Hydrogenolysis of Alkanes

Part 1.—Hydrogenolysis of Ethane, Propane and n-Butane on 6% Pt/SiO₂ (EUROPT-1)

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The hydrogenolysis of ethane, propane and n-butane has been studied on a 6.3% platinum /silica catalyst (EUROPT-1); for ethane the rate and other kinetic parameters agree well with literature values. Treatment of the catalyst in hydrogen between 623 and 1173 K leads to a loss of capacity for hydrogen chemisorption greater than that attributable to an increase in particle size, and to an even greater loss of activity for n-butane hydrogenolysis, partly restorable by oxidation. Extensive reorganisation of the metal occurs during a short oxidation at 873 K.

Product selectivities to methane, ethane and propane are interpreted by a simple but comprehensive reaction network due to Kempling and Anderson; this is thought to be more informative than the usual approach of assuming that two or more reactions proceed in parallel. Selectivities are not much changed by the thermal treatments. This observation, coupled with the fact that the activity for ethane hydrogenolysis, according to the literature, varies greatly from one platinum catalyst to another while the activation energy and reaction orders scarcely alter, strongly suggests that each hydrogenolysis reaction demands a uniquely defined active site for initiation of the reaction, whereafter it proceeds in a uniform manner.

The hydrogenolysis and skeletal isomerisation of alkanes has been widely studied on many metals and alloys,¹ and it may perhaps be wondered whether anything useful remains to be said on the subject. However, a survey of the literature relating to platinum reveals the following. (i) The principal emphasis has been on the mechanisms of skeletal isomerisation¹ and cyclisation,² their dependence on metal particle size³ and morphology,⁴ and on the relative rates of rupture of the various C-C bonds in molecules containing five or more carbon atoms.^{5, 6} (ii) The reactions of ethane, propane, n-butane and isobutane have been effected on platinum black,⁷ platinum films^{8,9} or platinum particles in zeolites,¹⁰ which while meriting study are esoteric; traditional supported-platinum catalysts have only rarely been used.^{5,7} (iii) The reaction of n-butane, the simplest alkane able to show skeletal isomerisation as well as selectivity in hydrogenolysis, is frequently cited and used as a structure-sensitive test reaction,^{10, 11} but the product yields are usually interpreted by a simplistic kinetic formalism which inhibits deeper understanding of the correlation between mechanism and surface structure. A further examination, using a more responsive kinetic model, of the precise meaning of the term 'structure sensitive' as applied to alkane hydrogenolysis therefore seems to be in order. Ethane hydrogenolysis of course only provides a single rate measurement.

A 6% Pt/SiO₂ catalyst designated as EUROPT-1 has been studied in a number of laboratories in Europe^{12–14} and its physical characteristics are well known.¹⁵ As part

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of a programme to establish this catalyst as an international standard of reference, we have employed it for the hydrogenolysis of ethane, propane and n-butane. In addition to examining an alternative kinetic formalism to describe the results, we have treated the catalyst in hydrogen at high temperatures to try to induce the kind of strong metal-support interaction observed by Martin *et al.*¹² with the same catalyst. Emphasis has been placed on the distribution of hydrogenolysis products from n-butane as a means of describing the active site, but the isomerisation to isobutane has been followed in a limited range of conditions.

MECHANISM OF HYDROGENOLYSIS

The reaction on n-butane with hydrogen affords a mixture of methane, ethane and propane; isobutane may also be formed, and the methane: propane ratio is sometimes^{5, 8} but not always unity. This situation is occasionally discussed qualitatively in terms of selectivity for central and terminal bond fission,⁷ but more usually by means of reactions expressed as

$$C_4H_{10} + H_2 \to CH_4 + C_3H_8$$
 (1)

$$C_4 H_{10} + H_2 \to 2C_2 H_6.$$
 (2)

When the methane: propane ratio exceeds unity, a third reaction is invoked:

$$C_4 H_{10} + 3H_2 \rightarrow 4CH_4. \tag{3}$$

A further possible reaction, rarely called upon, is

$$C_4 H_{10} + 2H_2 \rightarrow C_2 H_6 + 2CH_4$$
 (4)

since this can be expressed as a combination of reactions (2) and (3). If skeletal isomerisation is considered, yet another equation is needed. A corresponding but simpler reaction set can of course be written for propane. Numerous treatments of the n-butane reaction^{5, 8, 10, 11} employ a kinetic formalism based on reactions (1) and (2), expressing variation of the rate and product yields with reactant pressures or temperature through orders of reactions and activation energies for these reactions.

On reflection this appears to be a sterile approach, for it explains neither why the kinetic parameters for the two (or three or four) reactions should differ nor why their values alter from one catalyst to another. It does not provide a means of interpreting the dependence of product selectivities upon conversion, and it does not allow this information to be used constructively. Moreover, if one desires to recalculate the raw results, their recovery from the kinetic parameters is a virtual impossibility. The implications of formulating the process in this way have also not be explored. The only rational interpretation would be that there are two (or three or four) different types of site, such that an n-butane molecule landing on one type is bound to transform to the appropriate products, and no others. What distinguishes these sites, and how the intermediates on them differ, has never been discussed.

USE OF THE KEMPLING-ANDERSON REACTION NETWORK

A more constructive approach is that adopted by Kempling and Anderson.¹⁶ Some years ago they developed a simple but comprehensive reaction framework which avoids the *ad hoc* assumptions made in the procedure just described and which permits a deeper insight into how variation of the catalyst structure and composition, and of

G. C. BOND AND XU YIDE

reaction conditions, affects the reaction mechanism. The reaction network is as follows:

$$C_{4} \stackrel{k_{4}}{\underset{k_{4}}{\longrightarrow}} C_{4}^{*} \stackrel{k_{4}^{*}}{\underbrace{ \begin{array}{c} 1-F \\ F \end{array} }} C_{3}^{*} + C_{1}^{*}} \\ C_{3} \stackrel{k_{3}}{\underset{k_{3}}{\longrightarrow}} C_{3}^{*} \stackrel{k_{3}^{*}}{\xrightarrow{}} C_{2}^{*} + C_{1}^{*} \\ C_{2} \stackrel{k_{2}}{\underset{k_{2}}{\xrightarrow{}}} C_{2}^{*} \stackrel{k_{3}^{*}}{\xrightarrow{}} 2C_{1}^{*} \\ C_{1} \stackrel{k_{1}}{\underset{k_{2}}{\xrightarrow{}}} C_{1}^{*} \\ \end{array}}$$

 C_i represents a linear alkane containing *i* carbon atoms in the gas phase and C_i^* its adsorbed form. By inference there is only one type of site on which n-butane can adsorb, the relative probabilities of central and terminal bond-breaking being described by the parameter *F*, the value of which is presumably characteristic of the geometric or electronic structure of the site. The relative amounts of propane, ethane and methane formed then depend upon the chance of a given hydrocarbon fragment desorbing with the aid of hydrogen atoms, forming the alkane, to its chance of further rupture (except of course in the case of C_1 fragments, which can only desorb).

Steady-state analysis of this scheme leads to equations which express the yields or selectivities for each product as a function of conversion and of the disposable parameters. Treatment of the results proceeds as follows. Let c_i be the number of moles of product *i* formed, then

fractional conversion = $X = A/(A + c_4)$ moles of C₄H₁₀ transformed = $A = (c_1 + 2c_2 + 3c_2)/4$ selectivity to product $i = S_i = c_i/A$.

The constants of the reaction scheme can be grouped in various ways, the following consolidated constants being found most useful:

$$Y = X/(1-X)$$

 $k''_i = k_i k_i^*/(k'_i + k_i^*)$
 $T_i = k'_i/(k'_i + k_i^*)$
 $G_i = k''_i/k''_4.$

The steady-state analysis then leads^{16, 17} to the following expressions for the variation of S_2 and S_3 with conversion and their dependence on the various rate coefficients:

$$S_2 = (1 + F - S_3)T_2/(1 + G_2Y)$$

$$S_3 = (1 - F)T_3/(1 + G_3Y)$$

where F is defined as the chance of breaking the central C—C bond. Simpler equations result from a similar treatment of the reactions of propane,¹⁷ while the same principles may be used to describe the reactions of isobutane¹⁶ (including its isomerisation¹⁸) and of higher hydrocarbons.¹⁸ While this approach has chiefly been used by Anderson and coworkers to describe alkane hydrogenolyses catalysed by ruthenium, there is no reason why it should not be generally applicable.¹⁸

It is not, however, a simple problem to extract all the rate coefficients, even the consolidated ones, from the experimental results. In principle the variation of the selectivities with conversion over a sufficient range permits the evaluation of F, T_2 ,

 T_3 , G_2 and G_3 . In practice, however, selectivites often do not change significantly until conversions (based on n-butane to methane) exceed 50%,¹⁷ and it is necessary to have results in the 60–90% conversion range to make accurate curve-fitting possible.¹⁸ This is not always convenient in a continuous-flow system. We have therefore had to resort to expedients. We have sometimes confined our measurements to low conversions (< ca. 20%) where, because G_2 and G_3 are likely to be less than unity, the above expressions for the selectivites simplify to

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

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

However, this still does not allow the estimation of the three constants. In theory it should be possible to evaluate T_2 either from the selectivities observed under the same conditions with propane (where $S_2 = T_2$) or with isobutane [where because there is no splitting factor T_2 and T_3 can be deduced unambiguously from the equations $S_3 = T_3$ and $S_2 = (1 - S_3)T_2$]. We have used the first of these approaches in this paper. Finally, when this additional effort was not merited we have simply set T_2 equal to unity and calculated the modified parameters F' and T'_3 : the sense of their changes is probably significant, even if their absolute magnitudes are in doubt. We shall make extensive use of the above approach in later papers in this series.

EXPERIMENTAL

All reactions were studied in a continuous-flow system, the flows of hydrogen, alkane and nitrogen being adjusted to give the required gas composition. For ethane hydrogenolysis, hydrogen was purified by passage over Pd/Al_2O_3 and 5A molecular sieve, and nitrogen over MnO/Celite;¹⁹ gas-chromatographic analysis used a silica column (3 m) at 303 K and hydrogen as carrier gas. The catalyst (0.2 g) was prereduced at 473 K for 30 min in hydrogen (30 cm³ min⁻¹).

For the reactions of propane and of n-butane, nitrogen was purified by passage over Cu/SiO₂; analysis was performed with a silica column (3 m) at either 453 K or, when separation of isobutane from n-butane was desired, at 353 K with nitrogen as carrier gas. Conversions as low as 0.01% could be detected, but accurate product distributions were only obtainable at conversions > 0.05%. Selectivities were reproducible to better than 1% (see fig. 2 for an example). Conversions never exceeded 5%. Samples of catalyst (*ca.* 0.2 g) were reduced under various conditions and sometimes heated in air (see text). Total flow rates were 105 cm³ min⁻¹ for the other reactions, where the standard gas mixture contained 0.833 atm hydrogen and 0.042 atm alkane.† The alkanes were obtained from B.D.H. Ltd and used without further purification.

The catalyst was 6.3% Pt/SiO₂ designated as EUROPT-1. It is a coarse powder and its preparation and characteristics have already been described:¹⁵ the mean particle diameter is ca 1.8 nm and the dispersion ('percentage exposed') ca. 60%. The effect of thermal treatments described in the text was followed by measuring the hydrogen chemisorption isotherm in a conventional high-vacuum system equipped with a Texas precision transducer and capable of evacuation to better than 10^{-5} Torr.[‡] Samples (ca. 0.3 g) were reduced under 100 Torr hydrogen at 623 K for 1 h and then evacuated at the same temperature for 1 h before being cooled while pumping continued. Isotherms were obtained having equilibrium pressures up to 40 Torr and 15–30 min was allowed for equilibration. The amount adsorbed scarcely changed in the range 10–40 Torr, so extrapolation to zero pressure gave the monolayer volume with high precision. Heat-treated catalysts were also examined in a Jeol 100 electron microscope; suspensions, prepared by grinding and ultrasonic dispersion in actione, were placed on a carbon-coated grid. The instrumental magnification was 130000.

 $\dagger atm \equiv 101\,325 \text{ Pa.}$ $\ddagger 1 \text{ Torr} \equiv 101\,325/760 \text{ Pa.}$

G. C. BOND AND XU YIDE

RESULTS AND DISCUSSION

ETHANE

Rates were estimated from the flow-rate, the fractional conversion, the weight of platinum in the sample and the metal area per g (taken as $280 \text{ m}^2 \text{ g}_{Pt}^{-1}$). Orders of reaction were calculated from the power rate expression

$r = k p_{\mathrm{H}_2}^m p_{\mathrm{C}_2 \mathrm{H}_6}^n$

and activation energies from the Arrhenius equation using defined reactant pressures at the inlet. The results are shown in table 1, where they are compared with those obtained by Sinfelt^{20, 21} using a catalyst of much lower dispersion $(10\% Pt/SiO_2, metal)$ area 44 m² g_{Pt}, $d \approx 6$ nm). Using his orders and Arrhenius parameters, we calculated the rate which his catalyst would have given under our conditions: it is shown in the last line of table 1 and agrees closely with our value.

Our orders and activation energies are typical of those found with films,^{8, 9} platinum black⁷ and alumina-supported platinum.^{5, 20, 22} However, the rates (in molecule cm² s⁻¹ at 630 K) calculated from these publications vary enormously, from 3×10^8 for platinum black⁷ to 2×10^{15} for platinum/alumina.⁵ The similarity between the kinetic parameters, except for the pre-exponential factor, strongly suggests that the nature of the active site for ethane hydrogenolysis on platinum is more or less well defined and constant, while the concentration of such sites depends sensitively on the type of catalyst. This supports the popular notion that this is a structure-sensitive reaction, although the trends suggested in the foregoing do not at first sight fit the observation²² that with platinum/alumina larger particles show higher turnover numbers than smaller ones. The fact that turnover numbers depend upon the temperature of calcination before reduction, and on reduction temperature,²² casts some doubt on whether reported particle-size effects are always genuine. Further discussion of this interesting question is not, however, justified at the present time.

PROPANE

Hydrogenolysis of propane was examined on a catalyst reduced at 623 K for 16 h [R623(16)] and on the same sample after oxidation at 623 K for 1 h [O623(1)] and reduction at 578 K by the reactants at the start of the test. The catalyst showed constant activity after 30 min. The results are given in table 2. Unlike other catalysts, which are reported^{5, 8} to give methane and ethane in equal amounts at low conversion, this catalyst always showed values of S_2 larger than those of S_1 , showing that further cracking of C_2^* to $2C_1^*$ occurred during one residence on the surface. Only values of S_2 are quoted since $S_1 = 3 - 2S_3$. Selectivities did not change with temperature within the range studied. Orders of reaction were measured at 588 K on these catalysts, the conditions and the results being also shown in table 2. To test the kinetic expression developed by Leclercq *et al.*,⁵ reciprocal rates were plotted against reciprocal propane pressure; excellent straight lines were obtained (fig. 1). Selectivities were not much affected by reactant pressure variation and all values of S_2 fell in the range 0.897–0.916. The oxidation clearly had no effect on the properties of the catalyst.

There are few results for propane hydrogenolysis on platinum in the literature. Leclercq *et al.*⁵ found E = 188 kJ mol⁻¹ and n = 0.9, their order in hydrogen varying with the hydrogen pressure; Guczi *et al.*⁷ found a much lower activation energy (100 kJ mol⁻¹) over Pt black.

		Table 1. Kinetics	s of ethane hy	drogenolysis over	· platinum/silica ca	talysts		
p _{H2} /atm	P _{C₂H₅} /atm	T range/K	E/kJ mo	$ ^{-1} \log A^a$	log r ^a	ш	и	ref.
0.9375	0.0625	613-633	210 ± 10	30.06	12.58	-		this work
0.277	0.0454	603-630	199 ± 5	30.17	13.15	-1.5^{b}	0.95°	this work
0.2	0.03	617-658	226	31.76	13.06	-2.5	0.9	(20), (21)
a A and	in molecule cm ⁻² s	-1. r at 630 K b n	- 0.035 -	tm: n = 0.305	0 855 atm c n _	0.305 atm - 7	- 0.035	0.154.atm
		d	C2H6 - 0.000 6	$\mu_{\rm H_2} = 0.270^{-1}$	0.022 a uu PH2 –	d (1111 C/7.0	$C_2H_6 = 0.002$	
	Table 3. Kineti	ics of n-butane hyd	rogenolysis o	er variously trea	ted samples of plati	inum/silica (F	EUROPT-1)	
		nointertion						
set	treatment	$(\%)^{a,b}$	$r^{a,b}$	T range/K	$E/kJ mol^{-1b}$	$\log A^{a, b}$	m ^c	n ^c
-	R423(16) +	4.6	88	578–608	114±5	11.81		
12	R623(16) R623(16)	3.7	71	578-608	129 ± 2	13.02	-0.42	0.49
[3	0623(1)+	3.5	66	578-608	133 ± 3	13.34	-0.42	0.49
	R578							
4	R 873(16)	1.7	33	588-608	108 ± 3	10.87	ļ	1
15	O873(1)+	1.0	19	578-608	126 ± 2	12.19		
	R773(1)							
⁶ 6	R1173(1.5)+	0		up to 613				-
	R 1083(16)							
(7	O873(1) +	0.04	0.8	593-608	202 ± 6	17.39	1	
	R7/3(1)							

^{*a*} Conversion and rate *r* at 603 K; *r* and *A* in mmol g_{P1}^{-1} h⁻¹ (add 10.5 to log *A* to convert to *A* in molecule cm⁻² s⁻¹ for a metal area of 280 m²g⁻¹). ^{*b*} Conversion, *r*, *E* and *A* obtained using $p_{H_2} = 0.833$ atm and $p_{C_4H_{10}} = 0.0417$ atm. ^{*c*} Conditions as for propane, see table 2: error limits ± 0.05 .

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treatment	conversion $(^{o}_{o})^{a}$	$\log r^{b, c}$	$E/kJ mol^{-1c}$	$\log A^{b, c}$	
R623(16)	3.3	12.63	189 ± 2	34.9	
O623 (1)	3.4	12.65	181 ± 3	33.4	
treatment	S ₂ ^c	k_2^*/k_2'	m^d	n ^e	
R623(16)	0.906 ± 0.004	0.104	-1.4 ± 0.2	0.78 ± 0.05	
O623(1)	0.904 ± 0.012	0.106	-1.3 ± 0.2	0.83 ± 0.05	

Table 2. Kinetics of propane hydrogenolysis over platinum/silica (EUROPT-1)

^a Conversion and rate r at 608 K. ^b r and A in molecule cm⁻² s⁻¹ assuming Pt area = 280 m² g⁻¹. ^c r, E, A and S₂ obtained using $p_{H_2} = 0.833$ atm and $p_{C_2H_8} = 0.417$ atm; temperature range 578–608 K. ^d $p_{C_3H_8} = 0.0417$ atm; $p_{H_2} = 0.583-0.917$ atm. ^e $p_{H_2} = 0.833$ atm; $p_{C_3H_8} = 0.0208-0.0833$ atm.



Fig. 1. Plots of reciprocal rate against reciprocal propane pressure, $1/p_c$: \bigcirc , R623(16); \bigcirc , O623(1) (see table 2).

n-BUTANE

An extended study was made of the hydrogenolysis of n-butane after reducing and oxidising the catalysts under various conditions: the results are given in tables 3 and 4. Catalysts attained a satisfactorily constant activity after 2 h of use. Looking first at the rates and Arrhenius parameters (table 3), it is clear that reduction at 873 K leads to only a decrease in rate by a factor of about two and to no really significant change in activation energy (sets 1–4). This small loss of catalytic activity correlates with the loss of hydrogen chemisorption capacity as reported by Martin *et al.*¹² However, reduction at 1083–1173 K destroys the activity completely (set 6), but this cannot be

set	treatment	T/K	S_2	S_3	F	k_{3}^{*}/k_{3}'	F'	$(k_3^*/k_3')'$
1	R423(16)+	578	0.76	0.57		_	0.33	0.18
	R643(0.5)	608	0.85	0.52			0.37	0.20
(2	R623(16)	578	0.76	0.58	0.413	0.015	0.33	0.16
{		608	0.80	0.55	0.434	0.029	0.35	0.18
١3	O623(1) +	578	0.72	0.59	0.386	0.041	0.31	0.18
	R578	608	0.78	0.55	0.412	0.070	0.33	0.22
(4	R873(16)	588	0.52	0.71			0.23	0.09
{		608	0.60	0.66			0.25	0.14
5 ا	O873(1) +	578	0.76	0.61			0.37	0.03
	R773(1)	608	0.85	0.55		—	0.40	0.09
7	O873(1)+ R773(1)	613 <u>+</u> 5	0.72	0.60			0.32	0.14

 Table 4. Product selectivities and derived parameters for n-butane hydrogenolysis over various treated samples of platinum/silica (EUROPT-1)

ascribed primarily to growth in particle size (see below). Because of the evident lack of correlation between activity and particle size, as shown by electron microscopy or X-ray line broadening, rates and pre-exponential factors are given in units of mmol $g_{Pt}^{-1} h^{-1}$, a rate of one in these units corresponding to 4.3×10^{12} molecule cm⁻² s⁻¹ for a surface area of 280 m² g_{Pt}^{-1} . The reactivities of propane and of n-butane are thus almost the same (compare tables 2 and 3). The complete loss of activity (set 7) is unexpected in the light of the retention of some albeit decreased capacity for hydrogen chemisorption (*e.g.* 55 μ mol g_{cat}^{-1} after 16 h reduction at 1123 K, see below), and it must be concluded that whatever happens to the metal under these conditions affects the catalytic activity more severely than the hydrogen chemisorption.

We have observed by electron microscopy that the 873 K oxidation followed by 773 K reduction (set 5) produces a marked change in catalyst morphology. The metal particles are larger and fewer than before and clearly have the profile of regular hexagons of approximately uniform size (ca. 3.7 ± 0.7 nm). Uniform spheres of 3.7 nm diameter would have a surface area of ca. $75 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$, which is 27% of the metal area of the starting catalyst. Thus the activity decrease corresponds closely to the loss of metal area and the hexagonal particles may be presumed to have again acquired normal catalytic properties as a result of the oxidation treatment. Oxidation after the very-high-temperature reduction restores a low level of catalytic activity, but the activation energy is now much higher (set 7). Perhaps the oxidation here succeeds in revitalising only a small fraction of the metal particles after the high-temperature reduction.

There is a slight but quite significant change in product selectivities as a function of these heat treatments. Values of S_2 and S_3 for the highest and lowest temperatures used, and the derived parameters, are given in table 4, except for the catalyst of very low activity (set 7) where an average value is quoted. Values of S_1 are not shown since $S_1 = 4 - 3S_3 - 2S_2$. In each case where conversions are sufficient for accurate product distributions to be measured, S_1 is almost independent of temperature, while S_2 increases and S_3 falls with rising temperature. For reductions at temperatures not exceeding 643 K (the first three sets), selectivities are very similar. For reduction at 623 K, with and without subsequent oxidation, we may use the values of T_2 obtained



Fig. 2. n-Butane hydrogenolysis: plots of product selectivities, F and k_3^*/k_3' against temperature (set 3 of table 3): \bigoplus , S_1 ; \bigcirc , S_2 ; \bigoplus , S_3 .

from propane hydrogenolysis on the same catalysts to evaluate F and k_3^*/k_3' : this gives values of F of 0.39–0.43 and of k_3^*/k_3' of 0.03–0.07 (see table 4). Actually the values of F are slightly lower, and of k_3^*/k_3' slightly higher, after the oxidation, but in each case the effect of increasing temperature is to increase the values of them both (see fig. 2). The temperature dependence of k_3^*/k_3' corresponds to a value of $E_3^* - E_3'$ of *ca*. 30 kJ mol⁻¹. Although we cannot use this procedure for the other sets of results, we may obtain some idea of the relative changes induced by the heat treatments by assuming a value of unity for T_2 throughout, which gives the values of F' and of $(k_3^*/k_3')'$ shown in table 4. The former increases, and the latter decreases, consistently with rising temperature. The 873 K reduction (set 4), however, gives a significantly different product distribution from those already discussed: S_2 is lower and S_3 and S_1 are higher, owing chiefly to a lower value of F'. The subsequent oxidation and reduction, which increases the size and changes the shape of the metal particles, also gives back the higher values of F'. The low-activity catalyst (set 7) also has parameter values within the normal range, supporting the suggestion made above that the oxidation and lower-temperature reduction restores some of the particles to normal behaviour.

The values of k_3^*/k_3' and $(k_3^*/k_3')'$ are extremely sensitive to slight differences in the values of S_2 and S_3 . This is because T_3 and T_3' usually fall between 0.9 and unity, reflecting the fact that C_3^* species are much more likely to desorb than to react further to $C_2^* + C_1^*$. The sensitivity arises from the fact that $k_3^*/k_3' = T_3^{-1} - 1$ etc. (see above). Comparison of the results in table 4 for sets 2 and 5 at 578 K shows just how much the value of k_3^*/k_3' responds to slight differences in selectivities. It is therefore not always easy to draw quantitative conclusions from changes in this parameter.

Orders of reaction were obtained on the same catalysts as used for the propane reaction and under exactly the same conditions (see table 2); the results are in table 3. There are small but distinct effects on selectivities caused by reactant pressure changes. Use of the values for $S_2 = T_2$ from the propane reaction again permits the calculation of F and k_3^*/k_3' through the range of conditions used. The latter is invariant with hydrogen pressure (0.03-0.05) but increases with n-butane pressure. Although the results are scattered because the effects are small, k_3^*/k_3' tends to zero as the butane pressure decreases, suggesting that cracking is much less favoured than desorption when the concentration of adsorbed hydrocarbon species is low. This is understandable because the adsorbed alkane fragment is more likely to be surrounded by a complete ring of hydrogen atoms under these circumstances (*i.e.* at a high hydrogen: alkane ratio), and desorption by hydrogenation of a hydrogen-depleted hydrocarbon species will require more hydrogen atoms than its further cracking, for which it must remain in a dehydrogenated condition. Values of F decrease rather more smoothly with increasing hydrogen: butane ratio, however brought about, in the range 0.40-0.44, but the effect is small.

The isomerisation to isobutane was only examined with the sample of catalyst reduced at 423 and 643 K (corresponding to the first entry in table 2). There was no systematic change in the selectivity to isobutane during stabilisation ($S_{i4} \approx 0.17-0.22$), but it increased with reaction temperature (573 K, 0.22; 613 K, 0.41) so that E_{i4} was 156 kJ mol⁻¹ while E_{n4} (the activation energy for n-butane removal) was 114 kJ mol⁻¹.

For unsupported platinum catalysts⁷⁻⁹ activation energies lie between 88 and 96 kJ mol⁻¹ and activities between 10^{11} and 3×10^{13} molecule cm⁻² s⁻¹: values of *n* are 0.7–1.0 and of m - 1.4–1.6. Hydrogenolysis rates frequently pass through a maximum as the hydrogen pressure is varied, the location of the maximum depending upon the temperature⁷ and the alkane,⁵ so that either positive⁵ or negative order may be found according to the choice of conditions. Product selectivities have also been reported⁷ to change drastically with hydrogen pressure and temperature over platinum/silica, although the temperature range (486–593 K) is lower than that used by us. Platinum/alumina gives an activation energy similar to our values, but the activities are greater.⁵

EFFECTS OF HEAT TREATMENT ON EUROPT-1

The EUROPT-1 catalyst is remarkably resistant to the effects of heat treatment in hydrogen.^{12, 15} There is little indication of particle growth below *ca.* 1000 K, and even a 15 h treatment at 1200 K only raises the average size from 1.8 to 3.8 nm.¹² We have not performed accurate measurements of size distributions by electron microscopy, but treatments at 1123 K for 16 h and at 1173 K for 1.5 h + 1083 K for 16 h showed only a limited increase in average size to *ca.* 3 nm, as expected from published work.^{12, 15}

However, it has been shown¹² that capacity for hydrogen chemisorption is greatly diminished on heating to 1100 or 1200 K: thus for example after 15 h at 1100 K the H/Pt_{tot} ratio is 0.12, whereas the average size of 2.8 nm from electron microscopy corresponds to a dispersion of *ca*. 50%. We find hydrogen monolayer volumes as

G. C. BOND AND XU YIDE

follows: after 1 h in hydrogen at 623 K, 166 μ mol g_{cat}^{-1} , which is in excellent agreement with others' values,¹⁵ and after 16 h at 1123 K it is 55 μ mol g_{cat}^{-1} , corresponding to an H/Pt_{tot} ratio of 0.34 or a mean size of *ca*. 4 nm, which is almost 50% greater than expected on the basis of the particle size from electron microscopy. The effect is not as large as that reported by Martin *et al.*,¹² but it is quite unmistakable.

EFFECTS OF HEAT TREATMENT ON CATALYTIC PROPERTIES

The effect of reducing and oxidising atmospheres on the structural and catalytic properties of supported metals are of concern in areas of application as diverse as petroleum reforming, including catalyst regeneration,^{23, 24} vehicle-exhaust treatment and steam reforming of alkanes. We have noted above that platinum/silica (EUROPT-1) is remarkably resistant to sintering in a hydrogen atmosphere, although changes occur which affect the hydrogen chemisorption capacity and even more so the hydrogenolysis activity (table 3); we thus fully confirm the observations of Martin *et al.*¹² There are other examples in the recent literature of substantial disagreements between particle sizes as estimated by hydrogen chemisorption and by electron microscopy, after treatment at high temperature.²⁴ Unexplained effects of reduction temperature on turnover number for platinum-catalysed hydrogenolyses have also been reported recently.^{22, 25} The product selectivities (table 4) are, however, surprisingly invariant [except after the treatment designated R873(16)]: this is despite the fact that the O623(1) treatment almost certainly oxidises the metal completely.^{23, 25} while the O873(1) treatment clearly produces a complete reconstitution of the particles.

There are number of possible reasons why chemisorption capacity and *a fortiori* catalytic activity should change with treatment in hydrogen at high temperature. The effect has been likened¹² to the so-called 'strong metal-support interaction' which affects titania-supported metals at lower temperatures, the cause of which is still in dispute. For platinum/silica the possibilities include the incorporation of hydrogen into the metal particles as suggested by Menon and Froment²⁶ with platinum/alumina, the formation of a platinum-silicide similar to the platinum-aluminium intermetallic compound detected by Dautzenberg *et al.*,²⁷ a restructuring of the surface of the metal particles as the surface atoms become mobile, as originally suggested by Boudart *et al.*,²⁸ and finally the migration of traces of toxic species from the support to the metal.

Any of these effects could account for the partial loss of capacity for hydrogen chemisorption and the greater loss of catalytic activity for a reaction which is structure-sensitive. They could also in principle account for the partial restoration of activity following oxidation. To allocate responsibility between them for the observed consequences of heat treatments must, however, necessitate further research. We conclude that the composition of the active site for n-butane hydrogenolysis is an almost fixed quantity, and that at most the splitting parameter F is susceptible to slight modification. There is supporting evidence⁶ that the product distribution from the hydrogenolysis of higher alkanes is not particle-size dependent. The frequency with which the site occurs, and thus the activity, changes with pretreatment; we reached the same conclusion in the case of ethane hydrogenolysis.

These observations require a reassessment of the value of classifying reactions as either structure-sensitive or structure-insensitive. There is indeed much other evidence to suggest that such a distinction is overly simplistic. It seems probable that it is the initial chemisorption of the alkane on platinum which calls for a large and perhaps complex ensemble of atoms; in this sense the reaction is structure-sensitive. Thereafter the reaction proceeds in a manner almost unaffected by the catalyst's history, yielding products in a ratio and exhibiting kinetic parameters which uniquely reflect the nature

of the active site: in this sense the reaction is structure-insensitive. Thus the reaction does not in general proceed less quickly on a site which is less than perfect, it simply does not proceed at all.

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(PAPER 3/1480)