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Alkane Transformations on Supported Platinum Catalysts

Part 3: The Stability of Pt/Al_2O_3 (EUROPT-3) and of $PtRe/Al_2O_3$ (EUROPT-4) during the Hydrogenolysis of Alkanes[1]

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The hydrogenolysis of ethane, propane and *n*-butane has been studied on Pt/Al_2O_3 (EUROPT-3) and $PtRe/Al_2O_3$ (EUROPT-4) catalysts between 520 and 660 K by a thermal cycling technique using a 10-fold excess of H_2. Analogous catalysts having higher metal concentrations have also been examined. With neither ethane nor propane does any progressive deactivation result from repeated thermal cycles, but with *n*-butane on Pt/Al_2O_3 catalysts initial loss of activity alters product selectivities, specifically by decreasing the probability of breaking the internal C–C bond. After this, they behave reproducibly. With $PtRe/Al_2O_3$ catalysts, product selectivities shown by *n*-butane are very different from those given by the Pt/Al_2O_3 catalysts but are unaltered by the somewhat greater initial deactivation; they show some sample-to-sample variation, which is attributed to differences in surface Re concentrations. These results are explained by a model in which sites on low-index planes in very small Pt particles are those that are first inactivated through the formation of strongly held dehydrogenated species; when Re atoms are present they preferentially occupy these sites and the operation of bimetallic centres explains why deeper hydrogenolysis occurs in this case. Reproducible rates of *n*-butane hydrogenolysis are obtained with Pt/Al_2O_3 below about 600 K, but not with $PtRe/Al_2O_3$; use of short (1 min) reaction pulses overcomes this difficulty. Partially deactivated catalysts can, however, be studied in the continuous-flow mode. © 1996 Academic Press, Inc.

INTRODUCTION

The reactions between alkanes and H_2 in the presence of supported metals of Groups 8 to 10 continue to attract attention for their practical importance as well as their theoretical interest, but their quantitative study is made difficult by the almost universal occurrence of some form of carbon deposition (1, 2), e.g., by the formation of strongly held dehydrogenated forms of the reactant alkane (3) or species derived therefrom. These species, which may adopt a variety of forms (3, 4), act as poisons for reactions such as hydrogenolysis or dehydrogenation, but, because the extent to which they cover the surface may change with reaction conditions, their presence hinders the quantitative study of alkane transformations. We have therefore begun a further study of the problem by trying to determine how the existence of a partial "carbon deposit" affects the *kinetics* of hydrogenolysis of the lower alkanes, especially the way in which the rate responds to H_2 pressure. Analysis of such results by means of an appropriate rate expression of the Langmuir–Hinshelwood type leads to estimates of the true activation energy and of the enthalpy changes associated with hydrogen chemisorption and of dehydrogenation of the alkane to the reactive form (5).

For such a study to succeed, it is necessary to have a clear understanding of the factors affecting the extent of "carbon deposition," so that the proper steps may be taken to avoid it, or at least to minimise it, when desired. Our experience (5–7) and the literature (1–4) suggest that the chief factors to consider include: the H_2/alkane ratio, time-on-stream, temperature, catalyst composition, and alkane chain length. Quantitatively, carbon deposition occurs faster at low H_2/alkane ratio, at high temperature, and with increasing alkane chain length, but for the particular catalysts we have selected to study, namely EUROPT-3 Pt/Al_2O_3 and EUROPT-4 $PtRe/Al_2O_3$ (8) and their analogs having higher metal concentrations, there is only limited information available (15). This paper therefore reports the results of a study of how operating variables affect the stability of these catalysts during their use for alkane hydrogenolysis. Examination of these reactions in the absence, or virtual absence, of a carbon deposit would be helped by using short reaction periods and we have developed and applied a procedure, due orginally to Galvagno and his colleagues (9), whereby a 1-min pulse of reactants is followed by a time of cleansing with pure H_2, while the products of the pulse are analysed. Some preliminary results showing the success attending this procedure are given below.

Furthermore, we need to be able to follow the kinetics of alkane hydrogenolysis on surfaces partially deactivated by

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[1] Part 1: G. C. Bond and Hui Lou, *J. Catal.* **137**, 462 (1992). Part 2: G. C. Bond and Hui Lou, *J. Catal.* **142**, 512 (1993).

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the carbon deposit. The preliminary study outlined above will indicate the conditions that need to be used with each catalyst and each alkane, but it is also necessary that the deposit remain more or less stable under the conditions selected for the kinetic study. We therefore also report some observations on the stability of carbon deposit.

The results of the kinetic study will be presented in a later paper.

EXPERIMENTAL

Many of the procedures used in this work have been described before (5–7): a brief summary of them therefore suffices. Reactions in the continuous-flow mode were performed at atmospheric pressure using H_2: alkane ratios of 10 : 1 *except where stated otherwise* (flow-rates: H_2, 100; alkane, 10; N_2, 30 $cm^3\ min^{-1}$). In thermal cycling, the temperature was raised in steps of about 10 K every 20 min, samples being taken for analysis at the end of each isothermal period and analysed during the following one. After typically 14 steps, constituting stage 1, and covering the range 520–665 K, the process was reversed, giving a further 14 read outs (stage 2). Most usually a second complete cycle, comprising stages 3 and 4, was carried out; it was then possible to judge whether a catalyst was deactivating progressively or whether it had achieved a steady state. In one series of experiments, the direction of the temperature was reversed, i.e., stage 1 started at 665 K. In isothermal experiments, samples were simply withdrawn for analysis at 20-min intervals. In one series of experiments, a thermal cycle was inserted between two isothermal phases.

A short reaction pulse (SRP) procedure was based on a method developed by Galvagno *et al.* (9). H_2 (100 $cm^2\ min^{-1}$) and N_2 (30 $cm^3\ min^{-1}$) were passed through the reactor, and the alkane flow (10 $cm^3\ min^{-1}$) was then introduced for 1 min, after which time a sample was taken for analysis, and the alkane flow was immediately diverted from the reactor. Thus only the H_2–N_2 mixture passed over the catalyst for the next 19 min while the sample was being analysed; it was hoped in this way to maintain the surface free from carbon deposits. Preliminary measurements showed that closely reproducible results could be obtained by this technique.

The catalysts used were 0.3% Pt/Al_2O_3 (EUROPT-3 (8), also coded CK303); 0.6% Pt/Al_2O_3 (CK306), kindly supplied by the AKZO Company; 0.3% Pt–0.3% Re/Al_2O_3 (EUROPT-4 (8), also coded CK433); and 0.45% Pt–0.45% Re/Al_2O_3 (CK455) kindly given by Prof. V. Ponec.

The behaviour of the PtRe catalysts is known to depend critically on the precise schedule used for their activation; in particular, the degree of interaction of the two elements is largely controlled by the water concentration, and is thus sensitive to heating rate and gas flow rate. In most of this work, the procedure recommended by Prof. G. Froment was used as before (6), but, to determine how responsive the results were to the conditions used, a slightly different method as suggested by the EUROCAT Group (8) was also tried with CK433. The essential differences were as follows:

Froment method		EUROCAT method	
Gas/flow rate	Operation	Gas/flow rate	Operation
Air/20 $cm^3\ min^{-1}$	1. Heat 298–763 K over 7 h 2. After 1 h, cool to 673 K over 2 h	Air/60 $cm^3\ min^{-1}$	1. Heat 298–673 K over 5.5 h 2. After 1 h, cool to 583 K over 2 h
N_2/20 $cm^3\ min^{-1}$	3. 1 h at 673 K	N_2/20 $cm^3\ min^{-1}$	3. 1 h at 583 K
H_2/20 $cm^3\ min^{-1}$	4. Heat to 763 K over 2 h 5. After 1 h, cool to reaction temp.	H_2/60 $cm^3\ min^{-1}$	4. Heat to 673 K over 2 h 5. After 1 h, cool to reaction temp.

Procedures for treating the results have also been described before, but for ease of reference a brief summary is provided. Rates are expressed in mmol alkane converted per gram catalyst per hour. Product selectivities, S_j, where j is the number of carbon atoms, are defined by the carbon atom balance: thus for the reaction of propane

$$\frac{1}{3}(S_1 + 2S_2) = 1$$

and for the hydrogenolysis of n-butane

$$\frac{1}{4}(S_1 + 2S_2 + 3S_3) = 1$$

Isomerisation selectivity S_i is simply the fraction of n-butane changed into isobutane; this is subtracted from the total products before calculating values of S_j.

Product selectivities in the n-butane reaction are then manipulated according to the Kempling–Anderson formalism (10), which treats the reaction as a rake mechanism; adsorbed intermediates C_j^* ($j = 2$ or 3) may either vacate the surface to give product alkane (k'_j) or may crack further (k_j^*). T_j is then defined as

$$T_j = k'_j/(k'_j + k_j^*).$$

The probability of central-bond fission in the opening step is F and of terminal bond fission $(1-F)$. Steady-state treatment (10) then leads at low conversion to the following relations:

$$(S_2/T_2) + S_3 = 1 + F$$

$$S_3/(1 - F) = T_3.$$

There are insufficient knowns to solve these equations, so we either (i) assume T_2 to be unity, when the resulting parameters are identified by primes, or (ii) substitute the value of S_2 from the propane reaction under the same conditions, since the same method of analysis equates T_2 to S_2.

RESULTS

Kinetic Parameters at 603 K

Table 1 summarises the results of the thermal cycles performed with the three alkanes: rates and selectivities are those found at 603 K, and the apparent activation energies are derived from rates measured within the stipulated temperature range.

In order to establish a firm basis for judging the reliability of these results, we first compare the mean values of the kinetic parameters for the propane reaction over the four stages obtained from (i) Table 1, (ii) from our earlier work (6), (iii) by repeating the measurements using the previous sample of CK433, and (iv) by using the activation schedule recommended by the EUROCAT programme (8). Table 2 shows this comparison. The quoting of mean values implies that they showed no important progressive change during the four stages. From these results we can judge the importance of the various variables in determining the results. Agreement between the three studies of the reaction on CK303 is very satisfactory, but with CK306 the activation energy is now lower and the rate higher. Larger variations are found with CK433; rates vary eight-fold and S_2 values also differ. There is an interesting inverse correlation between rate and S_2; recalling that Re alone is much more active and less selective in hydrogenolysis than Pt (11), we may conclude that the sample showing the lowest S_2 and highest rate has the largest concentration of Re ensembles, while that having the highest S_2 and slowest rate has a surface most closely resembling that of pure Pt.

We have observed no comparable differences with the *n*-butane reaction, which is surprising because it usually exhibits a higher degree of structure sensitivity. We have repeated the reaction using the original batch of CK433, the only material difference being in the F and T_3 parameters which at 0.344 and 0.785, respectively, are both somewhat lower than reported before (6), but are similar to those we find with the new batch (Table 1). We must remember that each sample is separately activated, and as we shall see below there are some problems in deriving the true F and T_3 for this catalyst. We should not therefore place too much emphasis on comparatively minor differences. However, bearing in mind our experience with the pronane reaction, we may conclude that exceptional care in controlling the activation of the bimetallic catalysts will be essential in obtaining meaningful and reproducible kinetic results. We may expect fewer problems with the pure Pt catalysts.

Neither ethane nor CK355 was used in the earlier work (6), so no comparison with our present findings is possible.

There are a number of further conclusions to be drawn from the results shown in Table 1. With the two Pt/Al_2O_3 catalysts, the kinetic parameters for ethane and propane show little if any effect of ageing, the S_2 values being absolutely constant. In the case of *n*-butane, deactivation is largely confined to stage 1, where its effect in lowering the activation energy (Fig. 1) and the value of F (but not T_3) is

TABLE 1

Kinetic Parameters for the Hydrogenolysis of Ethane, Propane, and *n*-Butane

		Ethane			Propane				*n*-Butane						
Catalyst	stage	T (K)	E (kJ mol^{-1})	r	T (K)	E (kJ mol^{-1})	r	S_2	T (K)	E (kJ mol^{-1})	r	F	T_3	F'	T_3'
CK303	1	583–712	230 ± 4	0.70	541–661	200 ± 5	1.08	0.993	523–583	149 ± 13	1.26	0.241	0.985	—	—
	2	712–613	236 ± 5	0.65	630–533	197 ± 2	0.94	0.992	663–523	134 ± 3	0.44	0.157	0.989	—	—
	3	—	—	—	533–632	195 ± 2	0.85	0.993	523–663	137 ± 2	0.43	0.160	0.985	—	—
	4	—	—	—	621–552	191 ± 2	0.85	0.991	663–523	139 ± 1	0.40	0.159	0.986	—	—
CK306	1	—	—	—	532–633	177 ± 3	3.47	0.986	523–583	145 ± 7	12.4	0.293	0.983	—	—
	2	—	—	—	632–522	177 ± 4	3.54	0.986	582–523	150 ± 8	8.42	0.166	0.981	—	—
	3	—	—	—	522–633	178 ± 3	3.40	0.986	523–583	150 ± 6	7.92	0.181	0.983	—	—
	4	—	—	—	622–522	176 ± 5	3.43	0.986	573–523	154 ± 4	7.94	0.152	0.983	—	—
CK433	1	574–663	195 ± 4	7.35	540–610	184 ± 7	7.37	0.849	539–590	185 ± 21	15.2	0.406	0.759	0.262	0.611
	2	662–573	167 ± 6	11.0	613–534	189 ± 8	6.82	0.844	590–529	145 ± 5	5.91	0.392	0.740	0.245	0.596
	3	593–663	184 ± 7	7.22	544–614	186 ± 5	5.47	0.853	529–601	146 ± 6	6.16	0.388	0.745	0.251	0.609
	4	644–574	173 ± 3	12.0	613–543	182 ± 5	6.03	0.843	—	—	—	—	—	—	—
CK455	1	—	—	—	543–623	180 ± 5	6.14	0.845	517–594	143 ± 5	6.59	0.445	1.12	0.319	0.913
	2	—	—	—	622–522	174 ± 3	5.89	0.834	613–533	140 ± 4	3.44	0.443	1.13	0.311	0.917
	3	—	—	—	522–622	172 ± 2	5.22	0.837	523–633	144 ± 2	3.48	0.439	1.13	0.308	0.921
	4	—	—	—	622–531	169 ± 3	5.05	0.835	622–533	145 ± 2	2.09	0.433	1.13	0.303	0.921

Note. Rates in mmol g_{cat}^{-1} h^{-1}; rates and selectivities at 603 K.

TABLE 2

Mean Values[a] of Kinetic Parameters for Propane Hydrogenolysis

Catalyst	E (kJ mol^{-1})	r^b	S_2
CK303			
From Table 1	196	0.93	0.992
From previous work (6)	191	1.35	0.990
EUROCAT pretreatment	183	1.36	0.992
CK306			
From Table 1	177	3.46	0.986
From previous work (6)	207	1.00	0.990
CK433			
From Table 1	185	6.42	0.848
From previous work (6)	189	1.66	0.930
Previous sample repeated	169	1.71	0.936
EUROCAT pretreatment	177	0.83	0.961

[a] There were no significant changes in the values of these parameters over four stages.

[b] In mmol g_{cat}^{-1} h^{-1} at 603 K.

apparent. Steady-state rates are some four times faster with CK306 than for CK303, although the metal content is only doubled; there are also differences in activation energy that do not relate simply to metal content. The characteristic fingerprint of Pt is, however, shown by the steady-state values of S_2, F, and T_3.

With the PtRe/Al_2O_3 catalysts, there is a curious alternation in the rate and activation energy for ethane hydrogenolysis with CK433, and this must be caused by a deactivation at *low* temperature; there is no comparable effect in the reactions of propane or *n*-butane, where rates suffer a slow decrease (perhaps progressive in the case of CK455), but activation energies are in the main quite constant, and values of F do not change with deactivation as they did with the Pt/Al_2O_3 catalysts. The characteristic fingerprint of the PtRe/Al_2O_3 catalysts is the lower values of S_2 and the higher values of F compared to those shown by the Pt/Al_2O_3 catalysts.

A comment on the values of T_3 shown by the PtRe/Al_2O_3 catalysts is necessary. Values exceeding unity, as are recorded in Table 1 for CK455, are of course impossible. We have only *assumed* that the value of the S_2 obtained from the propane reaction may be substituted for T_2 in the *n*-butane reaction in order to obtain true values of F and T_3, and this assumption clearly fails in this case. It may also have failed with CK433, because it is unusual to find values of T_3 less than T_2. CK455 gives, for the *n*-butane reaction, $S_2 = 0.68 \pm 0.02$ and $S_3 = 0.63 \pm 0.01$, independent of stage number; thus if T_3 were to have its maximum value of unity, T_2 would be 0.92. It is unclear why the assumption so obviously fails in this case.

The fraction of *n*-butane converted to isobutane at 603 K very rarely exceeded 0.04 and was more generally about 0.01–0.02 with all catalysts.

Temperature-Dependence of Kinetic Parameters

Comparison of results at the standard temperature of 603 K only provides a kind of snapshot of the effects of temperature cycling; further information is gained by examining the way in which variation of the temperature affects what is found (Figs. 1–3). First, concerning the overall rates: the values of apparent activation energy given in Table 1 are in a temperature range which in some cases exceeds 100 K, but in others, especially with the reactions of propane and *n*-butane on CK433 and of *n*-butane on CK306, the range is small; this is because the Arrhenius plots deviate from linearity at quite low conversions (>5%). Figure 1 shows these plots for stages 1 and 2 of the *n*-butane reaction over each of the four catalysts; there are some marked differences. As noted before (7), the plots for CK306 show breaks at about 2.5% conversion, above which a second linear range, having a lower activation energy, is observed. Sometimes, as with CK303 and CK455, the change in slope is due more to deactivation, as it is less marked in stage 2 than in stage 1 (6, 7). With the catalysts having the lower metal loadings (CK303 and CK433), deactivation leads to a decrease in activation energy (see also Table 1), so that the extent of deactivation depends on the temperature of measurement: at about 525 K it would be almost zero. This suggests that reproducible kinetic results will be most easily obtained at low temperatures.

Important new information supplementing that shown in Table 1 is gained from the way is which product selectivities for the *n*-butane reaction and the derived Kempling–

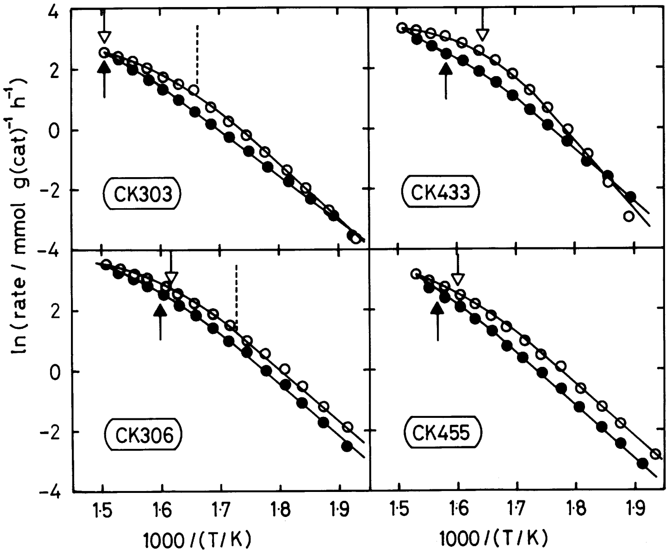

FIG. 1. Arrhenius plots for the hydrogenolysis of *n*-butane over the four catalysts. In this and the following figures, open points are for stage 1 (rising temperature) and filled points for stage 2 (falling temperature): the corresponding vertical arrows show the temperatures at which the conversion reaches ~10%. The deviation from linearity in stage 1 mentioned in the text starts at the temperature indicated by the broken line.

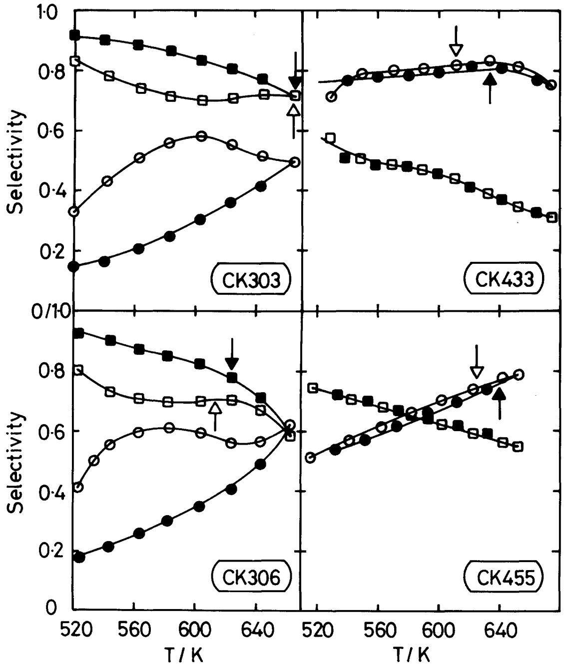

FIG. 2. Selectivity vs temperature plots corresponding to Fig. 1. Circles, S_2; squares, S_3 (see also legend to Fig. 1).

Anderson parameters change with temperature (Figs. 2 and 3). The marked differences shown between stages 1 and 2 by CK303 and CK306 persist over the whole temperature range: the changes in the temperature coefficients of S_2 and S_3 begin at the points at which the Arrhenius plots start to deviate from linearity (Fig. 1) and this indicates the regions in which carbon deposition is occurring (600–660 K for CK303; 575–625 K for CK306). These changes are entirely associated with changes in F and not at all with T_3, which decreases only very slowly with increasing temperature (Fig. 3). With both these catalysts, the isomerisation selectivity S_i increases with temperature, attaining values, respectively, of 6.0 and 2.4% at the highest temperature. Values of S_i are, however, markedly lower in stage 2, by, respectively, factors of 4 and 2 at 603 K. Whatever is causing the decrease in F is also suppressing S_i.

The initial deactivation shown by the PtRe catalysts (Table 1) is not accompanied by any significant changes in product selectivities (including isomerisation) or in the Kempling–Anderson parameters (Figs. 2 and 3). F' is almost temperature-independent in the low conversion region, while T_3' decreases smoothly in both cases (Fig. 3; note that in this figure we use F and T_3' rather than F and T_3, because of the uncertainty (noted above) in deriving "true" values).

In line with the smaller extent of the deactivation suffered by the Pt/Al_2O_3 catalysts during the propane reaction (Table 1), there is no detectable difference between stage 1 and stage 2 in the way in which S_2 varies with temperature (Fig. 4); the same is of course true for PtRe catalysts (see also Fig. 4). The only point deserving comment is the lower values of S_2 observed with the Pt catalysts at low temperature/conversion. The change with temperature is accurately measurable and is reversible; it cannot therefore be ascribed either to analytical error or carbon deposition.

The Formation of Carbon Deposits

When the intention is to deposit a partial layer of carbonaceous species on the surface before investigating its effect on reaction kinetics, it might make better sense to form it at a temperature higher than that to be used for the reaction, and to allow the equilibrium amount to form, than to create it by a normal thermal cycle starting at low temperature. We therefore next studied whether a thermal cycle begun at the highest temperature produced the same kind of deposit as judged by the kinetic parameters at 603 K: the results obtained for reactions of propane and of *n*-butane on CK303 and CK433 are summarised in Table 3 and compared with those found using the normal method (Table 1). With the former, as expected, there is no real difference between the results for the two stages, the parameters at 603 K being close to those found before (Table 1). Clearly the deposit is formed quickly at high temperature. However, with CK433, although rates and activation energies agree well with those from Table 1, the F' and T_3' are quite different;

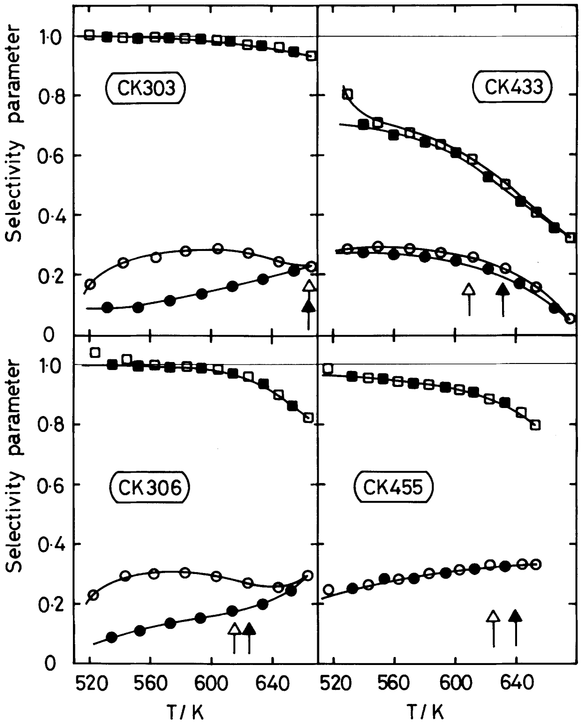

FIG. 3. Temperature-dependence of Kempling–Anderson parameters corresponding to Fig. 2. Circles, F'; squares, T_3' (see also legend to Fig. 1).

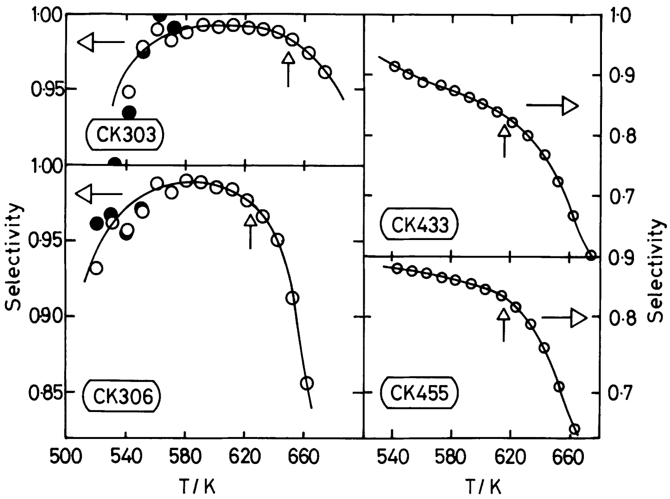

FIG. 4. Ethane selectivity vs temperature plots for propane hydrogenolysis for the four catalysts (see also legend to Fig. 1). Above about 560 K, values found with the Pt/Al_2O_3 catalysts in the rising and falling temperature sequences are indistinguishable.

there is obviously some way in which the temperature at which the deposit is formed controls product selectivities.

It is also of interest to know whether the carbon deposit is the same irrespective of the alkane from which it is formed, as judged by its effect on the ensuing hydrogenolysis. We have pretreated a sample of CK303 by performing a normal four-stage experiment with propane, followed, after thorough flushing, by a four-stage run with *n*-butane: the results show some interesting features. At low temperatures in stage 1 the value of S_3 greatly exceeds S_1 and only when the temperature is greater than 590 K is the position reversed; the effect decreases as the experiment continues, but is still just apparent in stage 4, results for which are shown in Fig. 5A. The same phenomenon may occur to a small extent with normally activated CK303 at the start of stage 1, but the effect is marginal; the behaviour of S_2 is quite normal. The most probable explanation is that C_1 species are being selectively incorporated in the carbon deposit, but why this only occurs *after* the propane pretreatment, and not in the reaction of propane, is not at all clear. Despite these differences, it is clear that the changes to the product selectivities in stage 1 of the *n*-butane reaction are caused by further carbon deposition, and that the prior treatment by propane has not eliminated it. After treating a sample of CK433 by the propane reaction for 3 h at 525 K, the same occurrence is seen in stage 1 below 560 K, above which temperature selectivities show no great change through the following stages (Fig. 5B). A similar experiment in which two complete thermal cycles were first performed with *n*-butane had no effect on cycles then made with propane, except to lower the activity.

A four-stage experiment was performed with *n*-butane and CK303 using an H_2:alkane ratio of 17:1 (H_2, 0.714 atm; *n*-C_4H_{10}, 0.042 atm) to see whether deactivation was any less than with the normal 10:1 ratio. The stage 1 rate was two times faster than that given in Table 1, and the extent of deactivation less (33% as against 56%, in stage 3); a smaller amount of carbon deposition in stage 1 is indicated by an absence of a maximum and a minimum, respectively, in the dependences of S_2 and of S_3 on temperature of the kind shown in Fig. 2. Activation energies and selectivities at 603 K were almost unchanged. With a 5 : 1 H_2 : alkane ratio, the rate decreased fivefold between stages 1 and 2, but thereafter kinetic parameters and selectivities changed only slightly.

Kinetic studies are most simply made at constant temperature, and it is therefore necessary to know how quickly deactivation and other changes occur under isothermal conditions. The *n*-butane reaction was carried out on CK303 at 574 K for 260 min; a decrease in rate and in F', and an increase in T_3', occurred only in the first 20 min. On raising the temperature to 594 K, the rate fell by only 6% over the next 260 min, and the selectivity parameters hardly

TABLE 3

Comparison of Mean Kinetic Parameters for Normal and Reverse Thermal Cycles and for Reaction of *n*-Butane on Catalysts Previously Used for Propane Hydrogenolysis (PUPH)

			Propane			*n*-Butane			
Catalyst	Thermal cycle	PUPH?	E^a	r^a	$S_2{}^a$	E^a	r^a	F'	T_3'
CK303	Normal	No	196	0.93	0.992	126^b	1.70^b	0.150^b	0.983^b
	Reverse	No	177	1.72	0.992	148	2.17	0.148	0.982
CK433	Normal	No	185	6.42	0.848	146^b	6.03^b	0.253^b	0.605^b
	Reverse	No	170^c	1.83	0.937	149	4.89	0.375	0.916
CK303	Normal	Yes	—	—	—	117^b	2.30^b	0.128^b	0.987^b
CK433	Normal	Yes	—	—	—	134^b	2.17^b	0.300^b	0.922^b

[a] E in kJ mol^{-1}; r in mmol g_{cat}^{-1} h^{-1}; r and selectivity parameters at 603 K.
[b] Steady-state values, i.e., average values for stage 2 and onwards.
[c] Excellent linearity.

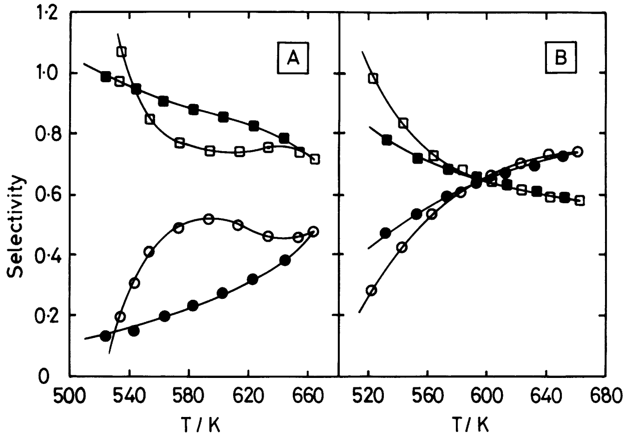

FIG. 5. Selectivity vs temperature plots for n-butane hydrogenolysis (A) on CK303 following four-stage reaction with propane and (B) on CK433 following reaction of propane for 3 h at 525 K. Open points, stage 1 (rising temperature); filled points, stage 4 (falling temperature); circles, S_2; squares, S_3.

TABLE 4

Kinetic Parameters for n-Butane Hydrogenolysis: Short Reaction Pulse Method at Constant Temperature

Catalyst	T (K)	t (min)	r^a	S_2	S_3	F'	T_3'
CK303	523	2	0.07	0.307	0.851	0.158	1.01
		202	0.07	0.272	0.846	0.117	0.958
	605^b	262^b	7.09	0.618	0.683	0.301	0.976
		442	6.17	0.593	0.695	0.288	0.977
CK433	582	2	3.26	0.818	0.539	0.357	0.838
		22	4.06	0.821	0.532	0.353	0.822
		362	3.87	0.823	0.531	0.353	0.821

[a] r in mmol g_{cat}^{-1} h^{-1}.

[b] Temperature raised to 605 K after 260 min.

changed; final values of F' at both temperatures were higher (∼0.18) than that obtained in a thermal cycle.

The purpose of the next series of experiments was to use thermal cycles to show whether a prior isothermal period was able to bring a catalyst to a stable state of carbon coverage; a second isothermal period was then performed to compare with the first. After using a sample of CK303 for 200 min at 523 K, during which time little change in activity occurred, the thermal cycle showed a deactivation of 16% at 603 K and a decrease in F' from 0.14 to 0.10. In a further 400 min at 543 K, the rate fell by 20% but F' and T_3' did not change. In a similar experiment with CK433, the rate at 533 K fell during 340 min by almost 10-fold, the change in selectivities arising through an increase in T_3' from 0.68 to 0.83. In the thermal cycle the rate fell by a further factor of two, but in the second isothermal phase the rate and selectivities were satisfactorily constant during 400 min.

These experiments suggest that in the continuous-flow mode one should be able to make reliable kinetic measurements with CK303 at low temperature (<550 K) on an essentially clean surface, and at higher temperatures (570–600 K) on a partially carbon-covered surface. Performing a thermal cycle does not, however, guarantee stable rates at moderate temperatures. With CK433 stable but low rates can be obtained after a thermal cycle.

The "Short Reaction Pulse" Technique

From this work it appears that it is only possible to obtain reliable kinetic results using the continuous-flow mode under very limited circumstances, and in particular its use may be confined to ethane and propane using Pt/Al_2O_3 catalysts, extended perhaps to n-butane at low temperatures. We have therefore made preliminary observations using the short reaction pulse (SRP) method, to see how far it helps in maintaining a clean surface. Table 4 shows the results obtained with n-butane using CK303 at 523 and 605 K and CK433 at 582 K; in each case there is only minor deactivation over prolonged periods. Selectivities are also well reproduced, and the ability of CK303 to retain the high value of F', normally only found in stage 1 of the thermal cycle (Table 1) is particularly noteworthy. Table 4 contains values for S_2 and S_3 as well as for F' and T_3' to make the point that small differences in the former produce larger differences in the latter, due to the form of the equations relating them. These quite satisfactory results with n-butane give us confidence that the method will work even better with ethane and propane.

The Stability of Carbon Deposits

In order to provide deliberately deactivated catalysts for kinetic studies, utilising the information obtained from the above work, samples of CK303 and of CK433 were exposed to the following H_2/alkane flows for 2 h at 713 K: (in cm^3 min^{-1}) $H_2 : C_2H_6$ ratio, 30 : 30; $H_2 : C_3H_8$ ratio, 40 : 10; $H_2 : n\text{-}C_4H_{10}$ ratio, 100 : 10. With n-butane, subsequent standard rates at 603 K were less than 2% of normal stage 1 rates; for propane the figure was ∼60%, but with ethane it was 4% because of the lower H_2: alkane ratio used. These activities did not change significantly during 3 h. However, it did not prove possible to obtain a stable coked sample of CK433 using ethane, because the activity increased continuously during the subsequent continuous-flow experiment.

DISCUSSION

Precise and methodical studies of the reactions of alkanes with H_2 on supported metal catalysts have as a prerequisite an understanding of the conditions under which strongly adsorbed carbonaceous deposits are formed and the effect they may have on the remaining clean surface. There have been a number of reviews (1, 2) and papers (3–7) on this subject, and they reveal a complex situation with numerous features awaiting clarification. For our purposes, and under the conditions we have used, it is adequate to regard the species responsible for loss of activity as having the same number of carbon atoms at the reactant alkane, but having lost more H atoms than is necessary to activate the molecule for hydrogenolysis; the formation of the additional carbon–metal bonds is the source of their stability and lack of reactivity. The clearest evidence for this model comes from the observation that tendency to deactivation increases in the sequence,

$$C_2H_6 < C_3H_8 < n\text{-}C_4H_{10},$$

and with increasing temperature (which on energetic grounds will favour dehydrogenation) and with decreasing H_2/alkane ratio.

Platinum/Alumina Catalysts

It appears to be a characteristic of Pt catalysts that they possess a certain type of site (denoted as Type I (6)) easily and quickly poisoned by the carbon deposit; that is to say, sites at which the excessive dehydrogenation occurs readily. Once these are removed, as happens in stage 1 of the thermal cycle, the remaining sites (Type II), which are characterised by a lower value of F but the same high values of T_3, retain their activity, and catalysts show a very satisfactory stability (Table 1). The same behaviour was seen with Pt/SiO_2 (EUROPT-1) (7). CK306, having 0.6% Pt, shows the same change in F as CK303, having only 0.3% Pt, but the deactivation is less and there is no change in activation energy (Table 1): the difference between the two catalysts is also shown by ways in which product selectivities change with temperature (Fig. 2). We may in accordance with the prior literature (12, 13) associate the Type I sites with flat low Miller index planes and the Types II sites with edges, corners, and steps, where it is less easy to form more carbon–metal bonds than are needed for reaction. An indication of the possible identity of these sites is shown in Fig. 6a and location of a C_4 residue blocking Type I sites in Fig. 6b. Skeletal isomerisation of n-butane is specifically associated with Type I sites.

The propane molecule, having only one sort of carbon–carbon bond, lacks the ability to reveal structural changes in Pt catalysts: the consistently high values of S_2 (Tables 1–

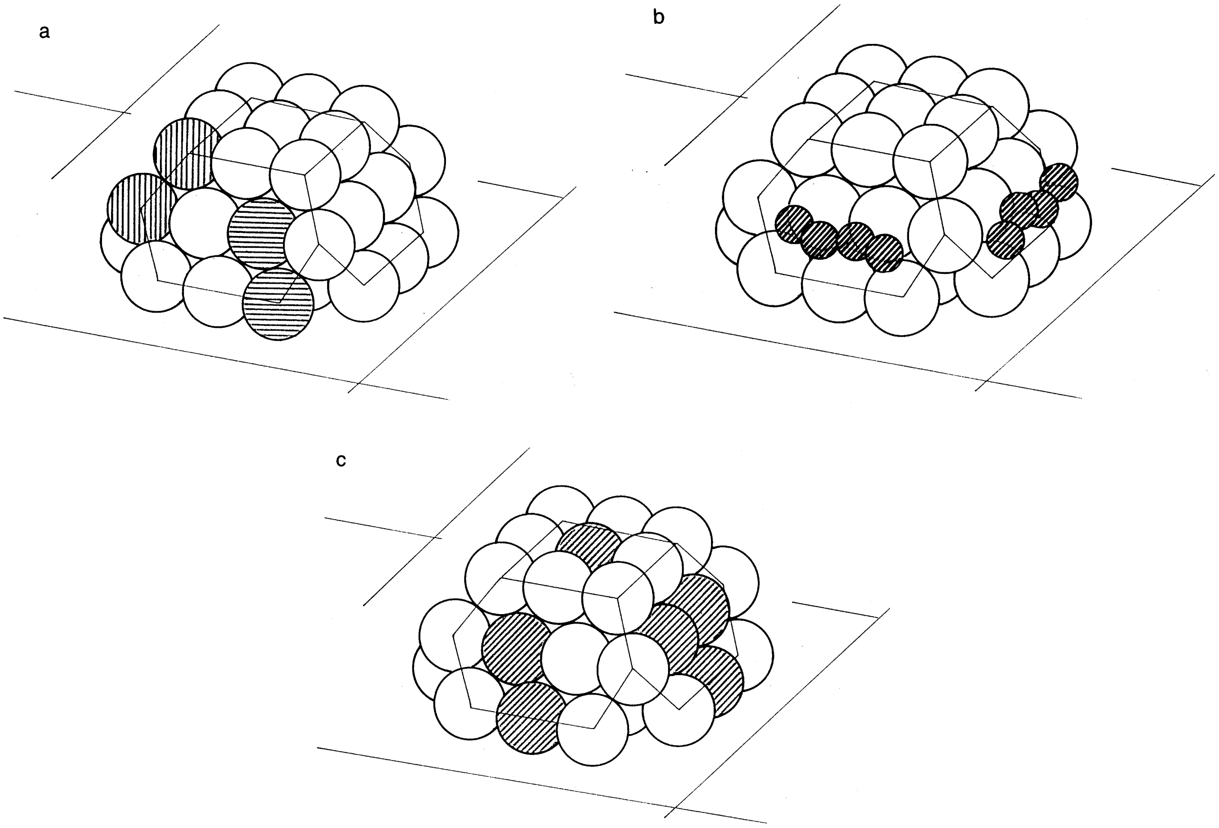

FIG. 6. Models of a small metal particle having fcc structure and resembling half a cubo-octahedron, applicable to CK303 and CK433 : 46 atoms, size $\simeq$1.2 nm, dispersion 72%. (a) Pt, showing Type I site (horizontal hatching) and Type II site (vertical hatching). (b) Pt, showing strongly adsorbed C_4 residues. (c) PtRe, showing location of Re atoms. In this particle there are 23 atoms each of Re and Pt; 13 Re atoms occupy internal positions, and 10 are external. Of these, six are visible and are in high coordination sites.

3) for both Pt catalysts is one of their most characteristic features. Although rates for ethane and for propane are not much different (Table 1), the adsorbed C_2 intermediate in the propane reaction has a very high probability ($\sim$99%) for forming gaseous ethane, which can then apparently not re-adsorb and react due to the stronger adsorption of propane. Literature reports support this observation (14, 15).

The Arrhenius plots for *n*-butane shown by CK303 and by CK306 are somewhat different (Figs. 1a, 1b): with the former, the change in slope in stage 1 at about 605 K coincides with the onset of carbon deposition as seen in the selectivity-temperature plot (Fig. 2a), but the lower activation energy in stage 2 shows that the deposit has changed both the Arrhenius parameters. With CK306, the change in slope begins at a lower temperature ($\sim$585 K, Fig. 1b), which also is that at which Fig. 2 indicates the onset of carbon deposition. However, stage 2 and later stages show two quite distinct linear parts, the reason for which is uncertain. The same behaviour was also shown with EUROPT-1 (7). It is unlikely to be due to diffusional problems, as the conversion where the change starts is quite low (2–3%).

The effect on the *n*-butane reaction of the Pt catalyst's prior use for the propane reaction (Fig. 5A) is curious. Clearly further carbon deposition occurs in stage 1, as might be expected, but it appears that adsorbed C_1 species may interact with C_3 species left by the propane reaction rather than appear as methane. The size of the effect decreases with stage number, but is still visible in stage 4.

Platinum–Rhenium/Alumina Catalysts

The problems involved in arriving at a detailed understanding of the behaviour of the PtRe catalysts are altogether more difficult. Notwithstanding the lack of reproducibility, particularly as shown by the selectivity parameters, there is no mistaking the influence that Re has (see Table 1). The values of S_2 for the propane reaction are always lower than those for the Pt catalysts, because the adsorbed C_3 species is more inclined to crack; the same effect is shown on T_3 (or T_3') in the *n*-butane reaction. The variability of the results most probably reflects differences in surface composition, and perhaps most particularly the number of Re_x clusters ($x > 2$). A further marked and consistent difference between the two types of catalyst lies in the behaviour of F and T_3 with stage number (Table 1) or time-on-stream (Table 4). The obvious changes seen with the Pt catalysts are almost absent with the PtRe catalysts, where initial deactivation is not accompanied by changes in parameter values. We might at once conclude that the Re atoms occupy the Type I sites, at least to the extent that Pt clusters of the kind that show Type I behaviour no longer exist. As noted above, however, Re_x ($x > 2$) clusters cannot be ruled out.

We have to try to reconcile this strong evidence for PtRe interaction with recent TEM/EDX information that seems to show no indication of it (16). The most probable explanation is that the catalysis is mainly due to very small particles of approximately 1 nm size and effectively 100% dispersed. Such particles are not easily detected by TEM, nor is the presence of Re in them necessarily seen by EDX, which is stated (16) to need 400–800 atoms for signal recognition. A further possibility is that, although the catalyst has been passivated after reduction, the components may disassociate in an oxidising atmosphere.

Joyner and Shpiro have pointed out (17) that by consideration of surface energies we should expect Pt to segregate to the surface; however, if most of the particles are so small that all atoms are superficial, then Pt atoms having the lower surface energy should preferentially occupy positions of lowest coordination number (18), i.e., edges and corners, allowing Re atoms to concentrate in small zones of lower Miller indices where with Pt catalysts the Type I sites would be located. This would account for the apparent absence of such sites in PtRe catalysts. The most logical model explaining why PtRe catalysts differ from pure Pt catalysts would invoke mixed Pt_xRe_y ensembles as the active centre in the former; the stronger binding of part of the molecule to the Re atoms(s), expected on the basis of its much greater activity for hydrogenolysis (11), would then explain the lower values of the selectivity parameters.

Figure 6c shows a possible model for a PtRe particle: it contains a total of 46 atoms and would appear in projection to be about 1.2 nm in size. Thirty-three atoms are on the outside, giving a dispersion of 72%. If the 13 interior atoms are all Re, then there must be 10 external Re atoms if equal numbers of each kind are present. The figure shows six of these, located in high coordination number positions, and possible PtRe bimetallic sites. Some small ensembles of Pt atoms may still be present, influenced perhaps by neighbouring Re atoms, as suggested by Joyner and Shpiro (17). This model would predict that PtRe catalysts would show a lower isomerisation selectivity S_i than the pure Pt catalysts. This is certainly true for CK433 (S_i at 603 K $= 0.002$) compared to CK303 (S_i at 603 K $\simeq 0.017$).

The CK455 catalyst, having a high loading of both metals, differs in some respects from CK433; while values of F' are similar, the former shows much higher values of T_3', approaching those shown by the Pt catalysts (Fig. 3). We may expect that the mean particle size for CK455 will be larger than that of CK433, so that a higher fraction of the Re atoms will be located in the interior, and the surface will have a more Pt-like composition. This would account for the higher values of T_3', and incidentally for the somewhat greater values of S_i (0.03 at 603 K), which is closer to that shown by CK306 (0.015 at 603 K).

It is also necessary to appreciate that, at reaction temperatures, particles comprising at most a few tens of atoms will experience severe thermal stress, and the component atoms will be undergoing vigorous oscillation, resulting in continual exchange of positions. The comparatively stable behaviour sometimes seen in functioning catalysts represents a time average of numerous different configurations, each of short duration. The formation of strongly held carbonaceous species may, however, lead to an increased surface stability.

The behaviour of CK455, having higher metal contents than CK433 (Table 1), suggests that its surface may be somewhat richer in Pt, because the rate is lower and the selectivity parameters are higher. The greater values of T_3' shown by CK433 after reverse cycling and after prior use by propane (Table 4) also suggests that these pretreatments may promote a Pt-like surface, perhaps through selective coating of the Re atoms by carbonaceous species.

Conditions for Kinetic Measurements

Thermal cycling in its various forms, as described above, is informative concerning the circumstances under which carbon deposition occurs, its extent and its effect on the residual reaction: it teaches us what situations to avoid if maintenance of a clean surface is desired and *per contra* how to obtain a partially poisoned surface when this is wished for. However, kinetic measurements, i.e., examination of effects of reactant concentrations on rates, will be made at constant temperature. We have shown with CK303 that deactivation at 532, 574, and 595 K is slight, and that performing a thermal cycle, which leads to some loss of activity, does not significantly change it. With CK433, however, at 533 K there is substantial loss of activity which is lessened by the deactivation produced by a thermal cycle. While the short reaction pulse technique does not succeed in arresting deactivation during thermal cycling, it is successful in preventing activity loss with CK433 at 582 K.

We conclude that the short reaction pulse method should be successful in minimising deactivation during kinetic measurements performed with either CK303 or CK433 at moderate temperatures, but that continuous flow operation will generally succeed with catalysts that have received a prior deliberate poisoning.

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