

Alkane Transformations on Supported Platinum Catalysts

Part 1: Reactions of Ethane, Propane, and *n*-Butane on 6.3% Platinum/Silica (EUROPT-1)

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In a continuous-flow system in which the temperature is first increased and then decreased in a stepwise manner, EUROPT-1 (6.3% Pt/SiO₂) loses ~60% of its activity for the hydrogenolysis of *n*-butane during the first high-temperature excursion (to 655 K), and 80% of its activity for isomerization to isobutane. Selectivities for hydrogenolysis products are only slightly altered due to a small increase in the probability of central C-C bond fission, which is close to statistical. In similar experiments, hydrogenolysis activity for propane falls less (~33%) and for ethane hardly at all. Arrhenius plots for *n*-butane hydrogenolysis are distinctly nonlinear, showing somewhat higher activation energies (~120 kJ mol⁻¹) above 605 K than below it. Activation energies for reactions of propane and of ethane are ~150 and ~190 kJ mol⁻¹, respectively. It appears that the species responsible for the loss of activity are highly dehydrogenated forms of the reactant alkane. These results for EUROPT-1 are contrasted to those recently published for EUROPT-3 (0.3% Pt/Al₂O₃); the later, although having a similar dispersion, is more active in hydrogenolysis but much less active in isomerization, and differs from the Pt/SiO₂ catalysts in a number of other respects. © 1992 Academic Press, Inc.

INTRODUCTION

A central question in research into the properties of supported metal catalysts is the nature of the active centres responsible for each catalysed reaction. Considerable progress has been made in assigning different roles to surface atoms depending on their coordination number, but the theoretical basis for the degree of structure sensitivity shown by a reaction is still quite unclear, and indeed there is a dearth of sound experimental observations on which advances in theory can be based. The root of the problem lies in finding a way in which the surface structure can be altered in a controlled and measurable way, so that changes in mean ensemble size and in the population of atoms

of different coordination number can be produced and their catalytic effect studied (1).

Two procedures have traditionally been used in pursuit of these aims. (1) The mean *size* of the particles is altered by some convenient means, and the likely consequences for the surface structural parameters is deduced from some geometric model. (2) The mean *ensemble size* of active metal atoms is changed by incorporating an inert element which either forms a homogeneous alloy but may segregate to the surface, or which simply adsorbs onto the surface of the active particle. While both approaches have generated results of great importance, both suffer distinct drawbacks. It is for example only recently that the possibility of the inert atom occupying some class of surface site preferentially has been considered (2, 3). If the inert component has a lower surface energy than the active one, it will not only segregate to the surface, but its atoms will prefer to

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take sites of *low* coordination number where their effect in minimising the total energy of the particle will be greatest (2). It is not however clear that the thermodynamic factor is predominant, since in the Ru–Ge, Sn, and Pb systems there are differences not accounted for by surface energy considerations (3). Nevertheless, the concept of partially coating the surface of the active particle with catalytically inactive atoms is a sound one and is likely to be applied and developed in the future.

One further possibility, related to the latter, is to use the decorating effect of species implicated in Strong Metal–Support Interactions (SMSI) as a means of affecting metal surface structure. This is best done by using the modifier (TiO_2 , V_2O_5 , etc.) as a third component added to an SiO_2 -supported metal (4–7). Effects analogous to SMSI have been produced with a number of systems (TiO_2 –Ru/ SiO_2 (4, 5) V_2O_5 –Ru/ SiO_2 (6), etc.), and in some cases quite marked changes in product selectivities, as well as in rates, have been noticed. This technique has the advantage in principle that the extent of coverage of the metal particles by the modifier can be controlled.

If work of this type is to be undertaken, two things are important: (1) the base catalyst must be properly chosen, and (2) the catalytic measurements must be performed with the greatest care, as some of the effects generated by the modifiers may be subtle in character. In Part 2 we shall describe studies of the modifications to the standard Pt/ SiO_2 catalyst EUROPT-1 produced by additions of TiO_2 and of Al_2O_3 , and have used hydrogenolysis of propane and of *n*-butane to reveal the effects. Reasons for these choices are as follows. The structure of EUROPT-1 is very well documented (8–12), and its use may facilitate comparison with the work of others. There have been several studies of how TiO_2 affects the properties of Pt for alkane reactions under SMSI conditions (13, 14), although the conclusions are not all in harmony; there is nevertheless some literature to use as a point of reference. Al_2O_3 has

sometimes been reported to show similar effects to SMSI, usually (15) but not always (4, 16) after reduction at very high temperature (>773 K). There is the risk that some of these phenomena may originate with SO_4^- in the Al_2O_3 : this is a further reason for wishing to see whether addition of Al_2O_3 to Pt/ SiO_2 has any effect. SiO_2 was felt to be a sensible choice for the support, because based on the limited information available it appeared that the modifiers might not interact with it too strongly, hence ensuring that some if not all the modifier would act to coat the Pt particles to a useful extent.

The first part of this series is devoted to a detailed description of the hydrogenolysis of ethane, propane, and of *n*-butane over EUROPT-1, the purpose of which is to identify factors which may alter the behaviour of the catalyst, so that these may be taken into account when comparisons with the modified derivatives are undertaken. Particular stress is laid on the reliability and reproducibility of the experimental measurements.

EXPERIMENTAL

Methods

The physical and catalytic properties of the reference catalyst EUROPT-1 (6.3% Pt/ SiO_2) have been fully described in a series of papers (8–12). Samples (~0.2 g) were activated by heating at 5 K min^{-1} to ~750 K in H_2 , and after 2 h they were cooled to the initial reaction temperature (~525 K): this procedure is designated HTR. Catalytic behaviour was then measured in a continuous-flow mode at 1 atm pressure between ~525 and ~655 K, by raising the temperature in steps of 10 K and analysing a single sample of gas towards the end of the intervening 20-min isothermal periods. This constituted stage 1 of the reaction; as the temperature was decreased in a similar stepwise manner, results for stage 2 were collected, and if the whole cycle was repeated we obtained results for stages 3 and 4.

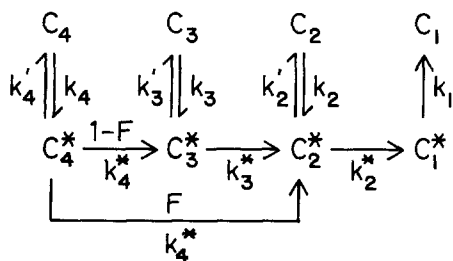
The catalyst was then heated in flowing

air for 1 h at 620 K and then (after purging with N_2) in H_2 for a further 2 h at 520 K before starting another series of reactions; this pretreatment is coded LTO/R. This treatment was applied to remove carbonaceous residues, and in the expectation that superficial oxidation, and reduction at only 520 K, might produce a rougher surface. A similar LTO/R procedure has made profound changes to supported Ru catalyst (4, 6). The reactant gas flow comprised: alkane, 10; H_2 , 100; N_2 , $30 \text{ cm}^3 \text{ min}^{-1}$: a conversion of 1% corresponds to a rate of $1.25 \text{ mmol alkane reacted g}_{\text{cat}}^{-1} \text{ h}^{-1}$. Full details of the procedures have been described previously (17).

Hydrogen chemisorption was performed in a standard vacuum system at room temperature. To obtain results compatible with the catalytic experiments, measurements were made in two stages. After HTR, the sample was outgassed at 750 K for 30 min and then cooled to room temperature, when an isotherm was measured. Then after LTO/R, the system was evacuated to 2×10^{-4} Torr and the catalyst heated under vacuum at 10 K min^{-1} from 525 to 750 K. Subsequent operations were as before.

Treatment of Results

The hydrogenolysis of n -butane can be treated as the successive reaction of adsorbed C_j^* intermediates which contain j carbon atoms ($j = 1-4$); the reaction scheme (see Scheme I below) allows fission of C_4^* to occur at either the central or a terminal C-C bond (18).



SCHEME I

The following definitions are then used:

$$\begin{aligned} \text{moles of } n\text{-butane converted} &= A \\ &= \frac{1}{4} \sum_{j=1}^{j=3} j C_j \end{aligned}$$

$$\text{fractional conversion} = x = A/(A + C_4)$$

$$\text{selectivity to product } j = S_j = C_j/A$$

where C_j is the molar fraction of products containing j carbon atoms ($j < 4$). The isomerization selectivity S_j is simply defined as the fraction of n -butane converted to isobutane. Furthermore,

$$T_j = k_j'/(k_j' + k_j^*)$$

Steady-state analysis (18) then leads to expressions for S_2 and S_3 as a function of conversion, and at low conversion these reduce to

$$S_2/T_2 = 1 + F - S_3$$

$$S_3/T_3 = 1 - F$$

Values of the three variables (F, T_2, T_3) cannot be derived from the two equations, but the corresponding treatment of the propane reaction shows, however, that

$$S_2 = T_2$$

If we assume the reaction probabilities implied by the quantity T_2 are the same for the C_2^* species formed both from propane and from n -butane, we can substitute the value measured with propane into the above equations and hence calculate T_3 and F . If central and terminal C-C bonds have the same chances of breaking, F will be 0.33; higher values imply preferential breaking of the central bond and vice versa.

RESULTS

Hydrogen Chemisorption

The general shape of the isotherms agreed well with those published earlier (11), the volumes adsorbed at zero and 40 Torr pressure being respectively 159.5 and $162 \mu\text{mol g}_{\text{cat}}^{-1}$ for the HTR pretreatment and 173.5 and $178 \mu\text{mol g}_{\text{cat}}^{-1}$ for the LTO/R pretreatment.

Of the 40-Torr values, that after HTR is at the bottom end of the previously cited range (11) while that after LTO/R is close to the median. Both isotherms also gave excellent linear plots when treated by the Langmuir equation for dissociative adsorption, these plots affording estimates of monolayer volume of $170.7 \mu\text{mol g}_{\text{cat}}^{-1}$ for HTR and $188.3 \mu\text{mol g}_{\text{cat}}^{-1}$ for LTO/R. These values translate into H/Pt ratios of respectively 1.064 and 1.170, and these are the values employed in converting rates to TOFs, i.e., rates expressed per surface Pt atom. As explained fully in the earlier publications (10, 11), dispersion as given by TEM is only about 60% and it is supposed that not all the H_2 adsorbed is utilised in covering the surface at a 1 : 1 H/Pt ratio. However, for consistency with later papers in this series, we use the measured H/Pt ratio for estimating TOFs, conscious of the limitations of the procedure.

Hydrogenolysis of Ethane

In a four-stage experiment, the rate at 573 K initially decreased very slightly (stage 1, 0.058; stage 2, $0.052 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$) and thereafter remained constant at $0.0515 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$; if the number of surface Pt atoms is taken as $2 \times 10^{20} \text{ g}_{\text{cat}}^{-1}$ (11), this last rate equates to a TOF of 0.15 h^{-1} , compared to the recommended value of 0.22 h^{-1} (19). The mean of four closely concordant values of the activation energy measured at 564–657 K (10^{-2} – 10% conversion) was $189.5 \text{ kJ mol}^{-1}$. There was no significant change of slope in the Arrhenius plots at conversions greater than $10^{-2}\%$, although there was an indication that the activation energy might have been lower below 550 K; however, the number and accuracy of the data points are insufficient to be certain of this.

Hydrogenolysis of Propane

Two experiments were performed, using different samples of catalyst. The HTR treatment was first applied in both cases; after the second experiment, one sample

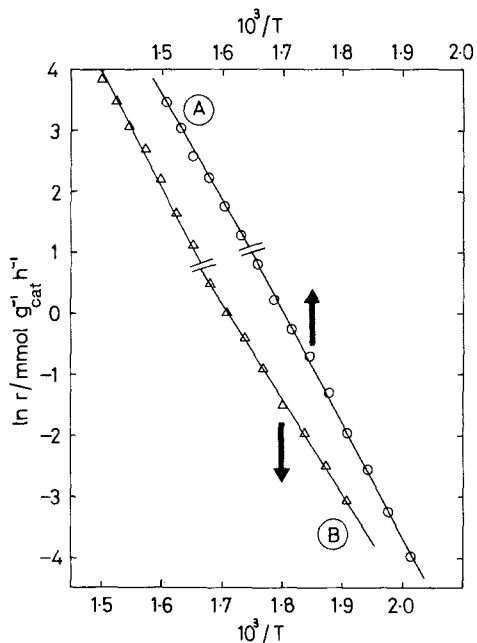


FIG. 1. Arrhenius plots (HTR, stage 2) using rates r for hydrogenolysis of (A) propane and (B) n -butane over EUROPT-1; kinetic parameters derived from these plots are given in Table 1.

was given the LTO/R treatment, and its behaviour re-examined. Following the HTR treatments, satisfactorily linear Arrhenius plots based on rate of reactant removal were obtained for stages 2 to 4 in the range 520–660 K (Fig. 1). The plots for both the first stages were however distinctly nonlinear because of deactivation which occurred above about 620 K; Arrhenius parameters for this stage were not well reproducible and are therefore not quoted. This loss of activity only occurred in the first high-temperature excursion.

Careful inspection of the Arrhenius plots for the later stages does however suggest that activation energies are slightly lower (by 7–18 kJ mol^{-1}) above 603 K than below it, but the differences between values derived from the whole set, comprising 15 points, and those derived for the nine points obtained at and below 603 K, are only 2–10 kJ mol^{-1} , and the correlation coefficients are on average no different, at about 0.9995.

TABLE 1

Differences in Arrhenius Parameters for Hydrogenolysis of Propane and of *n*-Butane above and below 603 K (HTR, stage 2)

Alkane	<i>T</i> range (K)	<i>E</i> (kJ mol ⁻¹)	ln <i>A</i> ^a	cc ^b
Propane	523–603	155.5 ± 4.7	31.84	0.9994
	603–663	146.5 ± 5.9	30.02	0.9994
	523–663	151.9 ± 2.3	31.05	0.9997
<i>n</i> -Butane	524–595	121.9 ± 3.1	24.94	0.9996
	595–666	145.5 ± 3.4	29.68	0.9997
	524–666	131.0 ± 3.8	26.90	0.9988

Note. The corresponding Arrhenius plots are shown in Fig. 1.

^a *A* in mmol g_{cat}⁻¹ h⁻¹.

^b Correlation coefficient.

Moreover the standard deviations on the activation energies for the high and low temperature parts of the plot overlap (Table 1), the lowest value being given by the whole set. The effect if it exists is therefore at the borderline of what is statistically significant, but Fig. 1 demonstrates how the change in slope manifests itself. It is therefore sufficient simply to record (Table 2) Arrhenius

parameters derived from the whole set. The agreement between the mean values of the activation energies for the two different samples is acceptable, but they are significantly lower than the mean value of 185 kJ mol⁻¹ given previously (19). This may be because our values relate to a partially poisoned surface.

Table 2 also quotes the rates measured at

TABLE 2

Kinetic Parameters for Hydrogenolysis of Propane over EUROPT-1
Reproducibility and Effect of Pretreatment Conditions

Sample	Pretreatment	Stage	Temp. range (K)	<i>E</i> (kJ mol ⁻¹)	ln <i>A</i> ^a	cc ^b	<i>r</i> ^{a,c}	<i>S</i> ₂ ^c
I	HTR	1	—	—	—	—	0.76	0.995
		2	676–532	148 ± 3.2	30.5	0.9994	0.54	0.996
		3	532–677	148 ± 3.0	30.3	0.9994	0.52	0.995
		4	655–532	146 ± 3.3	29.9	0.9994	0.49	0.995
II	HTR	1	—	—	—	—	0.72	0.994
		2	663–523	152 ± 2.3	31.0	0.9997	0.45	0.991
		3	523–663	154 ± 3.1	31.5	0.9994	0.46	0.993
		4	663–523	152 ± 2.2	31.0	0.9997	0.42	0.996
II	LTO/R	1	—	—	—	—	0.66	0.994
		2	663–522	151 ± 3.7	31.3	0.9992	0.65	0.995
		3	522–644	164 ± 1.8	34.1	0.9999	0.72	0.995
		4	663–522	160 ± 2.9	33.5	0.9996	0.87	0.996

Note. The value of the rate may not be exactly that derivable from the Arrhenius parameters as quoted, because they are given only to three significant figures.

^a *A* and *r* in mmol g_{cat}⁻¹ h⁻¹.

^b Correlation coefficient.

^c At 573 K.

573 K after HTR in each of the four stages in the two experiments. They fall by 28–37% between stages 1 and 2, and thereafter remain sensibly constant; the sample-to-sample reproducibility is also very satisfactory. Assuming the number of surface Pt atoms to be $2 \times 10^{20} \text{ g}_{\text{cat}}^{-1}$ (11), the mean TOF for the stage 1 rates is 2.2 h^{-1} and for the later stages 1.45 h^{-1} ; these values are to be compared with the recommended value (19) of 1.5 h^{-1} at 573 K. Values of S_2 at 573 K do not change with stage number (Table 2), and are in the range 0.991–0.996, independent also of temperature up to 615 K. Lower values (~ 0.9) were reported previously (19), but the present ones are more in line with the normal behaviour of Pt catalysts (17).

The LTO/R treatment produces small but significant changes. It restores the stage 1 rate to almost its original value, presumably by removing the carbonaceous species which had caused the initial deactivation, and the Arrhenius plot for stage 1 becomes again distinctly nonlinear; in the subsequent stages the rate appears to rise slightly. Activation energies are a little higher than after HTR, but there is no change in the value of S_2 .

In all cases, the value of S_2 only starts to fall below 0.99 above about 620 K; from its temperature dependence above 620 K one can calculate ΔE_2 , the difference in activation energy between the processes of C_2^* desorption as ethane and its cracking to methane. The latter is the higher by about 155 kJ mol^{-1} .

Reaction of *n*-Butane with H_2

Since the reaction of *n*-butane with H_2 affords both isobutane and the lower alkanes, it is necessary to record information on the rates of both reactions. Isomerization is an important reaction on EUROPT-1 (19), the isomerization selectivity S_i attaining values greater than 0.4 at high temperature; however, in general the kinetic results for this reaction are less extensive and less reliable than for hydrogenolysis.

Duplicate experiments were performed

after HTR; Arrhenius plots for hydrogenolysis were in all cases quite clearly composed of two linear parts, with a break at about 600 K, and the activation energy above this temperature being on average 22 kJ mol^{-1} (range $14\text{--}30 \text{ kJ mol}^{-1}$) greater than below it (Fig. 1). Similar results were obtained after LTO/R (range $16\text{--}32 \text{ kJ mol}^{-1}$; mean 26 kJ mol^{-1}). In each first stage, however, Arrhenius plots (although of the same form) gave distinctly lower activation energies ($\sim 95 \text{ kJ mol}^{-1}$) than in the later stages, due presumably to the initially clean state of the catalyst, and so their precise values are not recorded. In Stages 2 to 4, the high temperature parts of the plots invariably gave excellent straight lines (Fig. 1) and the average correlation coefficient for the nine sets was 0.9998, based on seven or eight points. The low temperature part comprised nine points, with an average correlation coefficient of 0.9995. For the complete set (15 points), its mean value was only 0.9987. The differences in slope are thus larger than for propane, and are in the opposite sense; furthermore, the standard deviations on the activation energies derived from the two parts of the plot do *not* overlap (see Table 1 for an example), and the effect is in this case statistically meaningful. The Arrhenius parameters in Table 2 are only for the low temperature range. Activation energies are very consistent ($118\text{--}127 \text{ kJ mol}^{-1}$) and show no significant difference between the three experiments; they agree well with previously recorded (19) values based on reactant removal ($114\text{--}142 \text{ kJ mol}^{-1}$), mean 126 kJ mol^{-1}).

Rates at 573 K were about 60% less after stage 1, but again there was no progressive deactivation, and the rates measured in stages 2 to 4 were remarkably constant over the three experiments ($0.42\text{--}0.55 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$; mean $0.50 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$). Table 3 also contains values for the selectivities S_2 and S_3 , and the derived Kempling–Anderson parameters F and T_3 . The initial deactivation increases S_2 and decreases S_3 , this giving a small increase in F but no significant

TABLE 3
Kinetic Parameters for the Hydrogenolysis of *n*-Butane over EUROPT-1:
Reproducibility and Effect of Pretreatment Conditions

Sample	Pretreatment	Stage	Temp. range (K)	E_h (kJ mol ⁻¹)	ln A_h	r_h	S_2	S_3	F	T_3	S_i
I	HTR	1	—	—	—	1.21	0.692	0.640	0.335	0.962	0.200
		2	605–524	122 ± 3.1	24.9	0.52	0.770	0.600	0.373	0.957	0.106
		3	524–605	125 ± 2.2	25.6	0.55	0.770	0.597	0.371	0.949	0.094
		4	605–544	119 ± 5.2	24.3	0.48	0.776	0.594	0.374	0.949	0.085
II	HTR	1	—	—	—	1.22	0.628	0.674	0.306	0.971	0.197
		2	603–524	118 ± 3.3	24.1	0.52	0.708	0.632	0.346	0.966	0.108
		3	524–603	121 ± 3.9	24.8	0.55	0.709	0.633	0.347	0.969	0.158
		4	603–524	118 ± 2.8	24.0	0.48	0.714	0.626	0.343	0.953	0.131
II	LTO/R	1	—	—	—	1.22	0.680	0.643	0.327	0.953	0.298
		2	603–524	124 ± 3.4	25.2	0.47	0.738	0.613	0.355	0.950	0.123
		3	524–603	127 ± 3.3	26.0	0.50	0.729	0.613	0.346	0.937	0.102
		4	603–524	121 ± 3.3	24.6	0.42	0.739	0.610	0.352	0.941	0.220

Note. See footnotes to Table 1; all rates and selectivity parameters are at 573 K.

change to T_3 ; it is also responsible for a marked decrease in isomerization selectivity. Both the initial and the steady-state values of F vary slightly from sample to sample, and with the type of pretreatment. The consistency of the values of S_2 and S_3 in stages 2–4 shows that variations of F of only ± 0.01 are significant, and this parameter therefore reveals minor differences in surface structure which are not reflected in the rate measurements. As we found for Pt/Al₂O₃ catalysts (17), the differences in the T_3 values are much smaller and are close to what is statistically significant. The LTO/R treatment does give a markedly higher value of S_i in stage 1, but this quickly falls to more normal values for subsequent stages. Values previously given (19) at 573 K were: S_2 , ~ 0.7 ; S_3 , ~ 0.6 ; F , ~ 0.3 , in fair agreement with those we now find (Table 3).

Figure 2 demonstrates the effect of the initial deactivation over the whole temperature range; the values of T_3 are almost the same in the two stages, and there is no further significant change of any of the selectivity parameters in the subsequent two stages. T_3 has a small temperature coefficient, only falling from ~ 0.97 to ~ 0.92 as the temperature is raised; meaningful values of ΔE_3 (defined analogously to ΔE_2) could not there-

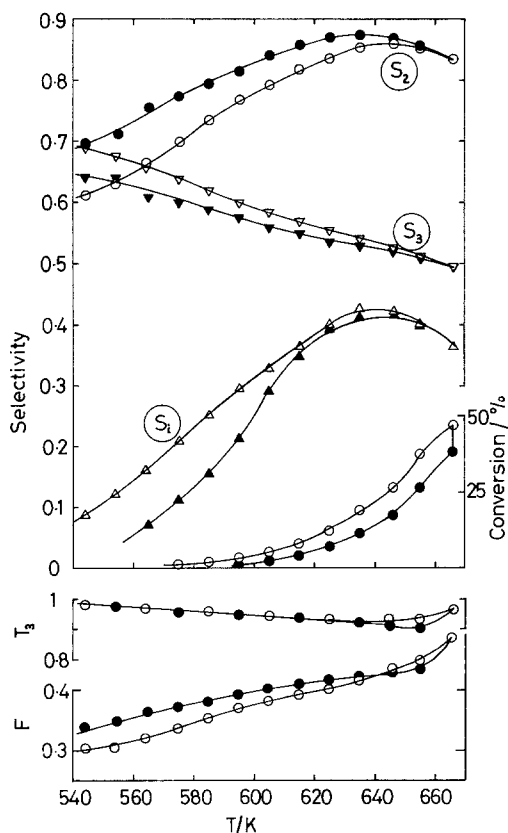


FIG. 2. Temperature dependence of conversion, product selectivities and parameters F and T_3 for *n*-butane hydrogenolysis on EUROPT-1. Open points, rising temperature; filled points, falling temperature.

TABLE 4
Kinetic Parameters for the Isomerization of *n*-Butane over EUROPT-1:
Reproducibility and Effect of Pretreatment Conditions

Sample	Pretreatment	Stage	Temp. range (K)	E_i (kJ mol ⁻¹)	ln A_i	r_i
I	HTR	1	—	—	—	0.28
		2	625–565	237	46.9	0.06
		3	575–615	253	50.3	0.06
		4	625–575	251	49.4	0.04
II	HTR	1	—	—	—	0.31
		2	623–574	232	46.0	0.06
		3	564–623	217	43.1	0.10
		4	633–574	218	43.1	0.07
II	LTO/R	1	—	—	—	0.49
		2	613–574	253	50.5	0.07
		3	574–603	286	57.2	0.06
		4	643–564	198	39.3	0.11

Note. See footnotes to Table 1.

fore be derived. The maxima shown by S_2 and S_1 at 630–640 K may be partly caused by the high-temperature coking, but stage 1 conversions exceed 25% above 625 K and secondary reactions of intermediate products are therefore to be expected.

Table 4 gives the Arrhenius parameters for isomerization. The plots for each stage 1 were nonlinear, and values of activation energy are not quoted. Those for stages 2 to 4 are, as expected from Fig. 2, higher than those for hydrogenolysis, but there is a greater scatter because of the larger error associated with measuring low rates of isobutane formation and the smaller number of points usable for estimating slopes. There is no reliable indication of alterations in the slopes of the Arrhenius plots for isomerization.

Mean values of TOF for reactant removal at 573 K are estimated as about 4.5 h⁻¹ in stage 1 and about 1.8 h⁻¹ in the later stages. The previously recommended value (19) of 5 h⁻¹ was clearly based on rates measured on catalysts not suffering from the initial deactivation brought about in this work by raising the temperature in stage 1 to ~660 K.

DISCUSSION

Deactivation due to Coking

It is extremely difficult to study the reactions of alkanes on Pt catalysts under conditions such that they do not quickly lose some of their activity due to "coking." By using low temperatures or high H₂/alkane ratios, the problem is minimised, but only small parts of the whole system are thereby examined. Use of the pulse-flow mode also lessens deactivation, but one is then deprived of the advantages of the continuous-flow or static modes in determining kinetics under steady-state conditions. Only in the case of ethane is deactivation unimportant. With higher alkanes, the progressive occurrence of coke formation as the temperature is raised in stage 1 is plain to see, but it is a striking characteristic of EUROPT-1 that, after this initial deactivation (by 33% for propane and by 60% for *n*-butane under the conditions we have used), the rates remain *perfectly steady* and almost exactly the same for the two alkanes. Initial and steady-state rates are closely reproducible from sample-to-sample (Tables 2 and 3), the

LTO/R treatment giving higher steady-state rates only with propane. Because of the initial deactivation, it is particularly important, when attempting comparisons with others' work, to define exactly the conditions under which rate measurements are made. Those recorded before (19) are however in quite good agreement with our stage 1 values.

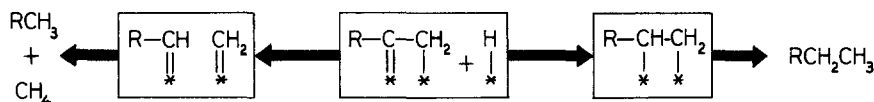
Careful and repeated measurements of the temperature-dependence of rates have revealed breaks in the Arrhenius plots in the second and subsequent stages, as illustrated in Fig. 1. The change in activation energy occurring at about 600 K is seen more clearly with *n*-butane than with propane, the changes being in the opposite sense with these two alkanes. This confirms that the effect is not a trivial one associated with mass-transport phenomena, but is more probably due to some alteration in the rate-determining step at about 600 K.

Effect of Coking on Product Selectivities

The issue of structure-sensitivity or particle-size sensitivity is normally discussed in the context of the rate of reactant removal, and it is only with higher alkanes, where isomerization and cyclization feature largely, or where, as with methylcyclopentane, different ring-opening routes are available, that product selectivities receive much attention. Carbon deposition is known (20) to change the composition of the products formed by *n*-hexane, although it is sometimes difficult to separate this factor from the effect due to temperature alone. We have previously shown (17) with Pt/Al₂O₃ that there is an initial deactivation similar to that found here with EUROPT-1, the difference with Pt/Al₂O₃ being that, while the value of *F* decreases to a lower stable value,

the rate continues to fall through all four stages. With EUROPT-1, the activity loss is accompanied by a small *increase* in *F* and by a significant decrease in *S_i* (Table 3). These effects are reversed by the LTO/R treatment, which apparently cleanses the surface; they are well reproducible from sample to sample, although the actual magnitudes of the parameters *F* and *S_i* do vary slightly with sample and with pretreatment (Table 3). We have previously attempted (17) to devise a model for these effects in terms of populations of active centres comprising atoms of different coordination number. It seems that particle structure is sensitively determined by the activation procedure, and the exact reproduction of the selectivity parameters provides a rigorous test of experimental control, more rigorous in fact than that afforded by the total rate.

It is also noteworthy that the *T* parameters (i.e., *T₂*, which is the same as *S₂* in the propane reaction, and *T₃* in the *n*-butane reaction) exhibit no structure sensitivity of any significance; the same was observed with Pt/Al₂O₃ (17). The relative probabilities of reactive desorption (i.e., of *C₂^{*}* to C₂H₆ or of *C₃^{*}* to C₃H₈) to further bond breaking (i.e., of *C₂^{*}* to 2*C₁^{*}*, etc.) are uninfluenced by carbon deposition, which we have previously assumed (17) to occur preferentially on low Miller index planes comprising atoms of high coordination number. The former probabilities are much the higher over all Pt catalysts; with Pt/Al₂O₃ catalysts we found (17) values of *T₃* at 573 K of 0.985–0.99, but with EUROPT-1 they are slightly lower (0.94–0.97, Table 3). The lack of sensitive response of the *T* parameters to surface conditions may reflect the essential similarity of the two processes; both for example might



SCHEME II

proceed by the addition of a chemisorbed H atom (Scheme II), the right-hand product being much the more favoured over Pt. There is however a very small but consistent tendency for T_3 to increase with stage number, attributable to a slight effect of coking on their rates. In addition to the variation of F with surface structure, previously noted, carbon deposition on EUROPT-1 clearly deactivates skeletal isomerization selectively (Table 3); comparable effects are not observable with Pt/Al₂O₃ because there the values of S_i are so very low (~ 0.02). Our tentative conclusion is that isomerization occurs most readily at sites where *n*-butane more readily undergoes *central* C–C bond fission. This statement does not imply that *all* sites (previously (17) designated Type II) comprising *high* coordination number atoms are equally active in both processes; indeed, S_i varies to a greater extent, and more erratically, with stage number than does F (Table 3), and so it is likely that isomerization takes place on some subset of the Type II centres. It is not, however, yet clear why with EUROPT-1 the initial deactivation causes an increase in F .

CONCLUSIONS

Quite detailed information on the kinetics of the reactions of the lower alkanes with H₂ is now available for two standard supported Pt catalysts, viz., EUROPT-1 (Pt/SiO₂ (19)) and EUROPT-3 (Pt/Al₂O₃ (17, 21)); further work on the latter by members of the EUROCAT group is now being prepared for publication. Some comparison of these two materials has been made in the foregoing discussion, from which it is clear that there are substantial differences between them, notwithstanding the fact that their dispersions are probably not greatly different. To those differences already noted, we may add the observations that (i) rates at 573 K are higher for the Pt/Al₂O₃ by factors of about two for ethane, six for propane and (in stage 1) about 16 for *n*-butane; and (ii) consistently higher activation energies are given by this catalyst.

While the latter observation could originate in a difference of dispersion, the former is unlikely to do so. We must therefore conclude that the EUROPT-3 Pt/Al₂O₃ probably contains sites of inherently greater activity than EUROPT-1, even although higher activation energies might have been expected to correspond to lower activities.

In one respect, EUROPT-1 seems to show behaviour not at all in line with its dispersion; it gives higher isomerization selectivities (before deactivation) than expected by comparison with Pt/C catalysts (22). The same effect has also been noted with the reactions of *n*-hexane (20).

Finally, the present results help to confirm our earlier speculations (17) on the nature of the species causing deactivation. It is quite clear that, within the range of conditions we have covered, neither EUROPT-1 nor EUROPT-3 loses any significant activity if exposed to a 10:1 H₂:ethane mixture at temperatures up to ~ 670 K. We believe therefore that excessive dehydrogenation, over and above what is needed to activate the molecule for hydrogenolysis, does not occur. With propane, however, and a fortiori with *n*-butane, there is an initial loss of activity with EUROPT-1, suggesting that the number of carbon atoms in the molecule determines the number of points at which it can be attached to the surface in consequence of breaking of C–H bonds. The greater the number of bonds so formed, the smaller the chance of rehydrogenation to an active structure, and hence the greater the probability of activity loss. The susceptibility of EUROPT-3 (17) to deactivation is somewhat less than for EUROPT-1, although the trends are the same.

Although a model was sketched to account for the effects of coking (and of Re) on the Pt/Al₂O₃ catalyst (17), its further refinement to embrace the behaviour of EUROPT-1 will most sensibly await the presentation of results on the deactivation of this catalyst by TiO₂ and Al₂O₃, and on the description of other supported Pt catalysts (23).

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