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Effects of Catalyst Regeneration with and without Chlorine on Heptane Reforming Reactions over Pt/Al_2O_3 and $Pt–Sn/Al_2O_3$

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The reforming of heptane over chlorine-free Pt/Al_2O_3 and Pt–Sn/Al_2O_3 catalysts has been studied as a function of Sn-content, coking, sequences of regenerative oxidation/reduction treatments after catalytic use, and sequences of regeneration by oxychlorination, involving an air/1,2-dichloropropane mixture, followed by reduction. Particle size effects on selectivities were dominant for Pt/Al_2O_3, decreasing size favouring hydrogenolysis at the expense mainly of aromatisation and favouring C_1 ring closure in cyclisation reactions. Electronic effects of added chlorine on metal catalysis were not important, although, unlike the effects of repeated oxidation/reduction treatments, regeneration involving chlorine gave reproducible Pt dispersions and hence reproducible selectivity behaviour. Tin also induced reproducibility of catalytic behaviour for Cl-free catalysts, but the presence of both Sn and Cl showed additional effects due to the promotion by chlorine of greater intimacy between Sn and Pt in reduced catalysts. In particular oxychlorinated $Pt–Sn/Al_2O_3$ gave low or zero aromatisation selectivity, and strongly promoted cyclisation and isomerisation reactions involving C_2C_6 rather than C_1C_5 or C_1C_6 cyclic intermediates. However, bond-shift mechanisms of isomerisation were also important. The results are discussed in terms of Pt site character, and geometric and electronic effects of Sn, Cl, and coke on catalyst structure and performance. The addition of Sn or Cl enhanced the occurrence of central rather than terminal C–C fission due to cracking reactions at acid sites on the oxide support. © 1999 Academic Press

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INTRODUCTION

The regeneration of Pt/Al_2O_3 catalysts after use in hydrocarbon reforming reactions can be achieved by an oxidation/reduction cycle (1), which removes deposited coke (2), or an oxychlorination/reduction cycle which not only removes coke (3) but also redisperses sintered Pt (4). Changes in dispersion induced by regeneration procedures are reflected in changes in both catalyst activity and selectivity (5). The addition of Sn to Pt catalysts enhances stability by hindering coking of active sites on Pt (6–10), but increasing coke deposition on the alumina support (7, 8, 11, 12). There are parallels between the effects of coke and Sn on catalytic behaviour (3, 10). The effect of chlorine during regeneration of Pt/Al_2O_3 in improving dispersion is less significant for $Pt–Sn/Al_2O_3$ (13), although chlorine has the additional effect of favouring $Pt^o–Sn^o$ alloy formation (14) at high metal loadings (15) or greater intimacy between Pt and Sn dispersed on SnO_x-modified alumina (14, 16, 17) at low metal loadings (13).

The character of Pt sites in Pt/Al_2O_3 and $Pt–Sn/Al_2O_3$ catalysts after series of oxidation/reduction and oxychlorination/reduction cycles (13) and the effects of coking by heptane/hydrogen reaction (3) have been monitored by infrared study of CO adsorption. The roles of Sn and Cl in influencing site character were discussed in terms of structural, electronic, and geometric effects. Five types of site in Pt/Al_2O_3, four adsorbing CO in a linear configuration differing in terms of Pt coordination or ensemble size and one involved in bridge-bonding with CO, gave distinguishable behaviour on coking (3). This should be reflected in differing changes in catalyst selectivity for structure-sensitive and structure-insensitive reactions as a function of time, Sn content, and Cl content (5, 7, 8, 10, 18–21). The present work was designed to test whether there were any recognisable links between catalytic activity and selectivity and the surface character of Pt sites in Pt/Al_2O_3 and $Pt–Sn/Al_2O_3$ as recognised by CO adsorption. Heptane reforming has been studied over Cl-free catalysts and after oxidation/reduction and oxychlorination/reduction cycles identical to those used in the infrared studies.

EXPERIMENTAL

Four γ-alumina-supported Cl-free catalysts were prepared from tin(II) oxalate and tetrammineplatinum(II) hydroxide as before (13) and, after calcination in dry CO_2-free air (60 ml min^{-1}; heated at 15 K min^{-1} to 673 K and held at 673 K for 1/2 h), flushing with nitrogen, and reduction in hydrogen for 1 h at 673 K, contained nominal loadings of Pt(0.3 wt%), Pt(0.3 wt%)–Sn(0.15 wt%), Pt(0.3 wt%)–Sn(0.30 wt%), and Pt(0.3 wt%)–Sn(0.45 wt%). The

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compositions of the last three catalysts correspond to mol Sn/mol Pt of 0.82, 1.64, and 2.47, respectively. Chemisorption of CO on the four catalysts gave CO/Pt values of 0.49, 0.36, 0.31, and 0.32, respectively. The initial calcination and reduction treatments are here jointly designated "calc." Samples were then subjected in various sequences to three additional treatments as follows.

(a) (Designated "ox") Oxidation in dry CO_2-free air (60 ml min^{-1}; heated to 823 K at 15 K min^{-1} and held at 823 K for 1 h) followed by flushing with nitrogen during cooling to 673 K and then the standard reduction at 673 K. The CO/Pt ratios for the four catalysts after calc followed by one ox treatment became 0.46, 0.29, 0.26, and 0.26, respectively. An ox cycle in the absence of chlorine decreased the dispersion of all the catalysts.

(b) (Designated "oxy") Catalyst was heated to 823 K at 15 K min^{-1} in air (60 ml min^{-1}), oxychlorinated (823 K, 1 h) in air (60 ml min^{-1}) containing 31 μmol h^{-1} 1,2-dichloropropane per 50 mg of catalyst followed by cooling to 673 K in a nitrogen flow prior to the standard reduction. The CO/Pt ratios after calc followed by a single oxy treatment were 0.58, 0.23, 0.24, and 0.23, respectively. An oxy cycle enhanced the dispersion for Pt alone (4) but worsened the dispersion of the Pt–Sn/Al_2O_3 catalysts.

(c) (Designated "react") Heptane reforming was carried out in a fixed-bed reactor at 623 K and atmospheric pressure with constant flow (GHSV 2030 h^{-1}, molar C_7H_{16}/H_2 ratio 1/10) and differential conditions under which conversions were in the range 5–10%. Analyses after various times involved on-line use of a Perkin–Elmer 8410 gas chromatograph with an FID detector and a 5.6 m column containing 15% squalane on chromosorb W-HP (80–100 mesh).

RESULTS

Pt/Al_2O_3

The activity of catalysts decreased with time due to coking (3), the decrease being large in the early stages of reaction but much less at longer times (3–8 h). "Initial" activity and selectivity results are therefore reported for the first analyses carried out after 5 min on stream, and "final" activities and selectivities refer to 8 h on stream. The effects of repeated ox and oxy cycles on the initial and final activities for Pt/Al_2O_3 are compared in Fig. 1 with CO uptakes, as measured by both pulse chemisorption and infrared band intensities (13). Raising the temperature of catalyst oxidation from 673 K (calc) to 823 K (first ox cycle) reduced the activities because of sintering (1, 4, 13), the effect being enhanced by repeated ox treatments. In contrast, oxy treatments maintained both catalyst dispersion and activity confirming the important role of chlorine in the redispersion of Pt/Al_2O_3 catalysts (4). This is further shown by the results

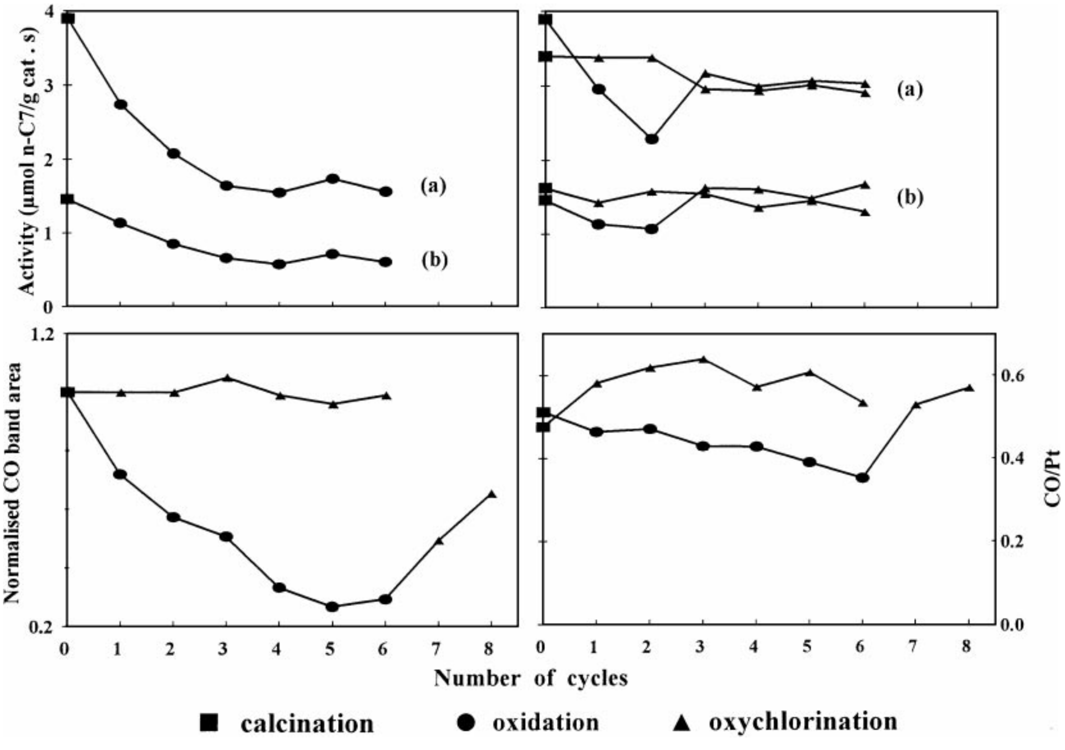

FIG. 1. (a) Initial (5 min) and (b) final (8 h) catalytic activities compared with CO adsorption data for Pt/Al_2O_3 after various sequences of calc, ox, and oxy cycles.

TABLE 1

Initial (i) and Final (f) Catalyst Selectivities after Specific Reduction Steps in Sequences of Consecutive Treatment Cycles

Step		%A[a]	%C[a]	%I[a]	%H[a]	C_1/C_3	2MH/3MH	3EP/2MH
(a) Pt/Al_2O_3								
Calc[b]	i	26	21	20	33	0.77	3.4	1.4
	f	22	23	18	37	0.67	0.8	3.5
Ox 1[b]	i	27	23	22	28	0.75	2.7	1.7
	f	23	24	18	35	0.73	0.9	2.9
Ox 6[b]	i	27	27	23	23	0.66	1.5	2.0
	f	22	25	26	27	0.68	0.5	2.5
Oxy 1[b]	i	17	18	19	46	0.65	3.9	1.2
	f	17	19	18	46	0.67	2.2	2.1
Oxy[c]	i	18	18	18	46	0.60	2.9	1.6
	f	16	18	17	49	0.70	1.4	2.5
(b) Pt–Sn(0.15%)/Al_2O_3								
Calc[b]	i	19	21	23	37	0.70	3.2	1.1
	f	16	23	21	40	0.53	1.6	2.2
Ox 1[b]	i	21	22	20	37	0.56	2.8	1.5
	f	16	23	19	42	0.49	1.5	2.3
Ox 6[b]	i	19	19	20	42	0.55	2.2	1.3
	f	16	22	17	45	0.47	0.8	2.3
Oxy[b]	i	4	17	23	56	0.25	1.8	0.8
	f	3	15	28	54	0.26	1.0	1.2
Oxy[c]	i	5	18	21	56	0.23	2.7	0.8
	f	4	17	25	54	0.22	1.5	0.9
(c) Pt–Sn(0.45%)/Al_2O_3								
Calc[b]	i	21	20	22	37	0.69	3.5	1.3
	f	19	23	19	39	0.61	2.3	1.9
Ox 1[b]	i	17	23	23	37	0.64	2.8	1.9
	f	17	24	23	36	0.60	1.6	2.7
Ox 6[b]	i	19	22	22	37	0.61	1.6	2.5
	f	16	22	26	36	0.51	0.7	4.0
Oxy[b]	i	0	15	68	17	0.34	0.4	1.9
	f	0	13	78	9	0.38	0.2	6.1
Oxy[c]	i	3	15	30	62	0.19	0.5	1.5
	f	3	10	32	55	0.20	0.3	3.1

[a] A for aromatisation, C for cyclisation, I for isomerisation, H for hydrogenolysis.

[b] From sequences calc, ox 1 – ox 6, oxy.

[c] Mean values after oxy steps in sequences calc, oxy 1 – oxy 6.

(Fig. 1) for catalyst subjected to two ox cycles followed by a series of oxy cycles. The presence of chlorine, however, had litttle effect on the extent of catalyst poisoning by coking during operation.

The wealth of selectivity data obtained in the present study cannot all be presented here. Table 1 shows representative results aimed at exemplifying the typical magnitudes of the selectivity values. Coking during time on stream had fairly small effects on selectivity, but in general favoured hydrogenolysis at the expense of aromatisation and isomerisation with a negligible change in cyclisation. Repeated ox cycles led to variations in selectivities, increasing cycle number initially favouring aromatisation and cyclisation at the expense of hydrogenolysis with a general trend towards more isomerisation. The presence of chlorine induced stability in that repeated oxy cycles gave nearly identical selectivities. However, comparison of Cl-containing and Cl-free catalysts showed that the presence of chlorine favoured hydrogenolysis at the expense of aromatisation and to a lesser extent cyclisation and isomerisation. This is borne out by the changes in selectivities after six ox cycles and a subsequent oxy cycle or after two ox cycles and subsequent oxy cycles. The first oxy cycle after ox cycles led to a marked increase in hydrogenolysis and clear decreases in the other three classes of reaction.

More sensitive selectivity information was derived from comparisons of the ratios of the hydrogenolysis products methane (C_1) and propane (C_3), and the isomerisation products 2-methylhexane (2MH), 3-methylhexane (3MH), and 3-ethylpentane (3EP). Overall 21 products were detected and analysed. Hydrogenolysis gave $C_1 > C_3 > C_2$ with the C_1/C_3 ratio slightly less for Cl-containing than for Cl-free catalyst, there usually being a slight increase in the ratio with time on stream, particularly after oxy treatment. Repeated cycles gave a stable result with or without the addition of chlorine. In contrast, the isomerisation product ratios were stable for repeated oxy cycles but varied appreciably throughout the series of ox cycles. In particular 2MH/3MH decreased in parallel to catalyst sintering induced by ox treatments and was considerably reduced with increasing time on line. Changes in 3EP/2MH and 3EP/3MH were more variable after ox treatments although clearly the former was increased with time on line whereas the latter was always decreased with enhanced reaction time. The effects of catalyst poisoning during reaction were the same for Cl-containing as for Cl-free catalysts. General comparisons of the absolute ratios after ox and oxy cycles showed that 2MH/3MH and 3EP/3MH were both slightly less for the Cl-free catalyst particularly after catalyst sintering, whereas 3EP/2MH was about the same.

The dominant product of aromatisation was toluene with a trace of benzene. Cyclisation primarily gave 1,2-dimethylcyclopentane (DMCP) and ethylcyclopentane (ECP), the latter being dominant, with less cyclohexane and considerably less methylcyclohexane. Again oxychlorination induced stability of performance with a small decrease in the amounts of both major products but an increase in cyclohexane. A single oxy cycle after a series of six ox cycles gave similar selectivities to those after the first oxy cycle following calcination and reduction showing that the conditions of oxychlorination were sufficient to attain the same result for catalysts which had been preoxidised at 673 or 823 K immediately before reduction and use in heptane reforming.

Pt–Sn/Al_2O_3

Activities as a function of ox or oxy cycles for Pt–Sn/Al_2O_3 correlated well with the corresponding CO uptake

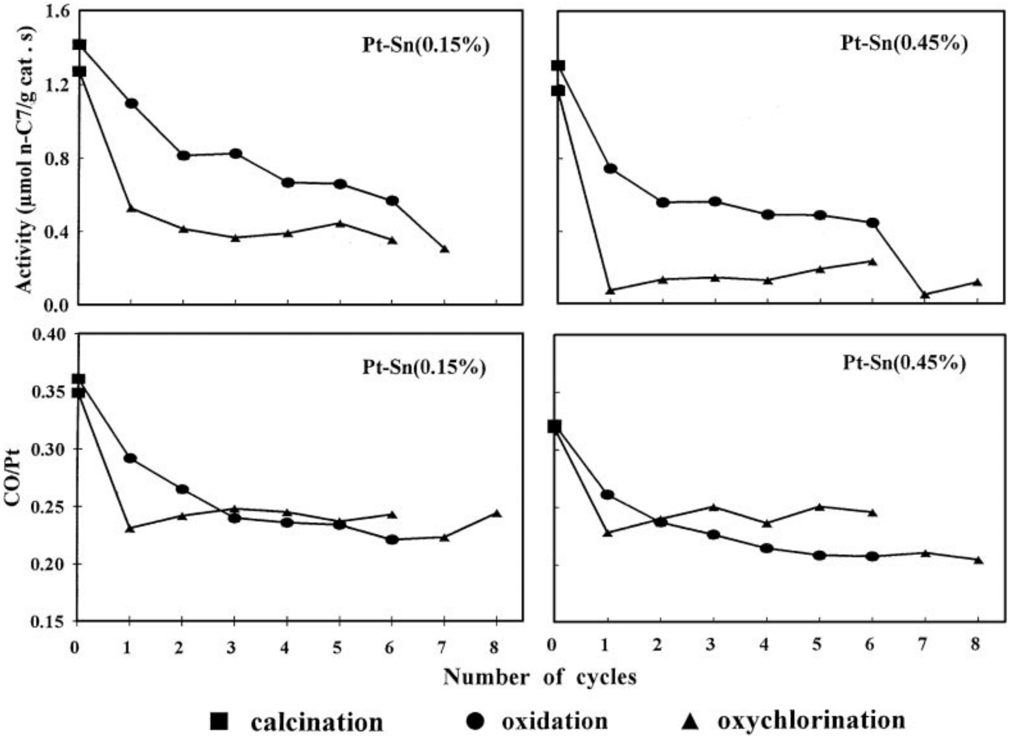

FIG. 2. Variations of activity and CO uptake for Pt–Sn(0.15%)/Al_2O_3 and Pt–Sn(0.45%)/Al_2O_3 after various sequences of calc, ox, and oxy cycles.

data (Fig. 2). As for Pt/Al_2O_3, raising the pre-oxidation temperature from 673 to 823 K led to sintering of the reduced ox catalysts and therefore a reduction in both activity and CO/Pt. Unlike the result for Pt/Al_2O_3, the addition of chlorine at 823 K led to a large decrease in activity because enhanced intimacy between Sn and Pt induced by Cl-content reduced the availability of Pt sites which were active for adsorption and reaction (13, 15). This effect was also apparent from the changes in activities, but not CO/Pt values, for oxy cycles immediately following a series of ox cycles. In general for the first oxy cycle after either calc or ox the percentage loss of activity was clearly greater than the percentage loss of CO uptake particularly for catalyst with 0.45% Sn. Notwithstanding the approximate nature of using CO uptake to assess Pt dispersion (13), the results suggest that the turnover frequency (TOF) was less for Cl-containing than for Cl-free catalysts.

Representative selectivity results for Pt–Sn(0.15%)/Al_2O_3 and Pt–Sn(0.45%)/Al_2O_3 given in Table 1 constitute only a small part of the total available data on which this discussion is based. Results for Pt–Sn(0.3%)/Al_2O_3 were similar or conformed with the trend for increasing Sn content. The addition of all three loadings of Sn reduced the aromatisation activity to toluene by about the same amount. Oxychlorination gave a bigger reduction in aromatisation, the effect increasing with increasing Sn content. Benzene was not detectable for Pt–Sn catalysts after oxy cycles. Selectivities for cyclisation were slightly reduced by Sn after ox treatments, and were reduced to a greater extent after oxy cycles particularly for the highest Sn loading. In contrast, isomerisation suffered different fates for the Cl-containing and Cl-free catalysts. Catalysts after ox cycles showed only small effects of Sn on isomerisation. However, after oxy cycles Sn-containing catalysts gave enhanced isomerisation activity particularly for Sn(0.45%). Hydrogenolysis was also enhanced for Sn-containing catalysts on adding Cl, but for Cl-free catalysts an enhancement on adding 0.15% Sn was not increased by further addition of Sn. Sn had a stabilising influence on the selectivities as a function of the number of ox cycles carried out. However, after repeated oxy cycles there were bigger variations in behaviour than for Pt/Al_2O_3. In particular for Pt–Sn(0.45%)/Al_2O_3 additional cycles increased hydrogenolysis selectivity primarily at the expense of isomerisation. However, a result which partly differed from the rest was after an oxy cycle following either calc or six ox cycles for Pt–Sn(0.45%)/Al_2O_3 for which isomerisation selectivity was greatly increased at the expense of not only aromatisation and cyclisation but also hydrogenolysis. In both cases a further oxy cycle restored the isomerisation selectivity back towards the value after calc and also increased the hydrogenolysis selectivity to a value well above that after calc. Further oxy treatments maintained fairly stable behaviour apart from the steady increase in hydrogenolysis.

After ox cycles C_1/C_3 ratios were less for Pt–Sn(0.15%) than for Pt alone although increasing the Sn content had little further effect. The decrease in C_1/C_3 on adding Sn was even greater for Cl-containing catalysts. Also, after ox and particularly oxy cycles the C_1 and C_2 selectivities were much more similar to each other for Pt–Sn catalysts than for Pt/Al_2O_3.

As for Pt/Al_2O_3 coking increased the 3EP/2MH ratios and decreased the 2MH/3MH and 3EP/3MH ratios for all three Pt–Sn/Al_2O_3 catalysts after all the ox and oxy cycles. The values of and trends in the three ratios with repeated ox cycles were similar for the Pt and Pt–Sn catalysts suggesting that the addition of Sn in the absence of Cl was not having a significant effect. However, bigger effects were observed for catalysts containing Cl after oxy treatments. Whereas the amounts of 3MH product did not vary greatly with increasing Sn content despite the overall decrease in activity induced by Sn, the progressive addition of Sn increasingly reduced the amounts of 2MH and 3EP formed by (for 0.45% Sn) up to 90% reduction even though the proportional loss of activity (Figs. 1 and 2) was much less. Thus with Cl present the 2MH/3MH and 3EP/3MH ratios were much less for Pt–Sn catalysts than for Pt/Al_2O_3. Comparisons of the results for Sn-free and Sn-containing catalysts and for Cl-free and Cl-containing catalysts show that the significant changes in selectivity were caused by a mutual effect involving both Sn and Cl. Catalyst behaviour was again nearly unchanged over a series of oxy cycles particularly for Pt–Sn(0.45%)/Al_2O_3.

The addition of Sn to Pt/Al_2O_3 had little effect on selectivities to the cyclisation products DMCP and ECP in the absence of chlorine. However, cyclisation selectivities to both DMCP and ECP were reduced by oxychlorination of Pt–Sn catalysts in sequences of oxy cycles following calcination and reduction. Under these conditions, unlike the result for much more highly loaded catalyst (15), the ratio DMCP/ECP (ca. 1/6) did not change significantly. However, for Pt–Sn(0.45%)/Al_2O_3 after one oxy cycle following six ox cycles there was a large increase in selectivity to DMCP and no ECP detectable as a product. This result parallels the effect of oxychlorination for Pt(3%)–Sn(4.5%)/Al_2O_3 (15). A second oxy cycle, however, reverted the selectivities to those for catalyst after oxy cycles following a calc cycle rather than an ox cycle. Methylcyclohexane was a minor product of catalysis over the Pt–Sn catalysts with or without Cl present.

DISCUSSION

Characterisation of the present catalysts following treatments identical to those used here are presented in detail elsewhere (13). Additional information resulted from spectra of CO on catalysts which had been coked by heat treatment in a heptane/hydrogen mixture (3).

Pt/Al_2O_3

The dominant factor influencing changes in catalyst activity on changing from calc to ox (activity down) or oxy (activities similar), or from ox to oxy (activity up), or in sequences of ox (activity falling) or oxy treatments (activity stable) was Pt dispersion. Changes in dispersion showed little change in the overall nature of exposed Pt surfaces, except for the calc catalyst which compared with the ox and oxy catalysts showed a slightly higher proportion of low coordination Pt sites at the expense of Pt atoms in low index planes (13). However, the change from calc to ox generated negligible changes in selectivities confirming the absence of significant catalytic effects involving any changes in the relative proportions of different types of active site. Results for Pt/carbon showed that TOFs for isomerisation and aromatisation were not a function of particle size, whereas that for hydrogenolysis increased with increasing Pt dispersion (22). The corresponding selectivities as a function of increasing dispersion increased for hydrogenolysis, decreased for isomerisation, and were unchanged for aromatisation (22). Here the losses in dispersion caused by successive ox cycles showed a similar pattern with hydrogenolysis selectivity trending downward, isomerisation (and cyclisation) trending slightly upwards, and aromatisation staying about the same. The better dispersions after oxy rather than ox cycles also gave trends in the same sense with hydrogenolysis being favoured at the expense of aromatisation, isomerisation, and cyclisation. The infrared spectra (13) showed that the Pt particles had similar external forms after ox and oxy cycles with no significant change in the relative proportions of different exposed forms of Pt site. The present results therefore also imply that the TOF for hydrogenolysis must have become more favourable than TOFs for the other reactions with decreasing Pt particle size.

Changes of the C_1/C_3 ratio in hydrogenolysis reactions have been used as an indication of the relative extents of catalysis by metallic and acidic sites in bifunctional catalysts, C_1 being the main product at metal sites and C_3 the main product at acid sites (23). However, this is probably an oversimplification. Despite the low reaction temperature used here acid catalysis cannot be discounted particularly for Cl-containing catalyst. The C_1/C_3 ratio was remarkably stable during the dispersion changes accompanying an ox cycle after calc, or repeated ox cycles. One contributing factor would be that the Pt surfaces were similar to each other as indicated by the infrared results (13), a second factor being that catalysis on acid sites was probably unaffected by the pretreatment conditions. The small decrease in C_1/C_3 accompanying the addition of chlorine in oxy cycles could be related to increased acid catalysis by an acid-strength enhancing effect of chlorine on alumina. However, chlorine on the support (24) or on the metallic Pt (13, 15) may also generate electron-deficient Pt sites which provide a route to hydrogenolysis products involving a lower activation energy and faster reaction rate (24). This effect would contribute to the overall enhancement in hydrogenolysis selectivity induced by oxy treatments, but in contradiction to the present result might be expected to favour C_1 rather than C_3 if only the balance between metal catalysis and acid catalysis is considered (23). However, variations in selectivity for different types of Pt site must also be considered.

As here, Coq *et al.* (25) reported for hexane hydrogenolysis over Cl-free catalyst that there was a slight shift from demethylation to central fission with improving Pt dispersion. However, here the change in C_1/C_3 may not have been solely dependent on particle size effects but there may also have been specific effects due to chlorine, either on the support, on the metal, or on both. Electronic factors are known to influence hydrogenolysis selectivity (26). The infrared results suggested that electronic effects of Cl on medium or large arrays of Pt atoms in Pt/Al_2O_3 were negligible, although an electronic effect involving high energy low-coordination sites was not ruled out (13). A possible analogy is the increase in hydrogenolysis activity induced by oxygen treatment of kinked Pt surfaces (27). If any electronic effect of Cl only influences low-coordination sites and these sites therefore become more active, then a resulting contribution in a positive sense to the observed trend in C_1/C_3 would require that central fission was more favoured relative to terminal fission on low coordination sites than on high coordination sites. This is unlikely as the addition of Sn, which preferentially blocks corner and edge sites, favours central fission and terminal fission is preferred at edge, kink, and corner sites (25). It therefore appears that electronic effects of Cl on the behaviour of the metal component of Pt/Al_2O_3 in heptane hydrogenolysis are small.

Increased selectivity for isomerisation with respect to hydrogenolysis with increasing particle size (5) is consistent with the present effects of both oxychlorination and repeated ox cycles. Variations in selectivities to specific isomerisation products also reflected particle size effects in that bigger particles, favoured either by repeated ox cycles or by ox treatments rather than oxy treatments, tended to cause decreases in both 2MH/3MH and 3EP/3MH whereas 3EP/2MH was insensitive to change. The implication if a cyclic mechanism was significantly influencing the formation of the isomerisation products is that decreasing particle size apparently favoured ring closure involving a terminal C_1 atom in heptane and either C_5 or C_6, thus giving adsorbed methylcyclohexane or ethylcyclopentane intermediates (27), in preference to ring closure involving C_2 and C_6 which would lead to 1,2-dimethylcyclopentane as intermediate (27). Cyclisation involving C_1C_6 giving adsorbed cyclohexane might be expected, however, to lead predominantly to toluene as the final product. No nonselective cyclic mechanism should statistically give 2MH > 3MH. The variations of 2MH/3MH ratio from ca. 3 for well-dispersed oxychlorinated catalyst to ca. 1.5 for sintered catalyst after several ox cycles suggest, therefore, that a bond shift mechanism must have been important for catalysts both after ox and oxy cycles. A similar conclusion has been reached for the corresponding hexane reaction over poorly dispersed Pt/Al_2O_3 (5, 25).

An effect resulting from oxychlorination may be related to the electron withdrawal from Pt induced by chlorine on either the support (24) or the metallic particles (13, 15). Decreasing electron density on Pt has been proposed to enhance adsorption involving C–H cleavage of terminal CH_3 groups rather than cleavage of central CH_2 groups (28, 29). Electron loss from Pt induced by oxychlorination might therefore be expected to enhance 2MH and 3EP over 3MH, in accordance with the present results, and to enhance ethylcyclopentane formation relative to 1,2-dimethylcyclopentane, which is contrary to the present results. However, the identity of the infrared band positions for CO on arrays of high coordination Pt atoms in Pt/Al_2O_3 after ox and oxy treatments (13) suggests that any electronic effect of Cl on Pt sites must have been specific to low coordination Pt atoms at steps, edges or kinks in exposed surfaces. Spectra of CO on ensembles of high-coordination Pt atoms did not suggest that the electron densities of the Pt atoms were influenced by surface chlorine.

Despite the large losses (ca. 55–60% decrease) in activity induced by catalyst coking during time on line and the significant changes in the relative proportions of different types of Pt site caused by coking (3), variations with time on line of the selectivities for aromatisation, cyclisation, isomerisation, and hydrogenolysis were only small. In view of conclusions that hydrogenolysis requires larger ensembles of Pt atoms than cyclisation or isomerisation (7, 20, 30, 31) and that coke is deposited preferentially on hydrogenolysis sites (32, 33) it is perhaps surprising that the small changes in selectivities with time were in the sense of an increase in hydrogenolysis and decreases in the other reactions for catalysts both with and without added chlorine. Infrared spectra of adsorbed CO showed that coking heavily poisoned large aggregates of Pt atoms in arrays akin to the surfaces of low index planes, partially poisoned medium size ensembles, and generally reduced ensemble size (3). The present results demand that the residual ensembles were as effective in hydrogenolysis reactions as the larger ensembles present before coking. A plausible implication of this conclusion and the infrared results (3) is that the coke was not evenly spread but existed in patches on medium-to-large ensembles of Pt atoms.

Coking may also affect low coordination Pt sites (3, 34). Opposing effects of coking of high and low coordination sites on isomerisation and central C–C splitting of butane over Pt/SiO_2 have been reported (34), coke generated isothermally favouring deposition at low coordination sites which led to an enhancement in isomerisation selectivity, whereas coke on low index planes decreased isomerisation selectivity. Low coordination sites may include edges and corners (34). However, spectra of adsorbed CO on Pt/Al_2O_3 suggested that whereas sites of intermediate coordination, possibly edges and steps, were heavily poisoned by coke, sites of the lowest coordination, possibly corner, apex, or kink sites, were resistant to coking (3). Thus, here, a balance between different influences of coke deposition on high coordination and intermediate coordination sites apparently resulted in only slight variations in selectivities with coking. This conclusion was independent of particle size effects induced by sintering or oxychlorination, and of electronic effects due to chlorine. One explanation would be that the isomerisation and hydrogenolysis products were derived from a common intermediate, for example, a $3C\alpha\gamma$ complex (35). A further requirement is that the availability of H atoms adjacent to the active sites (36) was not impaired by coking despite a reduction in the concentration of surface hydrogen (37, 38). The exposed lowest coordination Pt sites in the present catalysts were resistant to coking (3) and by analogy to the behaviour of kink sites on Pt (27) would have therefore retained their activity for the dissociation of hydrogen. A decrease in H atom availibility would have favoured isomerisation over hydrogenolysis (35). The enhancement in selective hydrogenolysis induced by surface oxygen on Pt has been linked specifically to the presence of kink sites (27). If an analogous effect occurred here due to surface chlorine in the presence of kink sites then this also would have been unaffected by coking.

A reduction of the C_1/C_3 ratio with coking has been attributed to greater deactivation of metal sites than of acidic sites on the oxide support (23). A small effect in the same sense occurred here after a calc cycle or the first three subsequent ox cycles. However, sintering which accompanied further ox cycles had the reverse effect in accordance with results for coking caused by butane hydrogenolysis over a Pt(111) surface (39). Here, as before for butane (39), multiple C–C bond breaking must have occurred since the *n*-alkane product ratios were in the sense $C_1 \gg C_6$, $C_2 \gg C_5$, and $C_3 > C_4$ and branched chain isomers with $<C_7$ were very minor products. Szanyi *et al.* (39) proposed that carbon on the Pt(111) surface increased multiple hydrogenolysis through an electronic accepting effect of carbon which strengthened the interactions between hydrocarbon molecules and surface Pt atoms. However, others have concluded that electron transfer from coke to Pt occurs (40–42), this being consistent with infrared band shifts for adsorbed CO (3). An alternative explanation would be that hydrogenolysis of the surface carbon deposit itself (43) would lead to lower hydrocarbons, particularly methane. The effects of coke on catalysts after oxy treatments were similar to those for the more highly sintered Cl-free catalysts despite the improvement of dispersion induced by chlorine. This apparent anomaly further suggests that it was not only particle size effects which affected the behaviour of chlorine containing catalysts. Chlorine was probably retained on the Pt surfaces after reduction (4, 13, 15) and therefore the combined effects of coke and electron-withdrawing Cl-adatoms may have enhanced hydrogenolysis selectivity involving the formation of methane. However, the infrared data showed that any electronic effect of chlorine was probably small and confined to low-coordination Pt sites. A further contributing factor might involve the poisoning by coke of sites on alumina whose acidity was increased by surface chlorine, and which were, therefore, more active for cracking reactions involving central fission (23). Chlorine favoured enhanced alumina acidity and reduced C_1/C_3, but poisoning of the sites by coke would favour an increased C_1/C_3 ratio.

The biggest effects of coking were on the ratios of isomerisation products. The marked decrease in 2MH/3MH ratio with coking parallelled similar effects which have been reported for reactions of other alkanes over both Pt/Al_2O_3 (44) and single crystal Pt (38). Christoffel and Paál (45) studied reactions of hexane over Pt/Al_2O_3 and reported a coking-induced decrease of the 2-methylpentane/3-methylpentane ratio. The relative amounts of poisoning of isomer formation by coking was in the sequence $2MH > 3EP > 3MH$. To be accounted for by a cyclic mechanism (27) this sequence would imply that coke preferentially poisons ring closure in the sequence $C_1C_6 > C_1C_5 > C_2C_6$, and hence coke poisons reaction of terminal CH_3 groups more than reaction of central CH_2 groups. However, high 2MH/3MH ratios (Table 1) emphasise that there were significant contributions from bond-shift mechanisms. The present results would also be consistent with a bond-shift mechanism for 2MH formation which would involve an adsorbed $3C\alpha\gamma$ intermediate (35). Although these effects were generally not reflected in the comparatively small effects of coking on the selectivities to cyclic products ECP and DMCP, the results for sintered Cl-free catalysts after ox cycles 4, 5, and 6 did show a significant increase in DMCP relative to ECP after coking which is consistent with the present conclusion. Furthermore, conclusions that coke donates electronic charge to Pt (40–42) and that enhanced electron density of Pt favours reaction of weaker secondary C–H bonds more than stronger primary C–H bonds in hydrocarbon reactions (28, 29) are also consistent with an effect of coke favouring fission of central rather than terminal C–H bonds. Electronic effects probably influenced, together with site-blocking effects of coke, the relative selectivities to isomerisation products. One reason for the poisoning effects of coke on ECP and 3EP formation might be that the 1,5-cyclisation pathway itself leads to coking (46).

$Pt–Sn/Al_2O_3$

The general loss in activity on introducing Sn to the Cl-free Pt/Al_2O_3 catalyst is consistent with the reduced uptakes of CO by Pt–Sn/Al_2O_3 and with infrared results (13) which showed that Pt^o clusters or particles were partly covered by Sn^o. In particular a proposal that step and kink sites are extremely active for bond cleavage reactions (27) is compatible with the losses of activity resulting from the high level of coverage of these sites on the addition of Sn (13). The latter effect was greater for Cl-containing catalyst in accordance with an effect of chlorine which promoted greater intimacy between Pt and Sn and a higher coverage of active low-coordination sites by Sn (13). This provides an explanation, at least in part, for the significant decrease in activity of Pt–Sn/Al_2O_3 caused by oxychlorination which is in contrast to the results for Pt/Al_2O_3 where oxychlorination promoted both improved dispersion and higher activity. Coq *et al.* (25) concluded for Cl-free catalysts that the Pt surface is diluted by Sn leaving smaller aggregates of Pt atoms and that low-coordination sites are selectively inhibited for catalysis. The present results combined with infrared data for the same catalysts (13) show that this effect is magnified for Cl-containing catalyst.

The addition of Sn to Pt catalysts may either increase or decrease hydrogenolysis selectivity (9, 46, 47). For catalyst containing small clusters of Pt adjacent to a tin oxide-modified alumina surface (13) the Pt atoms will be electron deficient and this would be expected to favour hydrogenolysis (9, 24) in accordance with the behaviour of Cl-free catalysts here, and also to influence selectivities to specific hydrogenolysis products (26). However, there is also a geometric effect of Sn (27, 39) which could account for the present results. The enhancement in hydrogenolysis selectivity and the reductions in cyclisation and aromatisation selectivities induced by the addition of Sn are the reverse of the effects of repeated ox cycles, which led to increasing Pt particle size in Pt/Al_2O_3, but are in the same sense as the effects of oxychlorination, which led to decreasing particle size. These results support the contention (25) that after the initial blocking of low-coordination Pt sites by Sn (13, 27), further Sn addition diluted the Pt surface with Sn and changed the catalytic properties towards those characteristic of smaller particles. In support of this conclusion the infrared data showed that Sn blocked sites for the adsorption of CO in a bridging configuration and for the linear adsorption of CO on highly coordinated Pt atoms in arrays akin to those in low-index planes (13). Smaller arrays of Pt atoms partially decorated by patches of Sn^o remained available for CO adsorption and hence also for catalysis.

In contrast to the present results, hexane hydrogenolysis over Pt(1.4%)/Al_2O_3 and Pt(1.4%)–Sn/Al_2O_3 catalysts containing much lower Sn/Pt molar ratios than those used here showed a slight shift from central fission to terminal fission on the addition of Sn (25). Here the decrease in C_1/C_3 on the addition of 0.15% Sn to Pt(0.3%)/Al_2O_3 and the subsequent stability of C_1/C_3 with further Sn addition may be related to the blocking effect of the initial addition of Sn on highly active low-coordination Pt sites and to an enhanced proportion of catalysis on acidic sites. High coordination sites on low-index planes favour central C–C hydrocarbon fission whereas terminal fission giving methane preferentially occurs at low-coordination edge, kink, or corner sites (25). The C_1/C_3 ratio was even less for Cl-containing Pt–Sn/Al_2O_3 catalysts in accordance with the Cl-induced additional blocking of low-coordination sites by Sn (13). However, unlike the result for Pt/Al_2O_3, Cl also had an electron withdrawing effect on high-coordination Pt atoms in small exposed arrays (13) and this could have led to an enhancement in hydrogenolysis activity (24) specifically involving central C–C fission (25). The overall effects of oxychlorination on C_1/C_3 derived from catalysis by metal sites may, therefore, involve both the geometric effect of enhanced site blocking by Sn and an electronic effect due to surface chlorine. Addition of chlorine would also increase the acidity of the alumina support, thus enhancing acid catalysis, which in accordance with the present result would favour C_3 rather than C_1 (23). However, the effect of chlorine in reducing C_1/C_3 was much smaller for Pt than for Pt–Sn, and, therefore, a dominant explanation of the Cl-effect on C_1/C_3 involving acid catalysis would require that Cl enhances the surface acidity of the SnO_x-modified alumina surface much more than for alumina alone. A further, at least contributing factor would be that, because the effect of Sn on Pt/Al_2O_3 is to reduce catalytic activity by a factor of ca. 3, the proportion of the total catalysis occurring on acid sites was higher for Pt–Sn than for Pt and this led to a larger influence of chlorine on Pt–Sn/Al_2O_3 than Pt/Al_2O_3.

Identically treated Pt–Sn/Al_2O_3 catalysts with a ten times higher Pt and Sn content than those here gave similar C_1/C_3 ratios in the absence of chlorine, when Pt^o particles were decorated with Sn^o, but gave much smaller amounts of C_1 compared to C_3 after oxychlorination had converted the majority of the Pt present to a 1 : 1 Pt^o–Sn^o alloy (15). As before (13), therefore, the present results could not apparently be attributed to a significant presence of Pt^o–Sn^o 1 : 1 alloy particles. Furthermore, unlike the enhancement in hydrogenolysis selectivity induced by oxychlorination here, hydrogenolysis selectivity decreased on oxychlorination for a much more highly loaded catalyst which contained 1 : 1 Pt^o–Sn^o alloy as the dominant metallic function (15). Alloy formation is known to suppress intermediate adsorbed complexes which lead to hydrogenolysis products (35). The enhancement in C_2 formation caused by the addition of Sn reflects similar effects of Sn (39) and Re addition (26) reported before.

The negligible effects on isomerisation selectivities of the addition of Sn to Cl-free Pt/Al_2O_3 suggests that the blocking effects of Sn on low-coordination Pt sites (13) had a less significant effect on isomerisation reactions than on hydrogenolysis. This implies that either, as for Pt/Al_2O_3, isomerisation selectivity was independent of the particular type of Pt site, or Pt sites which were dominant in the isomerisation reactions existed in two-dimensional arrays of high-coordination Pt atoms in exposed surfaces partially decorated with Sn^o (13). If interactions between the Pt atoms and alumina-supported oxidic tin caused electron transfer from Pt, then the results suggest that isomerisation reactions were relatively insensitive to the induced electron deficiency at active sites. This is also borne out by the similar isomerisation selectivities for Cl-free and Cl-containing Pt–Sn(0.15%)/Al_2O_3, Pt sites in the latter being affected by an e-withdrawing effect of adsorbed chlorine (13). However, despite reverting to the typical result after a second oxy treatment, Pt–Sn(0.45%)/Al_2O_3 was anomalous in that the first oxy cycle after calc or ox gave unusually high isomerisation activities. The infrared and chemisorption data gave no clear explanation for these results as there was nothing unusual about the CO adsorption uptakes or infrared spectra after the first oxy cycles as opposed to later cycles, apart from catalyst after the first oxy cycle giving the lowest CO uptake and infrared band intensities (13). One conclusion would be that the time of the first oxychlorination was insufficient to attain equilibrium between the bulk and surface species present for catalyst containing 0.45% Sn. The anomalous behaviour did not occur for Pt–Sn(0.30%)/Al_2O_3. A conclusion that hexane isomerisation selectivity is enhanced on very small Pt ensembles (48) suggests that here the first oxychlorination followed by reduction generated arrays of Pt atoms which were highly decorated by Sn^o and therefore gave small exposed Pt ensembles, whereas subsequent oxychlorination followed by reduction attained equilibrium spreading of tin species over the alumina support thereby enlarging Pt ensemble size by the partial clustering of Sn^o decoration on Pt surfaces. The generation of larger ensembles would also explain why the loss of isomerisation selectivity after the second oxy treatment was compensated primarily by an increase in hydrogenolysis selectivity which is favoured on larger ensembles (20, 31). Increased isomerisation relative to hydrogenolysis has been related to increasing particle size for catalysts containing Pt as the sole metal component (5). The CO uptake results for Pt–Sn(0.45%)/Al_2O_3 showed that the first oxychlorination generated a substantial loss in Pt surface which was partially recovered by subsequent oxy cycles. This loss can at least in part be attributed to loss of ensemble size resulting from Sn decoration (13). Increased particle size may also have been a contributing factor to the loss of Pt sites and therefore to the selectivity changes. However, this conclusion is confused by the oxychlorination-induced additional blocking of low-coordination Pt sites by Sn (13). Results for pentane reaction over Pt/SiO_2 (49) suggest that a reduction in the proportion of low coordination Pt sites might be expected to increase isomerisation relative to hydrogenolysis, a conclusion which is consistent with the present result for the first oxy treatment.

The similarity between the ratios of the isomerisation products 2MH, 3MH, and 3EP for Cl-free Pt/Al_2O_3 and Pt–Sn/Al_2O_3 contrasts with the results after oxy treatments for which the effects of chlorine were to induce decreases in all three ratios 2MH/3MH, 3EP/3MH, and 3EP/2MH. In addition to the formation of 2MH primarily by a bond-shift mechanism, 3EP is derived from a 1,5-cyclic intermediate whereas 3MH may be derived from routes involving 1,6-(low selectivity to toluene suggests this is negligible), 1,5-, and 2,6-cyclisation (27). Despite the uncertainty concerning the relative amounts of isomerisation products derived from bond-shift and cyclic mechanisms, the present changes induced by chlorine would imply, at least in terms of cyclic mechanisms, that oxychlorination favours 2,6-cyclisation relative to 1,6- or 1,5-cyclisation, as further evidenced by the promotion of DMCP over ECP as cyclic product. This is the reverse of the effect for Sn-free catalyst, for which improved dispersion after oxychlorination favoured ring closure at C_1. The effects of adding 0.15% Sn to Cl-containing Pt/Al_2O_3 or of adding higher amounts of Sn, however, also favoured 2,6-cyclisation showing that the enhanced extent of 2,6-cyclisation relative to cyclisations involving terminal C–H fission of heptane was a mutual effect of Sn and Cl. Sparks *et al.* (50) similarly reported for reactions of octane over Cl-containing catalyst that tin altered the cyclisation pathway to favour fission of two of the weaker secondary C–H bonds than a stronger primary C–H bond.

Oxychlorination of Pt–Sn/Al_2O_3 favours enhanced intimacy of Sn and Pt, increased blocking of low coordination sites by Sn, and the retention of small ensembles of Pt which are influenced by the e-withdrawing effects of chlorine (13). High Pt dispersion favours cyclisation involving C_1 in heptane implying that low-coordination sites favour C_1 cyclised intermediates in isomerisation. The blocking of these sites by Sn therefore would hinder the formation of 1,6- and 1,5-cyclic intermediates in accordance with the present results. Catalysts with ten times higher Pt and Sn loadings, for which a Pt^o–Sn^o alloy was formed after oxychlorination and reduction, gave a parallel result in that 1,2-dimethylcyclopentane became the only cyclisation product (15). For Pt–Sn(0.45%)/Al_2O_3, after a single oxy cycle DMCP was the sole cyclisation product with no ECP, although the latter reappeared as a product after further oxy cycles. Thus in terms of cyclisation selectivity the behaviour of the catalyst surface tended towards that of alloy, further supporting the view that the first oxy cycle generated a Pt surface which also contained a high proportion of Sn, but that further oxy treatments redistributed some of the Sn.

The electronic effects of chlorine (13) or of the SnO_x-modified alumina surface (9) were to withdraw electronic charge from exposed Pt, and this might be expected (28, 29, 51) to promote reactivity of terminal CH groups rather than central CH groups. This is the reverse of the observed result. Previous observations that, as here, Sn favours cyclisation pathways involving breaking of two secondary C–H bonds were attributed to less electron deficient Pt in Pt–Sn/Al_2O_3 than in Pt/Al_2O_3 (28, 29, 50, 51). Infrared spectra of CO on the present catalysts showed that the addition of Sn to Cl-containing Pt/Al_2O_3 in fact generated more e-deficient Pt (13). This apparent discrepancy is explicable in terms of whether (9) the Sn forms a 1 : 1 alloy with Pt (15) or, as here (13), the Pt interacts with an SnO_x-modified alumina surface. However, the similar oxychlorination-induced trends in selectivities to individual isomerisation and cyclisation products for the present low-loaded catalysts and a high-loaded catalyst containing Pt–Sn alloy (15) are not to be expected if the underlying cause is electronic because the electronic effect of Sn on Pt will be opposing for the two types of catalyst (9). Thus the changes in selectivity were apparently dominated by geometric effects of Sn in blocking Pt sites (13) rather than electronic effects. Changes in catalytic behaviour after repeated oxidation/reduction regeneration treatments following catalytic use have been reported for Cl-containing Pt–Sn/Al_2O_3 (52, 53), and in particular the balance between Sn^o on the Pt surface and Sn(II) on the support has been discussed (52). As here, the interaction of Pt with oxidic tin on alumina enhanced catalyst stability for catalytic conversions, and Sn^o inhibited catalytic activity of supported Pt–Sn catalysts (52). A further important factor, however, is the extent of catalysis on acid sites which would be enhanced in strength by Sn (54) or Cl leading to increased internal rather than terminal C–H fission in accordance with the present results.

The decrease in aromatisation selectivity on adding Sn to Pt/Al_2O_3 and the enhancement of this effect after the addition of chlorine is compatible with a geometric effect due to the partial decoration of Pt surfaces by Sn. A Pt(3%)–Sn(4.5%)/Al_2O_3 catalyst which contained 1 : 1 Pt^o–Sn^o alloy after oxychlorination/reduction gave no aromatisation products under the conditions of the present experiments (15). The similar extreme result for Pt(0.3%)–Sn(0.45%)/Al_2O_3 for the first oxy cycle after a series of ox cycles could be interpreted as implying that alloy had been formed. After a further oxy cycle (not shown) catalyst also retained zero aromatisation activity. However, the bulk of the infrared (13) and catalytic evidence is not consistent with alloy formation, although the enhanced intimacy of Pt and Sn induced by chlorine severely impeded cyclisation involving terminal C_1 atoms in heptane and therefore C_1C_6 cyclisation leading to toluene was inhibited. Davis *et al.* (38) concluded that low-coordination step and kink atoms were particularly effective at catalysing aromatisation of heptane. The blocking of low-coordination Pt sites by Sn and the enhancement of this effect in the presence of chlorine (13) is therefore consistent with the inhibition of aromatisation by Sn and Sn + Cl. Furthermore, if an ensemble of three Pt atoms is required for aromatisation (20) and this is more demanding than the site requirement of other reactions of heptane, then partial decoration of Pt surfaces which is enhanced by oxy treatments would have a greater inhibiting effect on aromatisation than the other reactions. Coq and Figueras (40) also reported the inhibition of aromatisation by tin but invoked an electronic effect of Sn on Pt as the prime cause of the effect.

The trends in Pt–Sn/Al_2O_3 catalyst selectivities with time on line may be attributed to coking (6–12) and in general resembled the corresponding trends induced by the addition of Sn or both Sn + Cl to Pt/Al_2O_3. Thus coking marginally enhanced central C–C fission compared with terminal fission in hydrogenolysis reactions, enhanced the formation of 2,6-cyclised intermediates relative to 1,6- and 1,5-cyclised intermediates in cyclisation reactions, induced the same trends as Sn in isomer selectivities, and partially inhibited aromatisation. Coke and Sn modify Pt in a similar way (10, 55), a contributing factor probably being increased acidity of the oxide support. The infrared spectra of adsorbed CO showed that coke heavily poisoned intermediate coordination Pt sites possibly at steps and edges, partially poisoned small ensembles of high-coordination Pt atoms, and heavily poisoned Pt arrays akin to low index planes (13). These effects were similar to the site blocking or decoration effects of Sn. Thus the dominant effects of coke appear to be geometric rather than electronic. In particular, the poisoning of step and edge sites by coke (13) would disfavour terminal fission relative to terminal fission since “end-on” impinging of heptane molecules on these sites may specifically favour C_1 splitting. Coke and Sn differed significantly in their behaviour towards the lowest coordination Pt sites present in Pt/Al_2O_3 which were resistant to coking. However, the sites were blocked by Sn and therefore did not influence the time-dependent behaviour of Pt–Sn/Al_2O_3.

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