The effects of Cl-induced alloying in Pt–Sn/Al_2O_3 catalysts on butane/H_2 reactions

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The effects of oxidation/reduction regeneration treatments, with and without 1,2-dichloropropane present as a chlorinating agent, on the structure of Pt(3%)–Sn(4.5%)/Al_2O_3 catalysts have been correlated with selectivities for butane/H_2 reactions. Particles of Pt^0 fin Cl-free catalysts were partly covered by Sn^0, but retained exposed ensembles of Pt atoms which were active for isomerisation, hydrogenolysis and dehydrogenation reactions, the latter becoming dominant at high reaction temperatures. Coking reduced Pt ensemble size and, hence, also favoured high selectivities for dehydrogenation as hydrogenolysis and isomerisation sites became poisoned. In contrast, the addition of 1,2-dichloropropane in an oxychlorination step before reduction promoted 1 : 1 Pt^0–Sn^0 alloy formation after reduction, the proportion of the total Pt in alloy being enhanced by increasing 1,2-dichloropropane concentration and oxychlorination temperature. The alloy surfaces were inactive for isomerisation and hydrogenolysis reactions, giving dehydrogenation as the sole catalytic reaction.

KEY WORDS: Pt–Sn/Al_2O_3 reforming catalyst; butane/H_2 catalysis on Pt–Sn; chlorination of Pt–Sn catalysts

1. Introduction

The use of Pt-containing catalysts in hydrocarbon reforming reactions leads to coking and metal sintering which result in loss of activity, change in selectivities and the need for occasional oxidative regeneration followed by reduction to restore catalytic efficacy. Heat treatment of used Pt/Al_2O_3 in oxygen will remove carbonaceous deposits [1] but in the absence of chlorine may induce further sintering after subsequent reduction [2,3]. Oxychlorination, however, not only removes coke but also favours enhanced Pt dispersion [3,4]. In contrast for Pt(3%)–Sn(4.5%)/Al_2O_3 oxychlorination/reduction treatment decreased Pt dispersion and reduced the catalytic activity for heptane/H_2 reactions [5]. Reduced catalytic activity after oxidative regeneration in the presence of chlorine was ascribed to the presence of Pt–Sn alloy particles [5]. Lieske and Völter [6] established that the presence of chlorine in the preparation of Pt–Sn/Al_2O_3 promoted Pt–Sn alloy formation. Arteaga *et al.* [5] showed that heating Pt(3%)–Sn(4.5%)/Al_2O_3 in oxygen at 823 K in the absence of chlorine gave Pt^0 particles with O-adatoms, and subsequent reduction in H_2 gave Pt^0 particles which were partially covered with Sn^0 [5]. In contrast, the addition of 1,2-dichloropropane in the oxidation step generated separate Pt^0 and SnO_2 crystallites, which on subsequent reduction gave 1 : 1 Pt^0–Sn^0 alloy. Studies of Pt–Sn/Al_2O_3 containing 0.3% Pt similarly showed that the presence of chlorine in the oxidative treatment favoured closer intimacy of Pt and Sn in the reduced catalyst [3].

Arteaga *et al.* [5,7] studied heptane/H_2 reactions over Pt–Sn/Al_2O_3 after oxidation/reduction and oxychlorination/reduction treatments in an attempt to correlate selectivities for isomerisation, cyclisation, aromatisation and hydrogenolysis reactions with catalyst structure. However, the high number of products formed hampered simple interpretation of the results specifically in terms of the effects of alloy formation. The present work has involved butane/H_2 reforming as a less complex test of the effects of alloy formation after a variety of catalyst pretreatments with and without chlorine present. Humblot *et al.* [8] studied isobutane/H_2 reactions over Pt–Sn/SiO_2 and contrasted the mechanisms for hydrogenolysis and isomerisation over non-alloyed Pt and for dehydrogenation to isobutene over Pt–Sn alloy surfaces. An intention here was to test whether a similar contrast of behaviour for butane/H_2 over Pt–Sn/Al_2O_3 could be correlated with changes in catalyst structure induced by the absence or presence of 1,2-dichloropropane during catalyst regeneration treatments and monitored by X-ray diffraction.

2. Experimental

Chlorine-free catalyst designed to contain 3 wt% Pt and 4.5 wt% Sn after reduction was prepared from a dispersion of Degussa non-porous γ-Al_2O_3 (surface area 110 $m^2\ g^{-1}$) in an aqueous solution containing tetraammineplatinum(II) hydroxide and tin(II) oxalate. Evaporation to dryness at 333 K was followed by heating in air (383 K, 15 h) and then dry CO_2-free air (673 K, 1 h). The catalyst was placed in a quartz reactor and heated in an air flow (673 K 1 h) before various sequences of treatments involving oxidation in a flow of air (1 h) and reduction (this constitutes an oxidation/reduction cycle and is designated *oxid*), oxychlorination (1 h) in a flow of air containing 1,2-dichloropropane and reduction (an oxychlorination cycle, designated *oxy*), or use as a catalyst for the butane/H_2 reaction (designated *react*). With one exception, reduction was always in a flow of H_2 for 1 h at 673 K. Temperatures were varied in the

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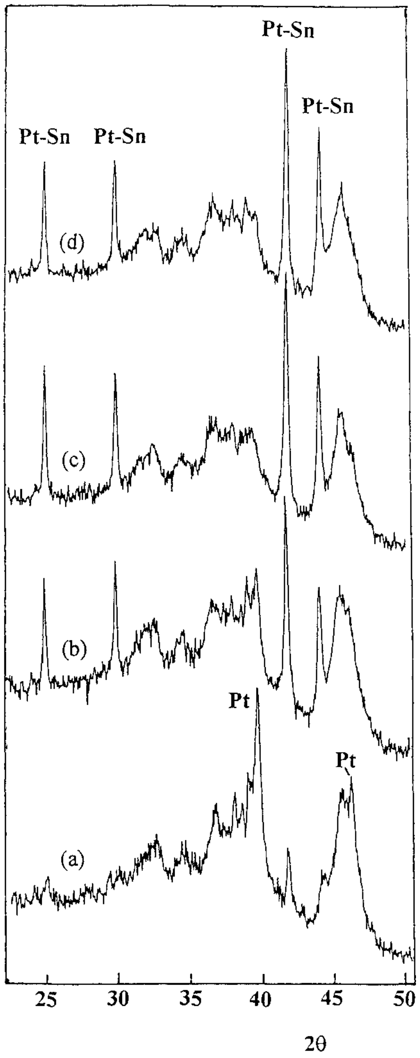

Figure 1. XRD patterns as a function of oxychlorination temperature: (a) 373, (b) 423, (c) 473 and (d) 788 K.

ranges 573–823 K for oxidation, 373–823 K for oxychlorination and 593–820 K for reaction. Specific experiments are referred to in the results section by including the oxidation or oxychlorination temperature, the amount of injected 1,2-dichloropropane in an oxychlorination step, and, where appropriate, the reaction temperature. For example, *oxy*823(15)/*react*673 means oxychlorination at 823 K with 15 $\mu l\,h^{-1}$ 1,2-dichloropropane, followed by the standard reduction and reaction at 673 K. Amounts of liquid 1,2-dichloropropane vaporized into the air stream during oxychlorination were in the range 4.2–77.0 $\mu l\,h^{-1}$. The Pt and Sn loadings in catalysts were consistent with a Sn/Pt molar ratio of 2.47/1.

Powder X-ray diffraction (XRD) patterns of samples after catalytic use were recorded using Cu K_α radiation at 1° 2θ min^{-1} . Catalysts were discarded after XRD analysis. A Hewlett–Packard 6890 GC System with a 5973 mass selective detector was used to analyse the products from butane/H_2 reactions over 150 mg catalyst in an H_2 flow of 25 $ml\,min^{-1}$ at 1 atm pressure and with (H_2/C_4H_{10}) molar ratios in the range (10/1)–(50/1). For all experiments other than those involving variation of (H_2/C_4H_{10}), the molar ratio of reactants was kept at (10/1).

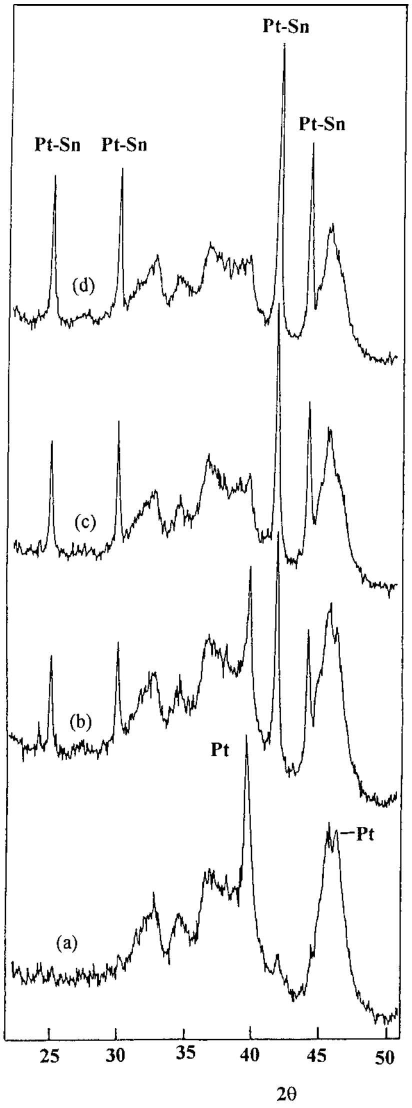

Figure 2. XRD patterns as a function of 1,2-dichloropropane injection rate during oxidative treatment at 823 K: (a) 0, (b) 4.2, (c) 10.2 and (d) 40.5 $\mu l\,h^{-1}$.

3. Results and discussion

3.1. X-ray diffraction analysis

Figures 1–3 exemplify the XRD results after a variety of catalyst pretreatments. All XRD patterns contained five peaks in the 2θ range 30–46° due to the alumina support. The patterns for *oxid*823 and *oxid*753 in figures 2(a) and 3(a), respectively, are typical of the results for catalyst that contained no chlorine. A pair of dominant peaks at 39.8° and 46.2° (both overlapping peaks for alumina) were due to Pt^0 crystallites. Maxima which could be attributed to Pt–Sn alloy [6,9–11] were very weak showing that *oxid* treatments of catalyst precursors which contained no Cl predominantly

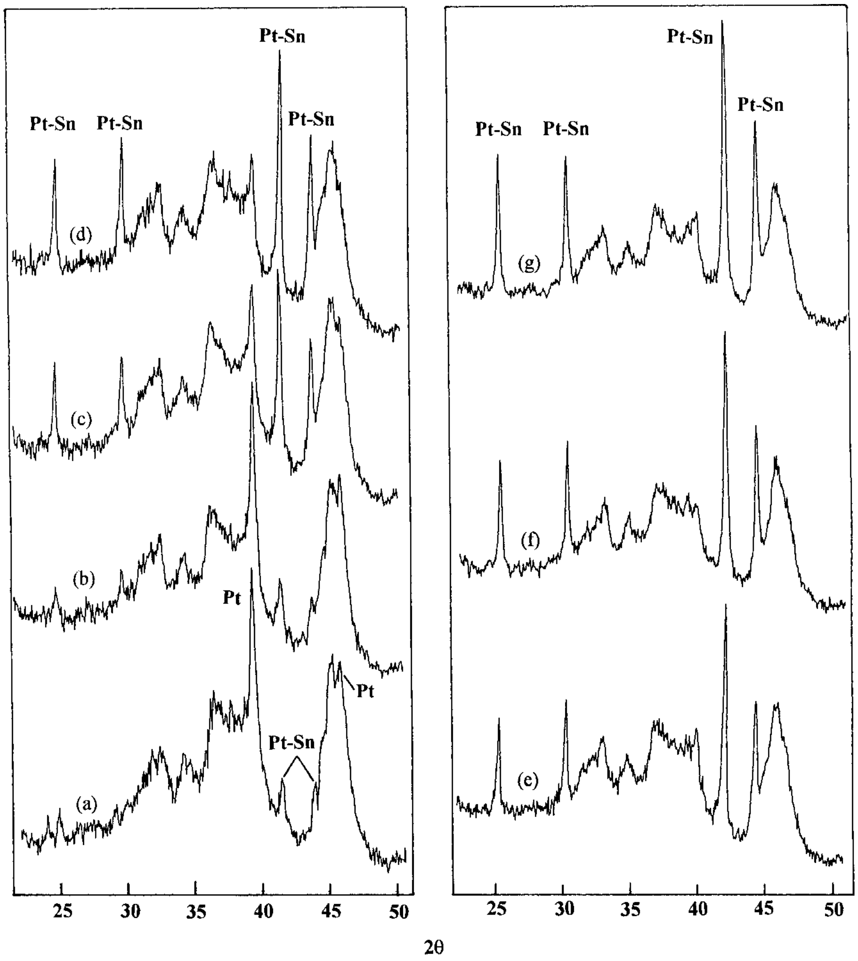

Figure 3. XRD patterns as a function of 1,2-dichloropropane injection rate during oxidative treatment at 753 K: (a) 0, (b) 1.73, (c) 3.7, (d) 7.9, (e) 11.4, (f) 22.9 and (g) 117 $\mu\mathrm{l\,h^{-1}}$.

generated Pt^0 particles with only very low amounts of Pt–Sn alloy.

XRD patterns were recorded for thirteen catalysts after *oxyT*(15) cycles with temperatures of oxychlorination T (K) in the range $823 \geqslant T \geqslant 373$. The result in figure 1(a) for 373 K shows Pt–Sn peaks that are more intense than those for catalyst with no added Cl, but non-alloyed Pt^0 remained the dominant form of Pt after reduction. However, raising the temperature of oxychlorination to 423 K reversed the relative intensities of the XRD peaks (figure 1(b)) showing that hexagonal 1 : 1 Pt^0–Sn^0 alloy [6,9–11] had become the dominant product containing Pt, although a proportion of the Pt was present as Pt^0. For $T = 473$ K all the reduced Pt was present in alloy form, figure 1(c) showing no peaks for Pt alone. An identical result was obtained for all higher temperatures up to 823 K (figure 1(d)). The efficiency of 1,2-dichloropropane as an “alloying agent” was therefore dependent on the oxychlorination temperature, too low a temperature favouring Pt^0 rather than Pt^0–Sn^0 alloy formation probably because of reduced 1,2-dichloropropane decomposition during the oxychlorination process. Insufficient Cl-liberation impaired the generation of mobile chloro-Pt and oxychloro-Pt complexes during oxychlorination [3,5] and hence the formation of alloy during the subsequent reduction treatment [5] was incomplete.

Figure 2 exemplifies the results for five *oxy*823 experiments involving injected amounts of 1,2-dichloropropane in the range 4.3–77 $\mu\mathrm{l\,h^{-1}}$. Figure 2(b) shows that 4.3 $\mu\mathrm{l\,h^{-1}}$ generated reduced catalyst containing substantial amounts of both Pt^0 and Pt–Sn alloy. However, raising the amount to 10.2 $\mu\mathrm{l\,h^{-1}}$ (figure 2(c)) gave Pt–Sn alloy as the dominant phase, this result being maintained for higher injection rates. A similar series of fourteen *oxy*753 experiments were carried out with injection rates in the range 1.73–117 $\mu\mathrm{l\,h^{-1}}$. The XRD patterns in figure 3 exemplify the smooth trend in behaviour shown by all the results from dominant Pt^0 with little alloy for 1.73 $\mu\mathrm{l\,h^{-1}}$ to dominant Pt–Sn alloy with only slight Pt^0 for 11.4 $\mu\mathrm{l\,h^{-1}}$. Amounts of Pt^0 were negligible for injection rates $\geqslant 22.9$ $\mu\mathrm{l\,h^{-1}}$.

In one experiment involving *oxy*753 170 $\mu\mathrm{l\,h^{-1}}$ of 1,2-dichloropropane was injected in the oxychlorination step and subsequent reduction was carried out at 753 K for 3 h. The level of Cl added was expected to be more than enough to ensure complete alloying of all the Pt in the catalyst. However, the XRD pattern showed that significant amounts of both Pt^0 and Pt–Sn alloy were present with the heights of

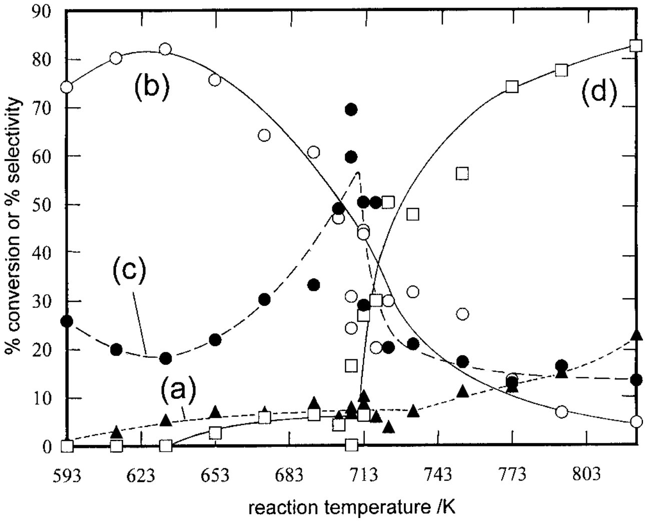

Figure 4. Variations with reaction temperature of initial (a) conversion, and selectivities for (b) isomerisation, (c) hydrogenolysis and (d) dehydrogenation for catalysts after *oxid*673.

the Pt peak at $2\theta = 39.8°$ and the Pt–Sn peak at 41.8° being nearly the same. This result suggests that the high reduction temperature and the long time of reduction promoted Cl loss from the catalyst during the reduction stage and, therefore, the promoting effect of Cl on alloy formation was partially lost.

Estimates of crystallite sizes from XRD peak widths showed that there were small changes with changing catalyst pretreatment. Diameters of Pt–Sn crystallites decreased from 34 ± 4 Å after *oxy*373(15) to 29 ± 4 Å after *oxy*823(15). Particle diameters were less sensitive to the injection rate of 1,2-dichloropropane during the oxychlorination treatment at either 753 or 823 K. Diameters of Pt^0 crystallites for catalysts after *oxy* treatment were 26 ± 2 Å, but were 21 ± 2 Å for catalysts which had not been treated with 1,2-dichloropropane. This is in the same sense as a previous conclusion that Pt^0 crystallites were bigger after oxychlorination (before reduction) rather than oxidation [5], but contrasts with results for Pt(0.3%)/Al_2O_3 [2,4] for which oxychlorination favours a better dispersion of Pt after reduction. For Pt(3%)–Sn(4.5%)/Al_2O_3 the existence of bigger Pt^0 crystallites after oxychlorination is also reflected in the retention of bigger crystallites after subsequent reduction under conditions for which alloying is incomplete.

3.2. Catalytic results for chlorine-free Pt–Sn/Al_2O_3

Typical results for catalysts containing hardly any Pt^0–Sn^0 alloy but consisting of dispersed Pt^0 particles partly covered in Sn^0 [5] were gained by studying Cl-free Pt–Sn/Al_2O_3 which had not been subjected to any *oxy* treatments. Reactions were followed for 255 min after which time further effects of coking [12,13] were small. Conversions and selectivities are reported as either "initial" or "final" values which refer to 7 and 255 min on line, respectively. Figure 4 shows changes in initial butane conversion and selectivities as a function of reaction temperature after *oxid*673 treatment. At ⩽633 K isomerisation dominated over hydrogenolysis and no alkenes were observed. Raising the temperature from 633 towards 700 K increased hydrogenolysis at the expense of isomerisation and also led to the appearance of alkenes. Similar trends in behaviour have been reported for hexane reactions at 563–663 K over Pt–Sn/Al_2O_3 which was prepared from Cl-containing precursor salts [14]. Kappenstein *et al.* [14] found that decreasing the Pt–Sn alloy content of catalyst increased the reaction temperature necessary for alkenes to become the dominant reaction products. Here, for Cl-free and largely alloy-free catalyst the onset of significant amounts of alkene occurred at 713 K, alkenes becoming the dominant products above 723 K. In general the alkene products were 100% butenes both in the initial stages of reaction and after coking had taken place. The only exception was for a reaction temperature of 823 K at 7 min when rapid coking was occurring and the dominant alkene formed was propene. However, as coking approached completion the alkene formed was ⩾95% butene. Ethene was never a detectable product.

The dramatic rise in alkene selectivity with increasing temperature may be attributed to decreasing metal surface coverage by hydrogen and to differences in the extent of coking at different temperatures [14]. Final conversion values showed that decreases in conversion through coking between reaction times of 7 and 255 min occurred at all temperatures and that coking led to enhanced selectivities to alkenes above 653 K. Catalysis on uncoked ensembles of Pt^0 atoms [5] at $T < 713$ K favoured dominant isomerisation and hydrogenolysis reactions. However, coking decreased the size of exposed ensembles [12,13] thus favouring dehydrogenation reactions which, unlike isomerisation and hydrogenolysis [14–16], can take place at single Pt atom sites [14,17]. Similar decreases in hydrogenolysis selectivity and increases in dehydrogenation selectivity with time-on-line have been reported for propane/H_2 reactions over Pt–Sn/Al_2O_3 at 792 K [18,20]. The effects of coking on the butane catalysis results support the conclusion from an infrared study of CO adsorption on a similar catalyst [5] that, although the surfaces of Pt^0 particles in freshly reduced Cl-free catalyst were partly covered by Sn^0, there remained clusters of exposed Pt atoms which did not contain Sn atoms as a surface diluent.

The effects of coking on conversions and selectivities are further exemplified by the results in figure 5 for changing H_2/butane ratio in the reactor feedstock. In the early stages of reaction when Pt ensembles [5] on metal particles were largely uncoked decreasing the butane partial pressure in the H_2 flow promoted hydrogenolysis selectivity largely at the expense of dehydrogenation. However, after 255 min when the Pt ensembles were highly coked, the catalytic conversions were much reduced, and isomerisation and hydrogenolysis reactions were attenuated by the lack of exposed Pt ensembles capable [14–16] of catalysing these reactions. Dehydrogenation at isolated Pt sites [14,17], therefore, became the dominant reaction taking place.

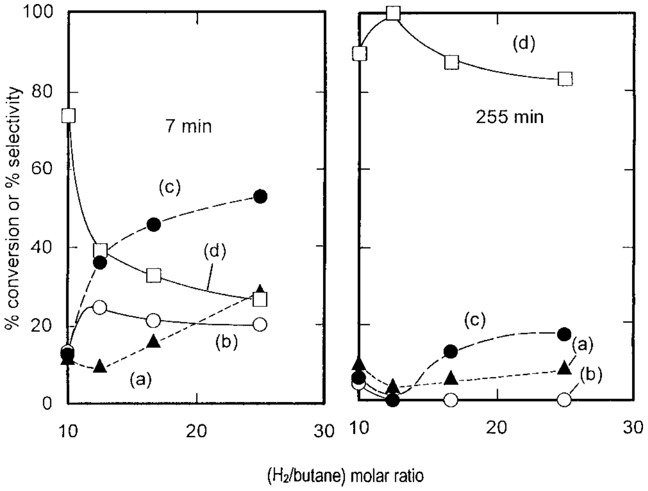

Figure 5. Variation with H$_2$/butane ratio of initial (7 min) and final (255 min) (a) conversions, and selectivities for (b) isomerisation, (c) hydrogenolysis and (d) dehydrogenation for catalysts subjected to *oxid*673/*react*773.

There were no significant changes in conversion or selectivities when the *oxid* temperature was varied in the range 573–823 K for *react*673. Both the surface area and nature of Pt^0 particles partly covered with Sn^0 but retaining arrays of exposed Pt^0 atoms [5] were insensitive to changing oxidation temperature prior to reduction at 673 K. This is consistent with nearly identical infrared spectra of adsorbed CO observed for a similar catalyst after *oxid*673 and *oxid*823 [5]. Spectra of adsorbed CO on the catalysts before reduction were significantly different from each other [5] showing, together with the present results, that the identity of surface behaviour for the reduced catalysts was established during the reduction step, and not in the preceding oxidation step, in the catalyst pretreatment.

3.3. Catalytic results for chlorine-containing Pt–Sn/Al$_2$O$_3$

Experiments involving *react*673 after *oxy*673(15), *oxy*823(70) or *oxy*823(170) showed that the generation of Pt–Sn alloy by oxychlorination followed by reduction had reduced the catalytic activity to an undetectable level. In one experiment involving *oxy*823(70) the reaction temperature was raised in increments which established that the onset of appreciable catalysis was at *ca*. 723 K where small amounts of butenes were detected with no products derived from isomerisation or hydrogenolysis reactions. This contrasts with the results for Cl-free catalysts for which isomerisation and hydrogenolysis were significant reaction pathways at 723 K and supports the contention that alloy formation favours dehydrogenation catalysis and not isomerisation or hydrogenolysis [8,10,12,19–21]. For *react*748 after *oxy*823(70) butenes were still the only products. For *react*773 catalysis became fast enough for reliable measurements of butane conversion and product selectivities and, therefore, 773 K was chosen as the reaction temperature for exploring the effects of alloying on catalytic behaviour.

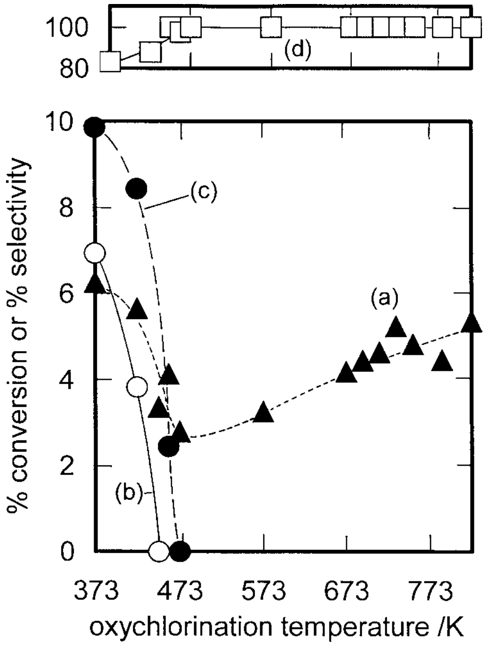

Figure 6. Variation with oxychlorination temperature of initial (a) conversion, and selectivities for (b) isomerisation, (c) hydrogenolysis and (d) dehydrogenation for *react*773.

The effects for *react*773 of changing the oxychlorination temperature T in *oxyT*(15) before reduction at 673 K are shown in figure 6 and in conjunction with the corresponding XRD results in figure 1 demonstrate a direct correlation between alloy formation and catalytic behaviour. The enhancement in alloy content at the expense of Pt^0 as the oxychlorination temperature was raised from 373 to 473 K was paralleled by decreases in activity, the disappearance of isobutane and hydrogenolysis products when all the Pt present was incorporated into alloy after *oxy*473, and the occurrence of dehydrogenation as the sole catalytic reaction. Butenes remained the only reaction products for oxychlorination temperatures in the range 473–823 K. Raising the oxychlorination temperature under conditions when alloying was complete increased catalytic activity, which may be correlated, at least in part, with XRD evidence that there was a parallel decrease in Pt–Sn particle size and, therefore, an increase in surface area. The corresponding "final" catalytic behaviour after 255 min on line was a close replica of the initial results in figure 6. However, coking induced small reductions in conversion and for oxychlorination temperatures below 473 K increased the dehydrogenation selectivities (for example, to 91% for *oxy*373) in accordance with the geometric effect of coking on the size of exposed Pt ensembles.

The effects on the catalytic results for *react*773 of varying the 1,2-dichloropropane injection rate during the the oxychlorination steps in *oxy*823 and *oxy*753 were determined for assessment in conjunction with the XRD data in figures 2 and 3. The results for the two oxychlorination temperatures gave exactly the same effects and led to similar conclusions and, therefore, only the data for *oxy*753 are shown in figure 7. The gradual trend from predominantly Pt^0 particles for Cl-free catalyst to all Pt incorporated into Pt–Sn al-

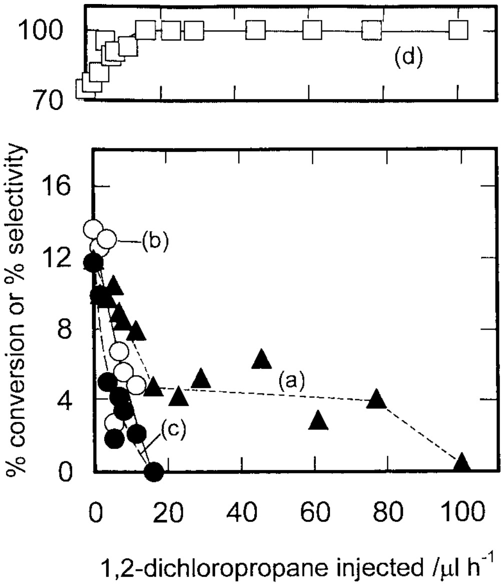

Figure 7. Variation with 1,2-dichloropropane injection rate during *oxy*753 of initial (a) conversion, and selectivities for (b) isomerisation, (c) hydrogenolysis and (d) dehydrogenation for *react*773.

loy occurred in the injection range 0–22.9 μl h^{-1} (figure 3). Increasing alloying reduced the butane conversion and the selectivities for isomerisation and hydrogenolysis reactions, and hence the selectivity for dehydrogenation rose to 100% when alloying was complete. The good correlation between the extent of alloying and the favourability of reaction to butenes rather than isobutane or hydrogenolysis products was also shown after 255 min reaction, with coking additionally enhancing dehydrogenation selectivity at the expense of the other reactions.

The enhancement in dehydrogenation selectivity on alloying in Pt–Sn/Al$_2$O$_3$ resembles results of a study by Humblot *et al.* [8] who showed that the generation of a Pt–Sn surface alloy on Pt particles dispersed on SiO$_2$ gave an increase to >99% selective dehydrogenation of isobutane to isobutene at 823 K. The build up of increasing amounts of alloy on the Pt surfaces progressively increased dehydrogenation selectivity in accordance with the present growth in selectivity which accompanied an increasing proportion of Pt in alloy rather than Pt^0 crystallites. The decreases in isomerisation and hydrogenolysis selectivities on alloying have been ascribed to geometric effects resulting from the absence of exposed vicinal Pt atoms capable of acting as active sites for these reactions [8]. Reductions in the sizes of clusters of exposed Pt atoms in passing from pure Pt surfaces to Pt surfaces partially covered by Sn and finally to Pt–Sn surface alloy decreasingly favour hydrogenolysis and isomerisation and hence dehydrogenation selectivity becomes enhanced. Kappenstein *et al.* [14] have discussed, in relation to results for hexane/H$_2$ reactions, the array of Pt and Sn atoms in low-index faces of the hexagonal Pt–Sn alloy consistent with the present XRD results. The decreased ability of Sn-rich surfaces to chemisorb H$_2$ [24] is also a contributing factor [14] to the catalytic behaviour.

4. Conclusions

The following conclusions follow from the present study of Pt–Sn/Al$_2$O$_3$ with a high Pt loading and a molar excess of Sn over Pt and a previous infrared and XRD study of an identical catalyst at various stages of oxidation, oxychlorination and reduction [5]. The catalytic results are interpreted in terms of catalysis at metal sites rather than bifunctional catalysis involving acidic sites on the alumina support. Studies of octane conversion at 755 K over Pt/Al$_2$O$_3$ containing various amounts of Sn led to the conclusion that bifunctional reaction pathways were eliminated because of the removal of acid sites by low loadings of Sn [22,23]. In accordance with the present conclusions, the effects of higher Sn loadings on catalytic behaviour were ascribed to Pt–Sn alloy formation [23]. Bariås *et al.* [18] similarly concluded that tin blocked or poisoned acid sites on the support and that this was a significant reason why the addition of Sn to Pt/Al$_2$O$_3$ enhanced selectivities to propene in propane/H$_2$ reactions at 700–792 K:

(a) After oxidation and reduction of Cl-free catalysts Pt exists predominantly as Pt^0 particles with a partial covering of surface Sn^0 but with exposed ensembles of Pt atoms which provide catalytic sites for hydrogenolysis and isomerisation reactions. The formation of Pt–Sn alloy on an alumina support is not favoured in the absence of chlorine during oxidation/reduction preparation or regeneration treatments.

(b) Oxychlorination/reduction treatment with 1,2-dichloropropane as the chlorinating agent promotes 1 : 1 Pt^0–Sn^0 alloy formation, the extent of alloying of the Pt depending on the temperature and the concentration of chlorinating agent present during oxychlorination. Increasing temperature and Cl-content favour increased alloying. This is consistent with previous conclusions that the presence of chlorine during catalyst preparation, derived either from Cl-containing precursor salts or from added HCl during impregnation of the support, promotes Pt–Sn interactions leading to alloy formation in reduced catalysts [6,19].

(c) Complete alloying of Pt with Sn reduces butane hydrogenolysis and isomerisation activities to zero, leaving dehydrogenation to butenes as the only detectable reaction. A study by Humblot *et al.* [8] gave a parallel result in that the generation of Pt–Sn surface alloy on Pt particles dispersed on SiO$_2$ gave an increase to >99% selective dehydrogenation of isobutane to isobutene at 823 K. Mechanisms were proposed.

(d) Coking of Pt–Sn alloy reduces the catalytic activity but does not change the selectivity from 100% dehydrogenation. In contrast, coking of ensembles of Pt atoms on Pt^0 particles produces a geometric effect which hinders isomerisation and hydrogenolysis reactions and increasingly favours enhanced selectivity for dehydrogenation to butenes. The effects of coking on specific Pt surface sites in Pt–Sn/Al$_2$O$_3$ catalysts have been monitored in detail by infrared study of CO adsorption [25]. Coke was deposited in part on arrays of Pt atoms which were partly diluted by surface Sn, the deposition of coke causing a reduction in exposed Pt ensemble size.

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References

[1] C.L. Pieck, E.L. Jablonski and J.M. Parera, Appl. Catal. 70 (1991) 19.
[2] J.A. Anderson, M.G.V. Mordente and C.H. Rochester, J. Chem. Soc. Faraday Trans. I 85 (1989) 2983.
[3] G.J. Arteaga, J.A. Anderson and C.H. Rochester, J. Catal. 184 (1999) 268.
[4] M.G.V. Mordente and C.H. Rochester, J. Chem. Soc. Faraday Trans. I 85 (1989) 3495.
[5] G.J. Arteaga, J.A. Anderson S.M. Becker and C.H. Rochester, J. Mol. Catal. A 145 (1999) 183.
[6] H. Lieske and J. Völter, J. Catal. 90 (1984) 96.
[7] G.J. Arteaga, J.A. Anderson and C.H. Rochester, J. Catal. 187 (1999) 219.
[8] F. Humblot, J.P. Candy, F. Le Peltier, B. Didillon and J.M. Basset, J. Catal. 179 (1998) 459.
[9] J. Llorca, P. Ramírez de la Piscina, J.L.-G. Fierro, J. Sales and N. Homs, J. Catal. 156 (1995) 139.
[10] J. Llorca, N. Homs, J.L.-G. Fierro, J. Sales and P. Ramírez de la Piscina, J. Catal. 166 (1997) 44.
[11] R. Srinivasan and B.H. Davis, Appl. Catal. A 87 (1992) 45.
[12] J. Völter and U. Kürschner, Appl. Catal. 8 (1983) 167.
[13] J. Beltramini and D.L. Trimm, Appl. Catal. 31 (1987) 113.
[14] C. Kappenstein, M. Guérin, K. Lázár, K. Matusek and Z. Paál, J. Chem. Soc. Faraday Trans. 94 (1998) 2463.
[15] F.M. Dautzenberg, J.N. Helle, P. Biloen and W.M.H. Sachtler, J. Catal. 63 (1980) 119.
[16] F.H. Ribeiro, A.L. Bonivardi, C. Kim and G.A. Somorjai, J. Catal. 150 (1994) 186.
[17] P. Biloen, J.N. Helle and W.M.H. Sachtler, J. Catal. 58 (1979) 95.
[18] O.A. Bariås, A. Holmen and E.A. Blekkan, Catal. Today 24 (1995) 361.
[19] S.M. Stagg, C.A. Querini, W.E. Alvarez and D.E. Resasco, J. Catal. 168 (1997) 75.
[20] O.A. Bariås, A. Holmen and E.A. Blekkan, J. Catal. 158 (1996) 1.
[21] P. Mériaudeau, A. Thangaraj, J.F. Dutel and C. Naccache, J. Catal. 167 (1997) 180.
[22] R. Srinivasan and B.H. Davis, J. Mol. Catal. 88 (1994) 343.
[23] D.E. Sparks, R. Srinivasan and B.H. Davis, J. Mol. Catal. 88 (1994) 359.
[24] M.R. Voss and B.E. Koel, Surf. Sci. 414 (1998) 330.
[25] G.J. Arteaga, J.A. Anderson and C.H. Rochester, Catal. Lett. 58 (1999) 189.
[26] D.A. Fletcher, R.F. McMeeking and D.J. Parkin, J. Chem. Inf. Comput. Sci. 36 (1996) 746.