Platinum–Tin Reforming Catalysts

II. Activity and Selectivity in Hydrocarbon Reactions

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A series of bimetallic catalysts has been prepared by impregnating a commercial Pt/alumina catalyst (series B catalyst in Part I, R. Burch, *J. Catal.* **71**, 348 (1981)) with solutions containing compounds of tin or lead in aqueous or nonaqueous solvents. The activity and selectivity of the catalysts have been determined under flow conditions at 750 K and 1 bar for the conversion of *n*-hexane, methylcyclopentane, cyclohexane, and at 373 K for the hydrogenation of hex-1-ene. Under these experimental conditions it has been established that the conversion of *n*-hexane into branched aliphatic isomers is catalysed by a bifunctional mechanism, but excess acidity gives lower selectivity due to enhanced cracking. Benzene and methylcyclopentane are formed directly from *n*-hexane on metal sites and do not require acidic sites. The conversion of methylcyclopentane into benzene is bifunctional. The results show that when tin is present the catalysts are much more stable, and have much higher selectivities for isomerisation and aromatisation reactions. The Pt–Sn catalysts produce more benzene from methylcyclopentane, they dehydrogenate faster, and they hydrogenate more slowly. At a given conversion the bimetallic catalysts produce much lower concentrations of cracked products. It is concluded that tin modifies the acidity of the support, resulting in higher selectivity for isomerisation and lower selectivity for cracking, and also modifies the properties of the Pt, resulting in less self-poisoning. Taking account of the fact that the tin is mainly present in these catalysts as Sn(II) (see Part I), stabilised by the alumina, it is concluded that the catalytic results cannot be rationalised on the basis of current geometrical models for bimetallic catalysts. It is proposed that the role of the tin is to modify the *electronic* properties of the small Pt particles. It is tentatively suggested that similar electronic effects may be important in other bimetallic catalysts.

INTRODUCTION

Catalytic reforming is a refinery process designed to increase the octane number of a naphtha or hydrocarbon. The process involves several different types of reaction, namely, isomerisation, dehydrogenation of cyclohexanes, isomerisation/dehydrogenation of cyclopentanes, and dehydrocyclisation of paraffins. Paraffin isomerisation occurs relatively easily, but contributes only a limited improvement in octane number. The most important reforming reactions are those which produce aromatics.

Bimetallic catalysts containing Pt and a second metal have been patented for reforming reactions. The major advantage of the bimetallic catalysts seems to be their lower rates of deactivation and their higher selectivity to aromatic products. In Pt–Re catalysts it has been observed that the Re is reduced to the zero-valent state, and the formation of Pt–Re alloy particles has been postulated to explain the modification of the catalytic properties (*1*). Pt–Sn catalysts also exhibit modified properties and it has been suggested that the formation of Pt–Sn alloy particles is again responsible (*2–4*). In both cases it is postulated that the atoms of the second metal divide up the Pt surface into small ensembles. It is thought that these ensembles are too small to catalyse hydrogenolysis and coke-forming reac-

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tions, whereas the ability to form partially dehydrogenated molecules, which can isomerise on acidic oxide sites, is hardly affected. However, the reduction results and the hydrogen chemisorption data presented in Part I (5) show that in Pt–Sn catalysts most of the tin is present in the 2+ oxidation state after a normal reduction treatment. It is possible that a solid solution of tin in Pt may be formed, but the tin content must be very low. Even allowing for surface enrichment the amount of tin present is too small for a geometric model to be applicable.

The purpose of the present paper is to present data showing that although Pt–Sn alloys are not formed, nevertheless, these catalysts still have very different properties from Pt/alumina.

EXPERIMENTAL

1. Materials

(a) Pt catalysts. The Pt/alumina catalyst used in this work was a standard reforming catalyst. (The reduction of this catalyst, and its interaction with Sn has been described in Part I, series B catalysts.) The extrudate as received was crushed and sieved and the 30–60 mesh portion retained for use. The base catalyst contained 0.3 wt% Pt and 0.6 wt% Cl. A single catalyst (B1.0K) was prepared by impregnating the base catalyst with a solution of KOH to give a catalyst containing 1.0 wt% K^+ after calcination. A further catalyst (B-Cl) was prepared by prechloriding the base catalyst by passing over the catalyst air which had been bubbled through 6 M HCl while the catalyst was being calcined. These two catalysts were used to ascertain the sensitivity of the various reforming reactions to the acidity of the support.

(b) Bimetallic catalysts. A wide range of catalysts were prepared, using the base catalyst as starting material, by impregnating with solutions containing tin or lead, either in aqueous or nonaqueous solvents. The procedure was to add the required amount of a solution of metal compound to a known weight of base catalyst, allow to stand for 1 h, and then remove the excess solvent by rotary evaporation. The impregnated catalysts were dried at 390 K overnight. The bimetallic catalysts were then either tested in an uncalcined form, or were given a standard calcination treatment by heating in air for 2 h at 770 K. Details of the metals content, the nominal chloride content, and the method of preparation are given in Table 1. Some blank catalysts were also prepared to observe the effect, if any, of just adding chloride ions to the base catalyst.

2. Equipment

The activity and selectivity of the catalysts were determined under conditions of constant flow in a Pyrex U-tube microreactor at 750 K and 1 bar pressure. The sample (300 mg) was supported on a glass sinter and the reactants were passed downstream through the reactor. The hydrogen flow from a cylinder was controlled by a Negretti and Zambra controller. The hydrocarbon (n-hexane, methylcyclopentane, cyclohexane, hex-1-ene, all Analar reagents) was injected into the hydrogen stream by a motor-driven syringe. The injection point was a stainless-steel T-piece and this, together with the stainless-steel tubing up to the reactor, was warmed with heating tape to 350 K to prevent condensation of the reactants. Samples from the reactor were analysed either by direct sampling with a gas sampling valve or by removing samples with a gas syringe and injecting into a gas chromatograph (Perkin–Elmer F33) linked to an Infotronics electronic integrator and recorder. The gas chromatograph used a 3-m column packed with silicone fluid on Chromosorb P. Complete separation of all the important products was easily obtained by operating the column at 400 K. The temperature of the reactor was maintained by a small electric furnace controlled by a West Gardian controller. The temperature of the sample was

TABLE 1

Composition and Method of Preparation of Bimetallic Catalysts[a]

Catalyst	Sn or Pb (wt%)	Chloride content	Method of preparation
B	—	0.6	Base catalyst
B1	0.3	0.6	$Pb(NO_3)_2$—aqueous solution
B2	0.3	0.8	$PbCl_2$—aqueous solution
B3	0.3	0.9	$SnCl_2$—aqueous solution
B4	0.3	1.0	$SnCl_4$—aqueous solution
B5	0.6	1.0	$SnCl_2$—aqueous solution
B6	0.6	1.6	$SnCl_4$—aqueous solution
B8	—	0.9	HCl blank
B9	—	1.0	HCl blank
B10	0.3	1.0	$SnCl_4$—acetone solution
B11	0.3	0.9	$SnCl_2$—acetone solution
B12	0.3	0.6	SnI_4—ether solution
B13	0.3	0.6	$Sn(NO_3)_4$—aqueous solution

[a] All catalysts contain 0.3 wt% Pt.

monitored with a thermocouple placed in a thermowell adjacent to the glass sinter.

The activity and selectivity of selected catalysts for the hydrogenation of hex-1-ene were determined using the same apparatus, but with only 30 mg of catalyst, at 373 K either under flow conditions or by removing the syringe unit and injecting pulses of hex-1-ene over the catalyst.

3. Procedure

Before determining the catalytic activity the catalysts were prereduced in flowing hydrogen (GHSV = 2500 cm^3/g catalyst/h) by first raising the temperature to 570 K, holding for 1 h, and then heating at 750 K for either 2 or 16 h. No significant differences could be detected between catalysts reduced for 2 or 16 h.

The standard test conditions were: hydrogen/hydrocarbon molar ratio = 5.4 : 1, LHSV = 2.7 cm^3 hydrocarbon/g catalyst/h; temperature = 750 K; pressure = 1 bar.

RESULTS

Under reforming conditions (especially at high temperatures) reactions of paraffins can occur either by metal-catalysed pro-

cesses or by a bifunctional mechanism involving both the metal and acidic sites on the oxide. The relative importance of the two processes depends on the acidity of the support, the activity of the metal, and the experimental conditions. Preliminary experiments with our bimetallic Pt–Sn catalysts showed that in addition to higher activity they had higher selectivity for the formation of isomerisation products. Since the most active catalysts were those prepared using chloride compounds of either Pb or Sn it was natural to suspect that the enhanced activity was caused by an increase in acidity when chloride counterions were added with the metal. Before proceeding with a study of the bimetallic catalysts it was necessary to establish the relative importance of metal- and acid-catalysed reactions *under our experimental conditions*. The objective of the first part of the work, now to be described, was to determine whether changes in acidity could produce similar variations in activity and selectivity, bearing in mind that the base catalyst already contains 0.6 wt% Cl.

1. Pt/ALUMINA CATALYSTS

(a) Reproducibility

Small variations in product distribution can give valuable information about the mechanism of catalysed reactions, so it is important to know whether such variations are outside the limits of experimental error. Table 2 shows data for the base catalyst obtained by three different operators using three different reactors. The reproducibility is very good, especially for the formation of benzene and methylcyclopentane, both of which later results will show to be important products in identifying the role of tin.

(b) Influence of Acidity on Product Distributions

(i) *Effect of pretreatment.* Table 3 shows the effect on the product distribution for the reaction of *n*-hexane of calcination either

TABLE 2

Reproducibility Test on Base Catalyst[a]

Product	Test		
	A	B	C
C_6 isomers	10.6	9.9	12.2
Benzene	1.8	1.8	1.8
Methylcyclopentane	1.4	1.4	1.6
$(C_1–C_5)$	7.0	7.5	7.0
Activity[b] (%)	22.3	22.6	23.1

Note. Values are expressed as percentages.

[a] Conditions: 750 K, 1 bar, n-hexane standard flow conditions, 5 h on stream.

[b] Activity (%) = fraction of feedstock converted into products.

with or without HCl present. The results show that the product distribution is hardly affected by pretreatment. There is a small change in selectivity from cracking to isomerisation when either calcination treatment is used. However, the product distributions for catalysts calcined in air or in air/HCl are the same within experimental error. We conclude that since prechloriding this catalyst has little effect on the *selectivity* of the catalyst the original catalyst already has about the optimum amount of acidity, and that all the strong acid sites are promoted by the chloride ions already present in the original catalyst. The activity of the catalyst calcined in air/HCl is about 25% higher than that of the air-calcined catalyst. However, since the product distri-

TABLE 3

Effect of Pretreatment on the Product Distribution Obtained with the Base Catalyst[a]

Product	Catalyst pretreatment		
	Uncalcined	Calcined in air	Calcined in air/HCl
C_6 isomers	44.5	49.0	47.0
Benzene	8.9	8.7	9.5
Methylcyclopentane	8.9	8.7	7.1
$(C_1–C_5)$	34.2	31.0	32.0

Note. Values are expressed as percentage selectivity. Selectivity = fraction of a specific product in outlet gas/activity.

[a] Reaction of n-hexane under standard conditions, steady-state data.

butions are the same, this may reflect an improved dispersion of the Pt during calcination in the air/HCl mixture.

(*ii*) *Injection of organo–chlorine and organo–nitrogen compounds.* Further experiments were performed to see if the level of acidity and hence the activity could be increased in other ways. Figure 1 shows the effect of injecting 5-μl pulses of CH_2Cl_2 into the hydrogen/hexane flow, at hourly intervals, 0.5 h before taking samples for analysis. The results show that as the acidity of the alumina is increased there is a progressive increase in cracking selectivity, even though the total activity only increases slightly. Propane makes up almost all the additional cracked products, a clear indication that the additional cracking is acid catalysed. The enhanced cracking selectivity is paralleled by a loss of isomerisation selectivity. The formation of benzene and of methylcyclopentane are hardly affected. This suggests that under our conditions the formation of benzene and methylcyclopentane from n-hexane does not require acidic sites. These results, together with other similar results which we have obtained using different organo–chlorine compounds and by varying the time of injection, show again that the base catalyst has about the optimum acidity level. No beneficial effects are observed by increasing the total acidity.
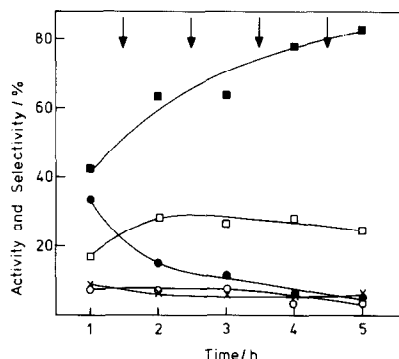

FIG. 1. Effect of injecting pulses of CH_2Cl_2 into n-hexane/hydrogen flow. Arrows indicate times when pulses were injected. Standard test conditions were used. ●, C_6 isomers; ×, benzene; ○, methylcyclopentane; □, $(C_1–C_5)$; ■, activity.

TABLE 4

Effect of Reducing the Acidity of the Base Catalyst by Injecting Triethylamine[a]

Product	Before injection	Time after injection (h)	
		0.25	0.75
C_6 isomers	13.4	3.9	6.4
Benzene	2.7	2.0	2.0
Methylcyclopentane	2.0	0.9	1.0
(C_1-C_5)	9.1	2.7	3.0
Activity (%)	28.3	10.8	13.5

Note. Values are expressed as percentages.
[a] Reaction of n-hexane under standard conditions.

A further test on the effect of *reducing* the acidity on the product distribution was made by injecting triethylamine (5-μl pulse) into the hydrogen/n-hexane stream. Table 4 summarises the results. It is found that the triethylamine poisons the catalyst for isomerisation and cracking. The rate of formation of benzene and methylcyclopentane is less affected even though the total activity is greatly reduced. With time the catalyst begins to recover, but most of the increase in activity is manifested as an increase in isomerisation activity.

(*iii*) *Addition of potassium hydroxide.* The effect of reducing the acidity by pretreatment with a solution of KOH, and the recovery of acidity by injection of CH_2Cl_2 is shown by the results in Table 5. Addition of potassium lowers the total activity giving less isomerisation and cracking. However, the rate of formation of benzene and methylcyclopentane is actually greater now. The first injection of CH_2Cl_2 raises the isomerisation activity very substantially, but the benzene and cracking activities are hardly affected. Less methylcyclopentane was produced. Further injections of CH_2Cl_2 increase the acidity too much so the formation of cracked products dominates.

It is clear from these various experiments that the activity of the catalyst for isomerisation and cracking is closely dependent on the acidity of the oxide. Benzene and

methylcyclopentane formation appears to be essentially independent of acidity. This implies that the conversion of n-hexane into cyclic products occurs mainly via a metal-catalysed reaction under our experimental conditions. This could be a direct ring closure process (*6*), or, in the case of benzene, may occur via the gas-phase cyclisation of hexatriene formed initially on the metal (*7*).

Methylcyclopentane is not an intermediate in the formation of benzene from n-hexane. Although this is often referred to as the route from paraffins to aromatics (see, e.g., (*8*)), there is evidence that at high temperatures (i.e., under typical reforming conditions) direct ring closure is possible and probably more important (*9*). This is certainly the conclusion to be drawn from our experiments.

(*iv*) *Reactions of methylcyclopentane.* Further evidence that methylcyclopentane is not involved in the formation of benzene from n-hexane under our conditions is shown by the data in Table 6, which compares the product distributions obtained from n-hexane and methylcyclopentane. The results show that the rate of formation of benzene is the same in both cases. Since the concentration of methylcyclopentane present is about 50 times lower in the case of hexane it seems highly improbable that a common intermediate involving adsorbed methylcyclopentane is involved. Whereas

TABLE 5

Effect of Impregnating Base Catalyst with Potassium Hydroxide and of Injecting CH_2Cl_2[a]

Product	Injection of CH_2Cl_2 (μl)				
	Base catalyst	Impregnated catalyst			
	0	0	5	15	25
C_6 isomers	15.4	5.5	13.0	5.3	4.1
Benzene	3.6	4.6	4.2	1.3	0.9
Methylcyclopentane	2.0	3.4	2.3	0.7	0.6
(C_1-C_5)	9.1	4.4	4.7	9.4	5.9
Activity (%)	33.2	21.0	27.1	18.2	12.8

Note. Values are expressed as percentages.
[a] Reaction of n-hexane under standard conditions.

TABLE 6

Product Distributions from *n*-Hexane and
Methylcyclopentane with the Base Catalyst[a]

	Methylcyclo-pentane		*n*-Hexane	
	Initial	Steady state	Initial	Steady state
n-Hexane	4.6	4.4	—	—
2- and 3-Methylpentane	2.3	0.9	20.6	9.4
Methylcyclopentane	—	—	3.0	1.4
Benzene	14.4	1.8	13.0	1.8
(C_1–C_5)	2.1	1.0	17.0	7.0
Olefins	12.3	7.0	1.5	0.4
Activity (%)	36.3	15.2	58.7	22.6

Note. Values are expressed as percentages.
[a] Standard test conditions.

when *n*-hexane was used as a starting material the rate of formation of benzene was unaffected by the acidity of the support, the results in Fig. 2 show that the rate of formation of benzene from methylcyclopentane is directly related to the acidity level. Acidification gives much more cracking, but also much more benzene. Similarly, on addition of triethylamine the cracking activity is reduced but the benzene activity is totally eliminated. We conclude that methylcyclopentane conversion to benzene is controlled by the rate of the acid-catalysed ring isomerisation step, but
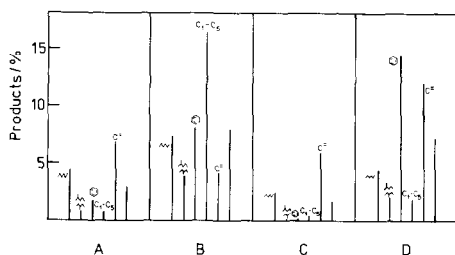

FIG. 2. Effect of additives on the reaction of methylcyclopentane over Pt catalysts. (A) Base catalyst before injection; (B) after injecting pulse of CH_2Cl_2; (C) after injecting pulse of triethylamine; (D) catalyst B10 (see text). For each catalyst the data represent from left to right the concentrations of *n*-hexane, 2- and 3-methyl pentane, benzene, (C_1–C_5), olefins, and the total activity × 0.2.
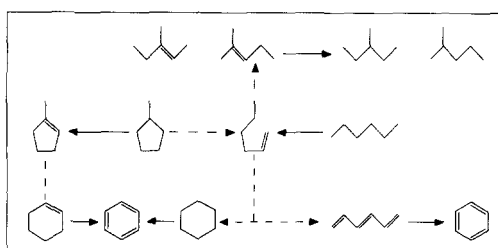

FIG. 3. Reaction scheme for the interconversion of *n*-hexane and methylcyclopentane. All reactions are reversible in principle. Vertical lines are acid-catalysed reactions; horizontal lines are metal-catalysed reactions. Broken lines indicate slow steps.

that *n*-hexane conversion to benzene is controlled by the Pt.

Figure 3 shows the reaction network which seems to be appropriate to the interconversion of *n*-hexane and methylcyclopentane under our conditions. This differs from conventional reaction schemes in having direct ring closure steps on metallic sites, and in distinguishing between *n*-hexane and methylcyclopentane as starting points for the formation of benzene. As pointed out at the beginning of this experimental section, the reason for establishing the relative importance of metallic and acidic functions in the catalysts under our conditions was to allow us to identify the role of tin in promoting Pt/alumina catalysts. Our conclusions are that benzene is formed by a metal-catalysed route from *n*-hexane, but by a bifunctional mechanism from methylcyclopentane; that methylcyclopentane is formed mainly by a metal-catalysed route; and that isomerisation requires a bifunctional mechanism. We now describe our results for the bimetallic catalysts.

2. BIMETALLIC CATALYSTS

The catalysts listed in Table 1 have been investigated and their activities have been determined for the conversion of *n*-hexane under flow conditions at 750 K and 1 bar pressure. For uncalcined and calcined catalysts, respectively, Tables 7 and 8 summarise the activity and selectivity data ob-

TABLE 7

Conversion of n-Hexane over Uncalcined Bimetallic Catalysts[a]

Catalyst	Activity (%)	Benzene (%)	C_6 isomers (%)	(C_1-C_5) (%)	Methylcyclopentane (%)
B5	53.5	4.5	32.2	11.5	1.6
B9	31.1	3.8	10.2	12.2	2.1
B6	30.6	3.0	11.0	11.8	1.8
B3	28.0	2.1	14.2	7.8	1.4
B4	25.9	2.7	10.2	8.5	1.7
B10	22.2	2.3	8.3	10.2	1.6
B8	15.3	1.3	6.1	5.4	1.4
B	14.6	1.3	6.5	4.3	1.3
B2	13.7	0.8	5.9	4.4	1.1
B1	12.3	0.7	5.4	4.1	1.0
B12	6.3	0.2	1.8	2.9	1.0
B13	4.2	0.3	1.6	1.7	0.6

[a] Standard test conditions.

tained under steady-state conditions after 5 h on stream. The results for the uncalcined catalysts show that all the catalysts prepared using tin chloride solutions, whether as Sn(II) or as Sn(IV) or aqueous or non-aqueous conditions, improve the activity and selectivity of the base catalyst. There is a considerable variation in the effect, however, with the aqueous solutions seemingly more effective than the nonaqueous solutions. This may reflect a greater degree of hydrolysis of the tin chlorides in aqueous solution and this in turn may result in a better distribution of the tin over the support. Both the lead-containing catalysts and the catalysts prepared from SnI_4 and $Sn(NO_3)_4$ have low activity. Addition of large amounts of HCl solutions gives a more active catalyst. However, in agreement with the data presented earlier for the Pt catalysts, the effect of acidifying with chloride ions is to increase the cracking

TABLE 8

Conversion of n-Hexane over Calcined Catalysts[a]

Catalyst	Activity (%)	Benzene (%)	C_6 isomers (%)	(C_1-C_5) (%)	Methylcyclopentane (%)
B10	55.0	4.6	37.5	12.6	2.3
B3	46.2	3.9	33.4	8.5	1.5
B5	45.1	4.2	31.0	8.7	1.5
B2	43.3	3.7	32.7	6.5	1.6
B6	40.8	3.8	26.2	8.5	1.8
B4	32.7	3.9	14.2	9.9	2.0
B12	28.3	2.2	16.9	5.1	1.5
B11	27.1	2.2	11.7	7.3	1.7
B	14.9	1.2	6.7	5.1	1.3
B8	13.9	1.2	5.8	5.0	1.3
B9	12.8	0.9	2.7	5.8	1.6
B13	8.4	0.4	3.1	2.1	0.8
B1	6.0	0.2	1.7	2.9	1.0

[a] Standard test conditions.

activity more than the isomerisation activity or the rate of cyclisation. In contrast, the most active bimetallic catalysts produce mainly C_6 isomers. The amount of benzene formed increases almost fourfold as compared with the base catalyst, but the amount of methylcyclopentane formed is only slightly higher. The C_6-isomer concentration is five times greater for the most active catalyst. It is notable that the SnI_4 and $Sn(NO_3)_4$ catalysts have much lower activities than the base catalyst. This is due to a change in selectivity towards cracking and away from isomerisation and benzene formation, and may reflect a poisoning of the metallic function. This would occur if these tin compounds decomposed during reduction to form bulk oxides which then reduced completely to form alloy particles with the Pt (see Discussion in Part I).

Calcination heightens the differences between the bimetallic catalysts and the base catalyst. The nitrate-based Pb and Sn catalysts are still less active than the base catalyst but the SnI_4 catalyst is now significantly more active, and has a high selectivity for isomerisation. Thus, although as stated earlier an obvious qualitative correlation exists between enhanced activity and amount of added chlorine we do not think this is the correct reason for the enhanced activity of the Pt–Sn bimetallic catalysts. We have established earlier that addition of chloride ions either does not affect the product distribution or moves it away from isomerisation. All the most active bimetallic catalysts shown in Tables 7 and 8 have higher isomerisation selectivi-
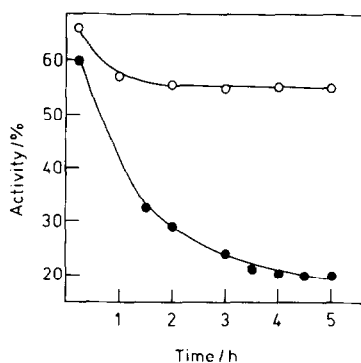

FIG. 4. Activity versus time for the conversion of *n*-hexane over catalysts B (●), and B 10 (○).

ties. Furthermore, comparison of Tables 1, 7, and 8 shows that calcination, which might be expected to result in a loss of chlorine, especially for the aqueous preparations, leads to higher activity in almost every case.

Differences between the base catalyst and the Pt–Sn bimetallic catalysts are further emphasised by the data in Fig. 4 which shows the variation in activity with time for catalysts B and B10. Similar trends, in varying degrees, have been found with the other bimetallic catalysts. Both catalysts have comparable activity initially but the greater stability of the bimetallic catalyst means that it has a much higher steady-state activity. Table 9 shows how the deactivation of these two catalysts differs in respect to different products. For all the individual reactions the addition of tin stabilises the Pt/alumina, but the quantitative effect differs in each case. With the bimetallic catalyst there is hardly any loss in activity for isomerisation or for the formation of

TABLE 9

Changes in Product Distribution during Deactivation of Catalysts B and B10[a]

Catalyst	Total activity	Products			
		Benzene	C_6 isomers	C_1–C_5	Methylcyclopentane
B	28	10	39	34	39
B10	84	34	97	70	92

[a] Values given calculated as (activity at 5 h/activity at 0.25 h) × 100.

methylcyclopentane, rather more for the formation of cracked products, and a decrease to one-third in the activity for benzene formation. Since the earlier experiments with the base catalyst showed that benzene and methylcyclopentane are formed by reaction on the metal it is clear that the tin has modified the metal. However, since the extent of deactivation is much greater for benzene than for methylcyclopentane this implies that the sites on the metal required for benzene formation are more demanding than those for methylcyclopentane formation. The production of methylcyclopentane from n-hexane requires the removal of two H atoms (one each from carbon atoms 1 and 5) and the formation of a C–C bond. The production of benzene requires the removal of eight H atoms and the formation of a C–C bond. This could occur either with the removal of six H atoms to give hexatriene before cyclisation occurs, or by removal of two H atoms followed by cyclisation to give cyclohexane. Later results will show that the dehydrogenation of cyclohexane is very fast over the bimetallic catalyst so, depending on which mechanism operates, the slow step in benzene formation seems to involve either the dehydrogenation to give hexatriene or the ring closure to give cyclohexane. Since the rate of the ring closure reaction to give methylcyclopentane decreases only slightly with time whereas the rate of formation of benzene decreases by two-thirds, it appears that the rate-determining step in the formation of benzene is the dehydrogenation of n-hexane to hexatriene.

In all the cases shown in Table 9 the tin improves the stability of the Pt/alumina. Since isomerisation and cracking reactions involve acidic sites as well as metallic sites it is possible that the tin modifies the oxide as well as the metal. Deactivation is generally taken to be due to coking via the formation of unsaturated hydrocarbon molecules which once formed on the metal sites migrate through the gas phase or across the surface to acidic sites where polymerisation can occur. It is mainly acidic sites which are seriously poisoned first. Consequently, the absence of any significant deactivation of the acidic sites in the Pt–Sn catalyst (as judged by the high activity for isomerisation) suggests either that the tin assists the Pt to provide spillover hydrogen to keep the acidic surface clean, or that the tin *directly* modifies the acidic properties of the alumina. While both mechanisms may operate the latter seems to be more important. Bacaud *et al.* (*3*) have shown previously that tin poisons the very acidic sites on alumina, but they have pointed out also that tin chloride is itself a strong acid. One role of the tin may be to destroy very acidic cracking sites on the alumina and to replace these with very selective acidic isomerisation sites. Some evidence for an improved selectivity in acid-catalysed reactions over the bimetallic catalysts is found in experiments using methylcyclopentane as feedstock.

Reactions of Methylcyclopentane

Table 10 compares the activity and selectivity of catalysts B and B10 for reactions of methylcyclopentane. The results show that

TABLE 10

Comparison of the Product Distributions for the Conversion of Methylcyclopentane over Catalysts B and B10[a]

Product	Catalyst	
	B	B10
C_1–C_5	5.5	7.6
Branched isomers[b]	6.2	1.9
n-Hexane	27.5	13.5
C_6 olefins	14.7	17.2
Cyclic olefins	31.4	30.7
Benzene	13.3	23.7

Note. Values are expressed as percentage selectivity.

[a] Standard test conditions, comparison made when total activity equal at 19%.

[b] Includes 2- and 3-methyl pentane and 2,2-dimethyl butane.

under steady-state conditions the bimetallic catalyst is much more likely to isomerise the C_5 ring to a C_6 ring than it is to open the ring: benzene is formed at the expense of C_6 paraffins. There is little difference in the amounts of cracked products or of aliphatic or cyclic olefins. The olefin levels are high and indicate a similar high activity for the metals in both catalysts. This fact, together with the data given earlier, indicates that methylcyclopentane ring expansion requires acidic sites and implies that the tin modifies the acidity of the alumina. However, this change in acidity occurs in a selective way because isomerisation is increased but cracking is not. Thus, the effect of tin differs in a very important way from that of adding halogen: compare Figs. 2A, B, and D. We conclude that the tin modifies both the Pt and the alumina. It stabilises the Pt against self-poisoning and so benzene formation is maintained (the *initial* activity for benzene formation is no higher for the bimetallic catalyst) and it improves the selectivity of the alumina for isomerisation versus hydrogenolysis (in the case of *n*-hexane this leads to C_6 isomers rather than C_1–C_5 products, whilst in the case of methylcyclopentane it leads to more C_6-ring formation and less C_6 aliphatic products).

Reactions of Cyclohexane and Hex-1-ene

Further differences between the Pt and Pt–Sn catalysts are shown by their activity towards the dehydrogenation of cyclohexane and the hydrogenation of hex-1-ene. Both these reactions are metal catalysed. For catalysts which have been previously deactivated in *n*-hexane for 5 h at 750 K Fig. 5 shows the variation in product distribution with time for the dehydrogenation of cyclohexane. The *deactivated* bimetallic catalyst is much more active and more stable for the formation of benzene than the corresponding Pt catalyst. Presumably the Sn weakens the adsorption of fully dehydrogenated species on the Pt surface and prevents self-poisoning. It is clear that ben-
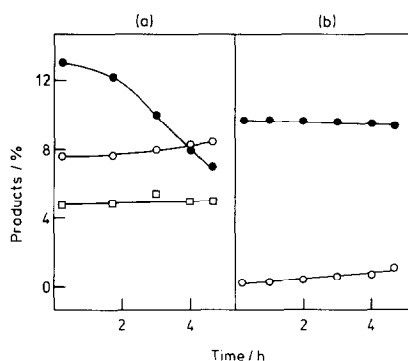

FIG. 5. Variation in product distribution with time for the reaction of cyclohexane over catalysts B and B10. (a) Catalyst B: ○, 0.1 × cyclohexane; ●, benzene; □, olefins. (b) catalyst B10: ●, 0.1 × benzene; ○, cyclohexane.

zene formation from *n*-hexane is more probable over the bimetallic catalyst, as observed experimentally.

For hex-1-ene the reverse order of activity is observed. For catalysts previously deactivated in hex-1-ene at 750 K the Pt catalyst gives 98 ± 1% hexane at 373 K, whereas the Pt–Sn catalyst gives only 79 ± 1% hexane (the error limits derive from two repeat experiments which agreed within these limits). The effect of tin is to decrease the hydrogenation activity of the Pt. Once again in reforming reactions this is beneficial since olefins once formed are more likely to leave the surface and migrate to acidic sites to become isomerised. It is also interesting that before deactivation at 750 K pulses of hex-1-ene injected over either catalyst were isomerised. However, under flow conditions the Pt catalyst no longer had any tendency to isomerise the hexene, whereas the Pt–Sn catalyst gave extensive isomerisation even after 2 h continuous flow. This again points to the fact that the tin stabilises the alumina against deactivation.

DISCUSSION

We have established that under our conditions the following processes occur over Pt catalysts: (i) *n*-hexane is isomerised by a bifunctional mechanism, but excess acidity

of the support gives lower selectivity due to enhanced cracking; (ii) benzene and methylcyclopentane are formed directly from n-hexane at metal sites; (iii) the conversion of methylcyclopentane into benzene requires acidic sites. Comparison of Pt–Sn bimetallic catalysts with the Pt catalyst shows that the tin increases the stability of the Pt for the formation of benzene, methylcyclopentane, C_6 isomers, and cracked products, but to differing extents for each reaction; the Pt–Sn catalysts produce more benzene from methylcyclopentane, they dehydrogenate faster, and they hydrogenate more slowly. The bimetallic catalysts, at a given conversion, produce a much lower concentration of cracked products. In many respects these results compare with those of other workers. Dautzenberg *et al.* (2), for example, found increased stability and higher selectivity to benzene over Pt–Sn catalysts. Moreover, the high selectivity of our Pt–Sn catalysts for mild dehydrogenation rather than for cracking is precisely the reason why industrial bimetallic catalysts have an advantage over monometallic catalysts (*1*). We believe, therefore, that our catalysts reflect reasonably accurately the behaviour observed in a real catalyst under reforming conditions.

A difference in interpretation of the role of tin exists. Whereas Dautzenberg *et al.* (2) interpret their results in terms of alloy formation with the tin atoms assumed to concentrate in the surface and so reduce the number of Pt atom ensembles which are large enough ($\geq$ three atoms) to self-poison (*10*), our data cannot be interpreted on this basis. We recall that in Part I (*5*) it was shown that the tin in these catalysts was present in an oxidized form, the average oxidation state being Sn(II). Moreover, hydrogen adsorption experiments showed that there is no suppression of hydrogen adsorption when tin is present; in fact the reverse is true at high tin loadings. These data exclude the possibility that proper Pt–Sn alloys are formed, or even that there is a large concentration of tin atoms present in a solid solution. We now consider possible models to explain the role of tin in our catalysts.

The Role of Tin

We conclude from our results that tin has two effects. First, it modifies the Pt and prevents or reduces self-poisoning. Second, it modifies the oxide support by eliminating very acidic cracking sites and replacing them with selective olefin isomerisation sites. These selective sites may either be low-acidity sites already present on the alumina, or may be new sites at Sn(II) ions in the surface.

The Effect of Tin on Platinum

The reduction in the amount of self-poisoning by adding tin to Pt is one of the main advantages of these bimetallic catalysts. Poisoning occurs when dehydrogenated hydrocarbon residues are adsorbed very strongly on metal sites. Therefore, any change in the surface properties of the Pt which decreases the binding energy of Pt to carbon should increase the stability. It is generally accepted that self-poisoning parallels deep hydrogenolysis in requiring several contiguous metal sites for reaction to proceed (*10–12*). In Ni–Cu alloys (*13, 14*), for example, the rate of hydrogenolysis of ethane decreases by several orders of magnitude when Cu is added, and this is explained on the basis of a reduction in the number of Ni ensembles large enough to catalyse this reaction. A similar explanation has been proposed to account for the greater stability of bimetallic Pt catalysts (2). However, in our catalysts there is not sufficient metallic tin present to significantly affect the surface geometry of the Pt particles, so we are forced to consider alternative models. Although, in general, the ensemble model is favoured, even in the classic case of Ni–Cu alloys Sinfelt has pointed out (*15*) that it is difficult to dismiss the possibility that the role of the copper is electronic rather than geometric. More-

over, in a number of other bimetallic systems, such as Ru–Cu and Os–Cu (16) or in Ir–Re and Ir–Cu (17) it has been necessary to invoke an electronic effect to account for the loss of hydrogenolysis activity since the degree of surface dilution by inactive atoms is much less than that required for a geometric model.

The reduction data for our catalysts place an upper limit on the amount of metallic tin present at a very few percent (certainly less than 5%). Even allowing for a high degree of surface enrichment it is difficult to see how the surface tin content could exceed about 10%. (This is supported by the fact that large amounts of hydrogen are adsorbed on Pt even when tin is present in our catalysts.) At this level the geometric effect would be small and could not explain the differences in activity and product distribution observed.

If we assume that a small amount of tin is present as a solid solution in Pt, the tin will either donate electrons to the Pt, or cause the Pt to redistribute its d electrons, so as to reduce the density of states at the Fermi level (18, 19). A lower density of states *localised* on a surface Pt atom would be expected to result in a weaker bond to carbon and so self-poisoning (and hydrogenolysis) would be reduced. Since tin has four valence electrons available a small amount of tin will be sufficient to modify the Pt.

On the other hand, if Pt interacts with tin via Sn(II) ions in the alumina surface the Pt would be expected to be electron deficient, and this in turn might be expected to result in an increase in the hydrogenolysis activity and amount of poisoning by increasing the binding of $Pt^{\delta+}$ to carbon. However, data for nickel supported on acidic silica–alumina show (20) that the hydrogenolysis activity is several orders of magnitude lower than for Ni/silica or bulk nickel catalysts, which seems to indicate that in this case electron withdrawal (by the acidic support) leads to lower activity for these destructive reactions. There is disagree-

ment in the literature as to whether electron donation or withdrawal will occur in particular cases and, indeed, as to which is beneficial for particular catalysed reactions (10, 21).

Our results (Part I (5)) suggest an interaction between Pt and Sn(II) ions stabilised by the alumina support, rather than the formation of a solid solution of Sn in Pt. Either way, however, it seems clear that the role of tin is electronic rather than geometric. Indeed it is possible that there is a common explanation for the stabilising effect of many other second-metal additives in terms of electronic modification of the active metal. The formation of a strong metal–carbon bond is essential for C–C bond breaking, and for self-poisoning to occur. The strength of a metal–carbon bond will depend on the electronic properties of the surface metal atom involved, and in an alloy the electronic properties of a surface atom must be affected to some extent by its ligand environment. If it is assumed that a metal, such as nickel, can only form a sufficiently strong bond to carbon when the Ni atom is surrounded exclusively by other Ni atoms, and if it is assumed that three adjacent Ni atoms are required for hydrogenolysis (10), the smallest number of Ni atoms necessary to give three central Ni atoms having exclusively Ni atoms as nearest neighbours is 11 for the (111) plane, 10 for the (100) plane, and 13 for the (110) plane. These values are close to the number of sites which have to be assumed in a geometric model to account for the decrease in activity when Cu is added to Ni (14). The true activation energy for the hydrogenolysis of ethane over Ni/SiO$_2$ catalysts has been determined by Martin (22) as 60 kJ mol^{-1}. At 600 K a change in activation energy of 25 kJ mol^{-1} would produce a change in rate of reaction of two orders of magnitude. A change in activation energy of this order of magnitude may result if a copper atom is substituted for a nickel atom as one of the nearest neighbours to the central Ni atoms.

Further evidence that ensemble effects may be *electronic* in origin comes from data on Ni–Pd alloys. Moss *et al.* (*23*) have found that even though Pd is essentially inert as compared with Ni (Pd has a similar dilution effect to Cu, therefore) the effect on the specific activity for ethane hydrogenolysis of substituting Pd for Ni is rather small. Even at 50% Pd the activity is only reduced by a factor of 3. These authors conclude that *small* ensembles of Ni atoms, or even mixed ensembles, can catalyse cracking. Clearly, if a Pd atom in a Ni matrix becomes active for cracking reactions there must be an electronic effect of the environment on a Pd atom.

In the case of other tin catalysts Masai *et al.* (*24*) have concluded (for Pd–Sn and Ni–Sn catalysts) that the tin is not just present as a diluent but that it also modifies the electronic properties of the active metal.

CONCLUSIONS

Tin modifies the properties of a Pt/alumina catalyst in two ways. It modifies the acidity of the support, and it modifies the Pt *electronically* with the result that self-poisoning is reduced, and selectivity for nondestructive reactions is increased. Although a strict interpretation of the data indicates that tin is present as Sn(II) ions and that it is interaction between Pt particles and Sn(II) ions which stabilises the Pt, the possibility cannot be completely excluded that a very small amount of tin may be incorporated as a solid solution into the Pt. However, the results cannot be rationalised on the basis of current geometrical models for bimetallic catalysts.

We suggest that the role of tin in Pt–Sn catalysts is to alter the local density of states at surface Pt atoms and that this modifies the catalytic properties of these surface atoms, the main effect being to reduce the activity in cracking/coking reactions.

ACKNOWLEDGMENTS

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