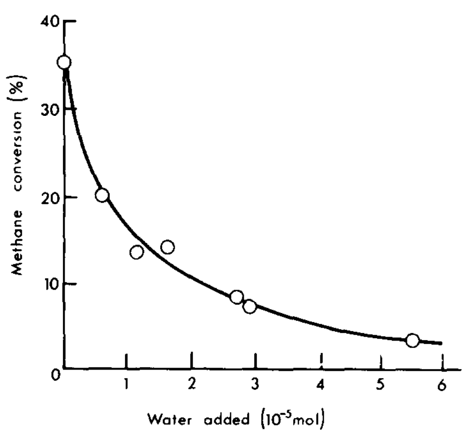

FIG. 1. The effect of water on the activity of an alumina-supported palladium catalyst. Temperature, 625 K, palladium loading, 2.7 wt%, composition of reactant pulse 1.8 × 10^{-6} mol CH_4, 3.6 × 10^{-6} mol O_2.

RESULTS

Effects of Water and Carbon Dioxide

Before studies were carried out of the influence of specific additives, measurements were made of the effects of the normal reaction products, viz H_2O and CO_2, on catalytic activity Relatively large quantities of water inhibit the oxidation of methane, the degree of inhibition increasing with the water content of the reactant pulse (Fig 1) However, amounts of water comparable with those formed by the total oxidation of the methane present were found not to have any appreciable effect on the activity of the catalyst Similar results were obtained with carbon dioxide

Inhibition by Halogenated Hydrocarbons

Small amounts of different inhibitors were mixed with a stoichiometric methane + oxygen pulse before the resulting gas mixture was passed through the catalyst, the initial activity of which had already been determined The decreased catalytic activity was then measured by passage of an inhibitor-free methane + oxygen pulse over the catalyst When the deactivated catalyst was placed in a stream of flowing helium and pulses of methane + oxygen were passed through it, the activity was often at least partially restored, experiments showed that methane-rich mixtures were more effective than oxygen-rich mixtures in promoting recovery of the catalytic activity If the initial activity of the catalyst is A_0, the decreased catalytic activity caused by the inhibitor is A_i and the activity of the subsequently restored catalyst is A_r, the extent of inhibition may be expressed as $(A_0 - A_i)/A_0$ and the extent of its recovery as $(A_r - A_i)/A_0$ Experiments with several halogenated hydrocarbons (Table 1) showed that both the loss of activity and the extent of its restoration depend not only on the nature of the inhibitor but also on the precious metal and the support The most marked loss of catalytic activity was found with trichloromethane and dibromomethane and there was little or no sign of subsequent recovery of activity when the bromine compound was used Palladium catalysts were more susceptible to poisoning than the corresponding platinum cata-

TABLE 1

The Effect of Some Halogenated Hydrocarbons on the Activity of Supported Precious Metal Catalysts[a]

Supported catalyst	Halogenated hydrocarbon	$\frac{A_0 - A_i}{A_0} \times 100$	$\frac{A_r - A_i}{A_0} \times 100$
2 7 wt% Pd on γ-Al_2O_3	$CHCl_3$	90	0
2 7 wt% Pd on γ-Al_2O_3	CH_2Cl_2	70	15
2 7 wt% Pd on γ-Al_2O_3	CH_2ClCH_2Cl	60	25
2 7 wt% Pd on γ-Al_2O_3	CH_2Br_2	70	0
2 7 wt% Pt on γ-Al_2O_3	$CHCl_3$	50	100
2 7 wt% Pt on γ-Al_2O_3	CH_2Br_2	30	0
2 7 wt% Pd on TiO_2	$CHCl_3$	95	25
2 7 wt% Pd on ThO_2	$CHCl_3$	100	5
20 wt% Pd on SnO_2	$CHCl_3$	95	80
20 wt% Pd on SnO_2 + γ-Al_2O_3	$CHCl_3$	70	0
25 wt% Pd on γ-Al_2O_3	$CHCl_3$	90	0
25 wt% Pd on γ-Al_2O_3	CH_2Br_2	75	0

[a] Temperature 650 K, catalyst weight 0 05–0 08 g, composition of each reactant pulse 1 8 × 10^{-6} mol CH_4, 3 6 × 10^{-6} mol O_2 together with 1 4 × 10^{-7} mol halogen compound during deactivation experiments

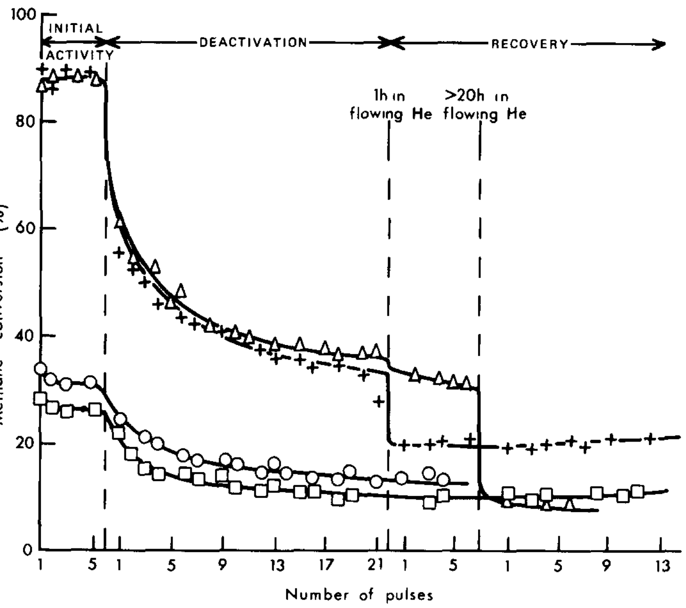

FIG 2 The deactivation of alumina-supported palladium catalysts by halogenated hydrocarbons and the subsequent recovery of catalytic activity Temperature, 650 K, composition of reactant pulse 1 8 × 10^{-6} mol CH_4, 3 6 × 10^{-6} mol O_2, together with 1 4 × 10^{-7} mol halogen compound during deactivation experiments △, CH_2Br_2, 0 064 g 25 wt% Pd on γ-Al_2O_3 catalyst, +, $CHCl_3$, 0 065 g 25 wt% Pd on γ-Al_2O_3 catalyst, ○, CH_2Cl_2, 0 079 g 2 7 wt% Pd on γ-Al_2O_3 catalyst, □, CH_2Br_2, 0 078 g 2 7 wt% Pd on γ-Al_2O_3 catalyst

lysts and those with a high metal loading were just as readily deactivated as catalysts with a relatively low palladium content It was also found that the surface area of the supports had little effect on the ability of the catalysts to resist deactivation

Figure 2 shows the progressive loss of activity of powdered Pd on γ-Al_2O_3 catalysts caused by some halogenated hydrocarbons Both trichloromethane and dibromomethane had comparable effects on catalysts with a relatively high precious metal loading and the same was true for dichloromethane and dibromomethane with a much lower loading of palladium In general the degree of inhibition found with the chlorinated hydrocarbons was dependent on the number of chlorine atoms present in the molecule, viz, $CHCl_3 > CH_2Cl_2 = CH_2ClCH_2Cl$ However, little subsequent recovery of activity was observed with any of the catalysts which had been poisoned by these compounds Although the exposure of fresh catalysts to halogenated hydrocarbons always resulted in an eventual decrease in activity, sufficiently small amounts of dichloromethane (<ca 10^{-7} mol) had an initially well-defined but transient promoting effect (Fig 3)

The action of the catalyst support had a considerable effect not only on the loss of initial activity but also on the subsequent recovery of palladium catalysts (Fig 4) A 20 wt% Pd on SnO_2 catalyst had the highest initial activity in the absence of inhibitors, it also exhibited the most rapid decrease in activity when exposed to trichloromethane and underwent the most pronounced recovery 2 7 wt% Pd on TiO_2 and 2 7 wt% Pd on ThO_2 catalysts both showed almost complete deactivation when exposed to this inhibitor, there was, too, very little subsequent recovery of activity in the latter system A 2 7 wt% Pt on γ-Al_2O_3 catalyst had a lower initial activity than the corresponding palladium catalyst but was never-

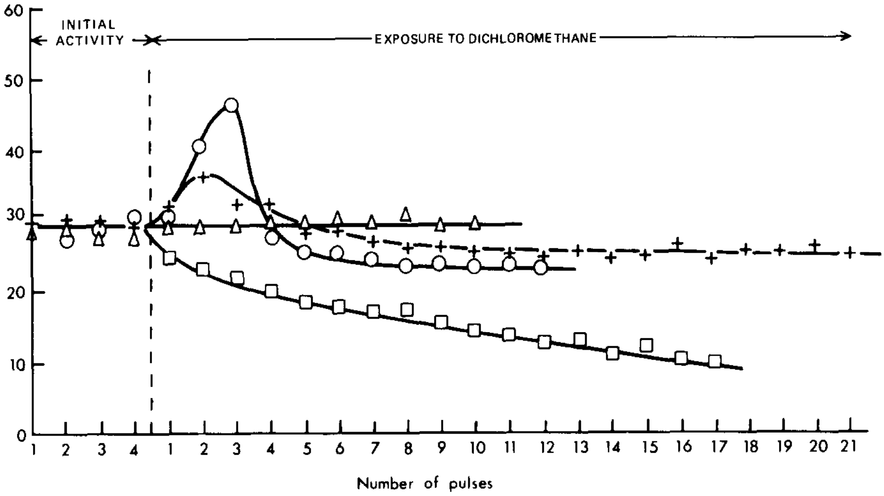

FIG 3 The effect of different concentrations of dichloromethane on the activity of an alumina-supported palladium catalyst Temperature, 650 K, palladium loading, 2 7 wt%, composition of reactant pulse, 1 8 × 10^{-6} mol CH_4, 3 6 × 10^{-6} mol O_2 △, No CH_2Cl_2 (catalyst weight, 0 079 g), +, 1 63 × 10^{-8} mol CH_2Cl_2 (catalyst weight, 0 084 g), ○, 2 72 × 10^{-8} mol CH_2Cl_2 (catalyst weight, 0 042 g), □, 1 36 × 10^{-7} mol CH_2Cl_2 (catalyst weight, 0 070 g)

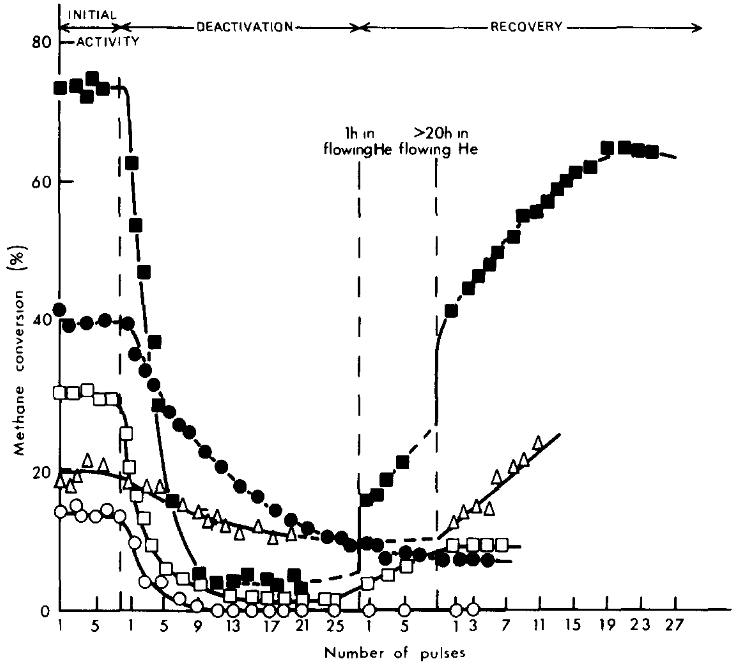

FIG 4 The deactivation of supported precious metal catalysts by trichloromethane and the subsequent recovery of catalytic activity Temperature, 650 K, composition of reactant pulse, 1 8 × 10^{-6} mol CH_4, 3 6 × 10^{-6} mol O_2, and 1 4 × 10^{-7} mol $CHCl_3$ ■, 0 054 g 20 wt% Pd on SnO_2, ●, 0 040 g 2 7 wt% Pd on γ-Al_2O_3, □, 0 058 g 2 7 wt% Pd on TiO_2, △, 0 044 g 2 7 wt% Pt on γ-Al_2O_3, ○, 0 033 g 2 7 wt% Pd on ThO_2

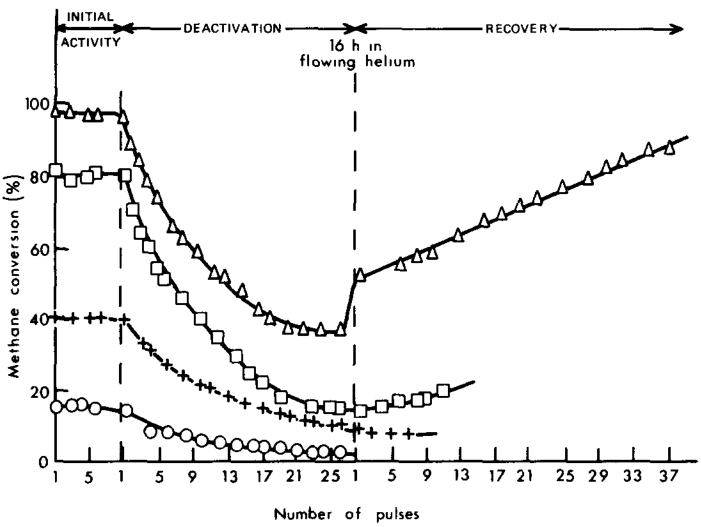

Fig 5 The effect of temperature on the deactivation by trichloromethane and the subsequent recovery of activity of an alumina-supported palladium catalyst Palladium loading, 2 7 wt%, composition of reactant pulse 1 8 × 10^{-6} mol CH_4, 3 6 × 10^{-6} mol O_2, and 1 4 × 10^{-7} mol $CHCl_3$ △, 730 K (catalyst weight, 0 041 g), □, 700 K (catalyst weight, 0 036 g), +, 650 K (catalyst weight, 0 040 g), ○ 625 K (catalyst weight, 0 043 g)

theless poisoned more slowly and, unlike its palladium counterpart, completely regained its activity

Changes in catalytic activity depended also on the temperature In general, the use of a higher temperature raised the initial activity of a given catalyst but also increased the rates of deactivation and of subsequent recovery (Fig 5) Similar behaviour was found when dibromomethane was used as an inhibitor, although with this compound there was little or no subsequent recovery of activity even at the highest temperature studied (730 K)

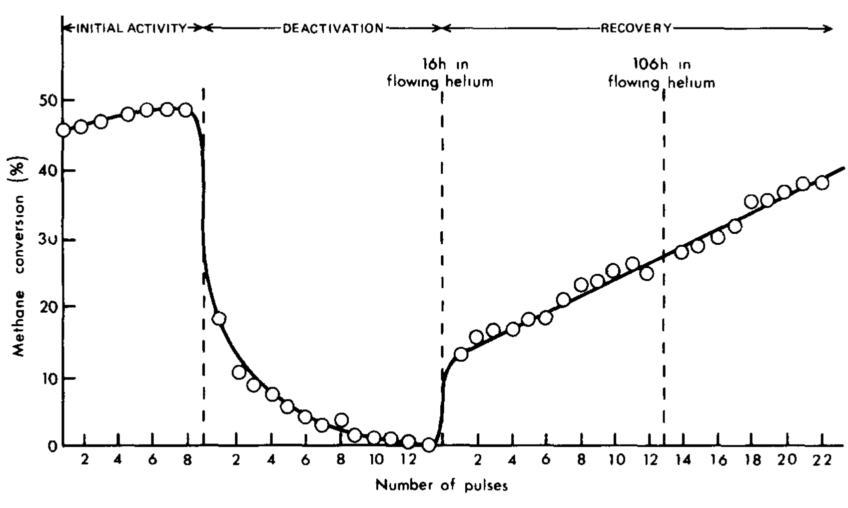

Fig 6 The deactivation of an alumina-supported palladium catalyst by hexamethyldisiloxane and the subsequent recovery of catalytic activity Temperature, 650 K, palladium loading, 2 7 wt%, catalyst weight, 0 038 g, composition of reactant pulse 1 8 × 10^{-6} mol CH_4, 3 6 × 10^{-6} mol O_2, together with 2 2 × 10^{-7} mol hexamethyldisiloxane during deactivation experiments

TABLE 2

The Effect of Hexamethyldisiloxane on the Oxidation of Methane over Catalyst Beads[a]

Concentration of hexamethyldisiloxane (mg m^{-3})	t_{50}[b] (min)	t_{75}[c] (min)	$\frac{A_r - A_i}{A_0} \times 100$ (methane oxidation)	$\frac{A_r - A_i}{A_0} \times 100$ (butane oxidation)
23	5 3	14 0	0	100
113	1 2	2 1	0	50
282	0 4	0 6	0	0

[a] Temperature 800 K

[b] Time taken for activity for methane oxidation to decrease by 50%

[c] Time taken for activity for methane oxidation to decrease by 75%

Inhibition of Hydrocarbon Oxidation by Siloxanes

A powdered 2 7 wt% Pd on γ-Al_2O_3 catalyst rapidly lost its activity when exposed to small amounts of hexamethyldisiloxane (Fig 6), indeed the initial activity was reduced to less than half its value as a result of the passage of the first pulse containing the inhibitor over the catalyst On removal of the siloxane from the gaseous reactant mixture, the activity of the catalyst was significantly restored The shapes of the deactivation and recovery curves were generally similar to those obtained with the halogenated hydrocarbons (Fig 3)

When hexamethyldisiloxane and oxygen on their own were passed over a palladium catalyst, the organosilicon compound decomposed to give methane at temperatures above 500 K, the yield of methane reached a maximum at 630 K but fell almost to zero at 725 K Carbon dioxide was also formed at 625 K, while carbon monoxide became a predominant product above 700 K

Studies were also made of the effect of small concentrations of hexamethyldisiloxane on the rate of hydrocarbon oxidation when the catalyst was in the form of a microcalorimetric bead A minimum of four beads was used for each experiment These were first exposed to a butane + oxygen + nitrogen mixture, usually for 1 hr, in a static reactor (vol 10 dm^3) and then to a methane + oxygen + nitrogen mixture for a similar period of time Measurements were made of the initial activities of the beads with respect to the oxidation of the hydrocarbons Exposure to reactant mixtures containing hexamethyldisiloxane caused a decrease in catalytic activity, the magnitude of which was dependent on the concentration of the inhibitor (Table 2) and was much larger with methane than with butane (Fig 7) Removal of the siloxane and introduction of

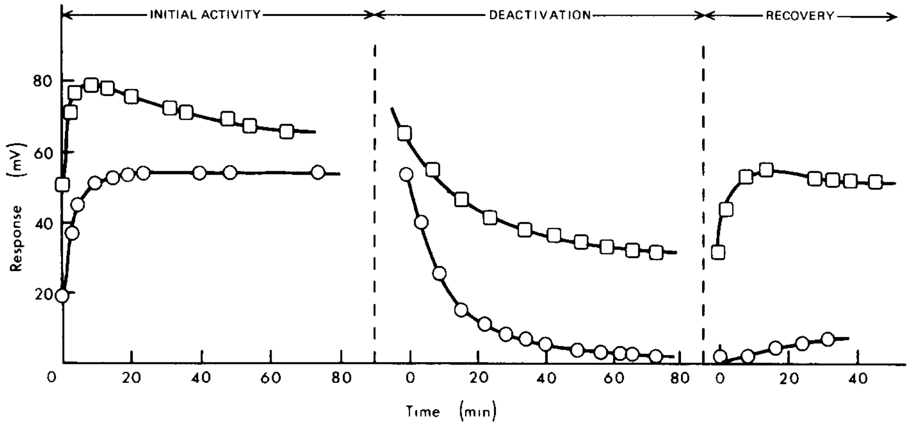

FIG 7 The deactivation of a palladium on thoria + alumina catalytic bead by hexamethyldisiloxane, and the subsequent recovery of catalytic activity Temperature, 800K ○, oxidation of methane (composition of reactant mixture 2 5 mol% CH_4, 20 5 mol% O_2 together with 2 5 × 10^{-4} mol% hexamethyldisiloxane during deactivation experiments, balance N_2) □, Oxidation of butane (composition of reactant mixture 0 75 mol% C_4H_{10}, 20 9 mol% O_2, together with 2 5 × 10^{-4} mol% hexamethyldisiloxane during deactivation experiments, balance N_2)

TABLE 3

The Effect of Halogenated Hydrocarbons on the Particle Size of Some Alumina-Supported Precious Metal Catalysts

Precious metal	Halogenated hydrocarbon	Temperature of exposure of catalyst to inhibitor (K)	Mean precious metal particle diameter (nm)
Pd[a]	—	—	9 6
Pd[b]	—	—	16 1
Pd	$CHCl_3$	580–730	20 1
Pd	$CHCl_3$	625	17 3
Pd	$CHCl_3$	650	19 8
Pd	$CHCl_3$	700	16 7
Pd	$CHCl_3$	730	18 6
Pt[b]	—	—	2 8
Pt	$CHCl_3$	650	3 2
Pt	CH_2Br_2	650	2 8

[a] Catalyst conditioned only

[b] Catalyst conditioned and then exposed to a $CH_4 + 2O_2$ mixture

pure methane + oxygen + nitrogen or butane + oxygen + nitrogen mixtures made it possible to determine the ability of the deactivated catalysts to regain their activity It was found that the catalysts were almost irreversibly poisoned for methane oxidation but that they generally recovered much of their activity with respect to the oxidation of butane (Table 2 and Fig 7)

Physicochemical Studies of Poisoned Catalysts

Transmission electron microscopy Particle sizes were obtained from transmission electron micrographs for catalysts containing palladium and platinum supported on γ-aluminium(III) oxide both before and after they had been exposed to inhibitors

Table 3 shows that the exposure to trichloromethane of a 2 7 wt% Pd on γ-Al_2O_3 catalyst did not result in any significant change in the average diameter of the palladium particles, even over a temperature range of 150 K Nevertheless the number of particles with diameter between 5 and 15 nm appeared to decrease, while there was a corresponding increase in the number in the 25–35 nm range Again no appreciable increase in mean particle size was observed when a 2 7 wt% Pt on γ-Al_2O_3 catalyst was exposed to halomethanes (Table 3)

X-ray photoelectron spectroscopy Supported palladium catalysts, both those which had and had not been exposed to inhibitors, as well as the materials used in their preparation, were examined using X-ray photoelectron spectroscopy with aluminium K_α radiation as the X-ray source Due to the insulating properties of the catalytic materials concerned, charging may occur on the surface of the samples causing shifts in the observed binding energies In order to reduce errors in measurements due to charging, a reference line (the O $1s_{1/2}$ line at 532 0 eV) was used as an internal standard from which other peaks were calculated

Exposure of the catalysts to halogenated hydrocarbons caused some changes in the carbon and palladium binding energies (Table 4) After a 2 7 wt% Pd on γ-Al_2O_3 catalyst had been exposed to dichloromethane, the C $1s_{1/2}$ line broadened and became a doublet The carbon peak at the lower binding energy may be ascribed to carbon–halogen residues, since it was absent before the inhibitor was introduced Samples of catalysts deactivated by dichloromethane were also found to be closer in composition to palladium metal than to the catalytically active palladium(II) oxide, this can be seen from the Pd $3d_{3/2}$ and Pd $3d_{5/2}$ electron binding energies, which lie close to those obtained for palladium metal (Table 4)

Recovery of the activity of Pd on γ-Al_2O_3 catalysts following exposure to pulses of methane + oxygen left the palladium in an oxidation state intermediate between those of the metal and the oxide This was indicated by a shift in the position of the 3d binding energies from those obtained for Pd^0 to those found for Pd^{II} and by a simplification of the C $1s_{1/2}$ signal The first step in recovery appeared to involve reoxidation of the palladium followed by removal of the carbonaceous residue This is shown in Table 4 for a 2 7 wt% Pd on γ-Al_2O_3 catalyst where a 10% recovery of activity was obtained, the palladium had Pd 3d binding en-

TABLE 4

The Effect of Halogenated Hydrocarbons on the Binding Energies

Catalyst	Binding energy (eV)			
	C $1s_{1/2}$	Pd $3d_{5/2}$	Pd $3d_{3/2}$	Cl $2p_{1/2}$, $2p_{3/2}$
Pd	284 5	335 1	340 5	—
PdO	285 5	338 2	343 6	—
2 7 wt% $PdCl_2$ on γ-Al_2O_3	284 9	337 3	342 5	199 3
2 7 wt% Pd on γ-Al_2O_3[a]	284 5	339 9	342 0	—
2 7 wt% Pd on γ-Al_2O_3[b]	283 8) 285 3)	335 5	340 7	199 6
2 7 wt% Pd on γ-Al_2O_3[c]	283 8[k]	337 2	342 4	197 1) 199 5)
2 7 wt% Pd on γ-Al_2O_3[d]	283 8) 285 3)	337 2	342 5	197 8) 200 4)
2 7 wt% Pd on γ-Al_2O_3[e]	283 7) 285 2)	336 9	341 7	—
2 7 wt% Pd on γ-Al_2O_3[f]	283 1) 286 0)	337 7	342 5	—
2 7 wt% Pd on SnO_2[g]	286 3	337 3	342 6	—
20 wt% Pd on SnO_2[h]	286 4	337 9	342 9	—
20 wt% Pd on SnO_2[i]	286 4	338 2	343 4	—
20 wt% Pd on SnO_2 + Al_2O_3[j]	284 8	338 0	342 7	—

[a] Catalyst conditioned and then exposed to CH_4 + O_2

[b] Catalyst after deactivation by CH_2Cl_2

[c] Catalyst after deactivation by CH_2Cl_2 and subsequent recovery

[d] Catalyst after deactivation by CCl_4 and subsequent recovery

[e] As *d* but after argon ion-etching and removal of ca 1 nm surface

[f] Catalyst after deactivation by CH_2Br_2 and 10% recovery

[g] Catalyst treated at 875 K

[h] Catalyst treated at 720 K

[i] Catalyst exposed to pulses containing 1 4 × 10^{-7} $CHCl_3$

[j] As *i* but catalyst activity not restored

[k] Shoulder

ergies typical of those for palladium(II) oxide, while the carbon retained a doublet for the C $1s_{1/2}$ signal A similar Pd on γ-Al_2O_3 catalyst which had been exposed to dichloromethane was subsequently reactivated, at the stage where its activity had recovered almost to the level obtained before inhibition, it had a simple C $1s_{1/2}$ peak at 283 8 eV with only a shoulder at 286 0 eV marking the presence of the other peak (Table 4)

After a 20 wt% Pd on SnO_2 + Al_2O_3 catalyst had been exposed to trichloromethane, the Pd $3d_{3/2}$ and Pd $3d_{5/2}$ binding energies observed were typical of those for palladium(II) oxide before reactivation (Table 4) This was not the case for Pd on γ-Al_2O_3 catalysts where palladium(II) oxide was found only after the activity was restored by means of methane + oxygen pulses and the inhibited catalyst contained only palladium metal

Some indication of the depth to which the inhibitor had penetrated below the surface of the precious metal was obtained by argon ion bombardment This technique involves erosion of the surface layers by ions of sufficient energy to remove successive atomic layers Fine control of the energy and time of bombardment provides a controlled depth of erosion and the exposed surface may then be analyzed The results in Table 4 refer to a 2 7 wt% Pd on γ-Al_2O_3 catalyst, from which ca 1 nm of surface had been removed No chlorine could be detected on the surface after this treatment but carbon was found to be present Inhibition by trichloromethane was thus shown to be a surface reaction only and no penetration of chlorine into the bulk of the palladium was observed

Auger electron spectroscopy Chlorine and bromine were found in catalysts which had been exposed to dichloromethane and dibromomethane respectively (Fig 7) However, whereas bromine was distributed more or less uniformly over the surface, chlorine was localised in a few areas The intensity of the chlorine peak was much lower than that obtained with supported palladium(II) chloride Carbon too was present on the catalyst surface although at 270 eV it was difficult to separate its peak from the Auger peak of palladium at 275–280 eV, its presence could be inferred only from a change in the expected height ratios of the three palladium peaks at ca 240, 275, and 320 eV After passage of a relatively large amount (2 3 × 10^{-5} mol) of dichloromethane through a 2 7 wt% Pd on γ-Al_2O_3 catalyst, carbon was relatively abundant on the surface Auger mapping of the surface of a palladium on γ-aluminium(III) oxide catalyst that had been exposed to trichloromethane revealed that the palladium was concentrated in certain areas Chlorine could be found where palladium was present but oxygen was absent from such areas, showing that the palladium is not in the form of the oxide but is associated with chlorine

The surface of a Pd on SnO_2 catalyst, which had been exposed to hexamethyldisiloxane (20 pulses of 3 × 10^{-9} mol in a methane + oxygen mixture) but which had partially recovered its activity at 650 K, was examined by Auger electron spectroscopy The results in Table 5 show that silicon and carbon were present on the outer surface only and that the removal of ca 1 5 nm of the surface layer by argon ion bombardment left little trace of these elements Included in Table 5 for comparison purposes are the results for a sample of silicon(IV) oxide

TABLE 5

Auger Electron Spectroscopic Analysis of the Surfaces of Powder Catalysts and Catalytic Beads Exposed to Hexamethyldisiloxane in the Presence of Methane + Oxygen Mixtures

Sample	Elements present[a]					
	Sn	O	Pd	C/Th[b]	Si	Al
Powder catalysts						
20 wt% Pd on SnO_2						
As received	0 95	(1 0)	0 16	0 07	0 44	—
After argon ion etching	1 03	(1 0)	0 21	—	0 05	—
SiO_2						
As received	—	(1 0)	—	—	0 14	—
After argon ion etching	—	(1 0)	—	—	0 15	—
Catalytic beads						
Pd on Al_2O_3 + ThO_2						
As received	—	—	0 31	0 55	0 25	0 24
After argon ion etching (15s)	—	—	0 57	0 49	0 22	0 22
After argon ion etching (390s)	—	—	0 27	0 20	0 10	0 36
Pd on SnO_2						
As received	0 46	(1 0)	1 25	0 60	0 15	—
After argon ion etching (15s)	0 61	(1 0)	1 88	—	—	—
After argon ion etching (390s)	0 43	(1 0)	1 23	—	—	—

[a] Peaks normalised to oxygen (1 0)

[b] Carbon and thoria peaks could not be identified separately

Table 5 also shows some results of the examination by Auger electron spectroscopy of catalytic beads that had been exposed to hexamethyldisiloxane, this treatment was found to destroy totally the activity with respect to methane oxidation The Pd on ThO_2 + γ-Al_2O_3 bead also contained silicon on its surface but bombardment with argon ions reduced the silicon and palladium levels The silicon had penetrated below the surface of the bead but its concentration decreased as successive atomic layers were removed Palladium on tin(IV) oxide beads which had been exposed to hexamethyldisiloxane showed differences in the Auger spectrum when compared with their counterparts supported on thorium(IV) oxide + aluminium(III) oxide (Table 5) Although silicon could be detected on the former beads, it was present only in the first few atomic layers as was carbon Argon ion bombardment for as little as 15 sec removed all the silicon as well as the carbon

DISCUSSION

Inhibition by Halogenated Hydrocarbons

The nature of the inhibiting species The species formed as a result of the interaction of halogenated hydrocarbons with precious metal surfaces depend both on the temperature and on the surrounding atmosphere Adsorption of chloromethanes on palladium and platinum involves an irreversible dissociative process in which C–Cl bonds undergo fission before C–H bonds (*11*) Thus at temperatures of 475–500 K, monochloromethane decomposes to give hydrogen chloride and methane as well as a carbonaceous solid on the catalyst surface

In this work the presence of a carbonaceous residue was confirmed by XPS The experimental finding that any associated bromine was widely dispersed on the catalyst surface, whereas chlorine was more localized, is not perhaps surprising in view of the difference in the bond strength of C–Cl (353 kJ mol^{-1}) and C–Br (294 kJ mol^{-1}) Thus brominated hydrocarbons may break down on the catalyst with the halogen being liberated well away from the carbonaceous residue, while the corresponding chlorine compounds tend to decompose in such a way that the chlorine remains associated with any solid carbon In the same way, studies of the thermal decomposition of hydrogen hexabromoplatinate(IV) and hydrogen hexachloroplatinate(IV) on aluminium(III) oxide (*12*) show that the Pt–Br bond is sufficiently weak to permit rapid dissociation and subsequent reaction of the dissociated species with surface sites on the alumina, whereas the stronger Pt–Cl bond undergoes little fission

It is not easy to assess the effect of carbon deposition on catalytic activity Twin carbon peaks were observed when XPS was used to study catalysts poisoned by chlorinated hydrocarbons, the extra peak gradually disappeared as the catalyst regained its activity and could no longer be detected when the activity had been fully restored The additional peak was absent when methane on its own was pyrolyzed over a reduced palladium surface and it may therefore perhaps be ascribed to the presence of carbon that is still attached to the halogen Carbon itself is thus unlikely to be wholly responsible for catalyst deactivation, although both a supported platinum catalyst (*13*) and a palladium sponge catalyst (*14*) temporarily lost activity with respect to methane oxidation after relatively large amounts of carbon had been deposited on their surfaces

The deactivating effect of the halogens, however, is likely to be considerably greater Hydrogen chloride and hydrogen bromide both inhibit the oxidation of hydrocarbons over palladium catalysts (*15*) With hydrogen bromide the loss in activity was the same as with 1,2-dibromoethane (*3*) Thus all the available evidence suggests that the loss of activity which occurs when supported precious metal catalysts are exposed to halogenated hydrocarbons is due solely to the chemical interaction of the halogen with the catalyst system

The effect of metal particle size Although supported palladium catalysts underwent a considerable loss in activity after exposure to chlorinated hydrocarbons, there was usually only a barely significant increase in metal particle size The diameter of the platinum particles in supported catalysts also increased slightly following such treatment but the loss in activity was much smaller than that found for the corresponding palladium catalysts The observed deactivation cannot therefore be connected solely with changes in the precious metal particle size, particularly as the decrease in activity is often reversible Any increase in the diameter of the metal particles is more likely to have been caused by the repeated passage of methane + oxygen pulses through the catalyst at high temperatures (*7*). In any case, the rate of reaction has been shown to be independent of precious metal particle size for the oxidation of methane over a Pd on γ-Al_2O_3 catalyst under methane-rich conditions (*7*).

The recovery of deactivated catalysts. The activity of supported catalysts poisoned by halogenated hydrocarbons could be most readily restored either by raising the temperature or by passing methane + oxygen pulses through the catalysts. Removal of halogen from the precious metal surface is probably the slow step in the recovery process. Thus a similarity may exist between the conditioning of a catalyst prepared from a precious metal–halogen salt and the recovery following deactivation by a halogenated hydrocarbon.

The atmosphere present during the preparation of catalysts by the thermal decomposition of precious metal salts has a profound effect on the subsequent activity of the metal. Water vapor accelerates the loss of chlorine from palladium chloride (*10*), allowing lower temperatures to be used for the decomposition of this salt than when either nitrogen or air is present. Hydrogen is more effective than halogen in activating the catalyst, partly because it removes chlorine from palladium chloride as hydrogen chloride. On the other hand, the activity of Pd on γ-Al_2O_3 remains low when oxygen on its own is passed over the catalyst during the conditioning process (*7*). Passage of methane + oxygen pulses through a palladium catalyst produces water and, also, in the case of methane-rich mixtures, some hydrogen, both of which accelerate the desorption of chlorine and thus cause more rapid recovery of catalytic activity.

The removal of chlorine from an alumina surface during the dehydrochlorination of chloroalkanes at 468–493 K is accelerated by the presence of water vapor (*16, 17*). That the support plays a part in the retention of chlorine is shown by the finding that a Pt on γ-Al_2O_3 catalyst adsorbs less chlorine than a corresponding Pt on η-Al_2O_3 catalyst (*18*). In general, however, the water content of the atmosphere and the temperature are the main factors controlling the rate of loss of chlorine.

The effect of the catalyst support. A Pd on SnO_2 catalyst underwent more rapid deactivation on exposure to chlorinated hydrocarbons than did other supported palladium catalysts. Tin(IV) oxide itself is a relatively efficient catalyst for the oxidation of methane (*7*). In addition, direct interaction has been shown to occur between this oxide and precious metals (*19*) and may be responsible for the loss of activity found Bond *et al.* (*20*), who observed transfer of oxygen from palladium to tin oxide during the oxidation of carbon monoxide, proposed a "spillover" mechanism

$$Sn^{2+} + Pd(O_{ads}) \rightarrow Sn^{4+} + O^{2-} + Pd,$$

the reverse of which has also been reported (*21*). Thus chlorine, formed by decomposition of chlorinated hydrocarbons, could, like oxygen, be readily transferred to the precious metal, thereby causing its deactivation. The equally rapid recovery of catalytic activity observed could be explained by the reverse reaction, i.e., the "spillover" of chlorine from the palladium on to the support.

A Pd on TiO_2 catalyst recovered more quickly than did a Pd on γ-Al_2O_3 catalyst after exposure to trichloromethane. This implies that the halogenated carbon residue is more difficult to remove when alumina is used as the support. This suggestion receives support from a study of the thermal decomposition of palladium(II) chloride on different supports (*22*). In a reducing atmosphere, the precious metal chloride was more stable on γ-Al_2O_3 than on TiO_2. It was found that, after being dried at 393 K, all the palladium was in the form of $PdCl_4^{2-}$ on alumina, while most of it was present as $PdCl_2$ on titanium dioxide.

Inhibition by Hexamethyldisiloxane

In contrast to the behavior observed with halogenated hydrocarbons, hexamethyldisiloxane generally causes rather complete poisoning of supported metal catalysts, but the deactivated powdered catalysts usually exhibit at least some recovery

At temperatures similar to those used in this work, hexamethyldisiloxane breaks down only slowly but the reaction yields a wide variety of products (*23*) The decomposition, however, is strongly catalysed by transition metals and under these conditions the main initial step is the cleavage of Si–CH_3 bonds, which is followed by liberation of gaseous methane and polymerization of the residual species to yield polyorganosiloxanes (*24*) Thus in the presence of hydrogen hexachloroplatinate(IV) hydrate, significant reaction occurs even at 473 K, and at higher temperatures some of the polymer is further oxidized to silicon(IV) oxide, the deposition of which on the catalyst surface is no doubt at least partly responsible for the observed deactivating effect

The extent to which both silicon and carbon, formed by the decomposition of the organosiloxane compound, penetrate below the surface of the catalyst is markedly dependent on the nature of both the precious metal and the catalyst support The readiness with which a catalyst loses its activity in turn increases with the degree of penetration of the inhibitor or its breakdown products Thus palladium, which readily absorbs silicon into its bulk, is more readily deactivated than platinum, and similar behavior has been found with regard to the extent of absorption of lead oxide (*25*) and the susceptibility to poisoning by lead (*26*) of palladium and platinum catalysts In the same way, Pd on Al_2O_3 + ThO_2 bead catalysts, into which silicon and carbon can penetrate significantly during the relatively long contact times between catalyst and inhibitor, are irreversibly poisoned, in contrast, Pd on SnO_2 beads, with which almost no penetration occurs, are quite resistant to deactivation This suggests that the reactant gases are adsorbed and undergo reaction in the interior of the catalyst as well as reacting on its external surface In spite of the relative resistance to poisoning of palladium supported on tin(IV) oxide, catalyst beads based on these materials do not recover their activity as rapidly as do Pd on Al_2O_3 + ThO_2 beads This behavior may perhaps be ascribed to some form of chemical interaction between the precious metal and tin(IV) oxide

The finding that hexamethyldisiloxane (HMDS) is a much less effective inhibitor of the oxidation of butane than of methane is probably a reflection of the well-known low reactivity of the simpler alkane The organosiloxane appears to be irreversibly adsorbed on the high-energy sites needed to catalyze methane oxidation but is only reversibly adsorbed on the lower energy sites which will nevertheless bring about the oxidation of butane, a similar explanation has been advanced for the selective poisoning of methane oxidation by HMDS in contrast to the less marked inhibition of the oxidation of propene (*4*) In the same way, lead compounds poison a catalyst for methane oxidation while leaving substantially unaffected the activity of the same catalyst for the oxidation of butane (*27*) In this connection, it is perhaps of interest that catalytic beads, in the absence of known catalyst poisons, gradually lose their activity with respect to methane oxidation but not to butane oxidation This is probably due to the gradual accumulation of water vapor which in a closed reactor is a powerful inhibitor of methane oxidation on the surface of catalytic beads (*28*)

Conclusion

The inhibition of methane oxidation by halogenated hydrocarbons is associated with a deficiency of oxygen at the catalyst surface This oxygen shortage is caused by the adsorption of the halogen compound on the sites normally needed for the adsorption and activation of oxygen, an equilibrium being set up between the inhibitor and the reactants adsorbed on the catalyst surface The extent of deactivation is decreased by raising the temperature of the catalyst bed Catalyst systems with which there is strong interaction between the precious metal and its support suffer the greatest loss in activity but also exhibit the most marked recovery

In contrast, hexamethyldisiloxane may cause total loss of catalytic activity The extent of recovery depends on the degree to which the silicon physically blocks active sites as a result of its penetration into the precious metal The oxidation of methane is inhibited to a much greater extent than the oxidation of butane Nevertheless, as with halogenated hydrocarbons, the catalyst support has an appreciable effect on the ability of the precious metal to resist deactivation

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