Hydrogenolysis of Propane and of *n*-Butane on Pt/KL Zeolite

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The reaction of *n*-butane with H_2 proceeds on a Pt/KL zeolite catalyst between 530 and 640 K, and, with a tenfold excess of H_2, the isomerization selectivity at 623 K lies between 0.40 and 0.75, depending on the form of pretreatment and prior use. In thermal cycling experiments, methane is initially the major product, but with the most active samples the propane selectivity is afterwards greater than that of methane; this strange behaviour may be a consequence of conducting the reaction in a microporous support. Isomerization selectivity increases with temperature. Propane is much less reactive than *n*-butane. The dependence of the rates of reaction of both these alkanes upon H_2 pressure is modelled by a rate expression derived from a mechanism in which the alkane is chemisorbed and activated by the loss of several H atoms. Rates are strongly inhibited by increasing the H_2 pressure, and values of K_H, the adsorption coefficient for H_2, obtained from the modelling are much higher than for other Pt catalysts. This may to some extent account for the activity of Pt/KL for aromatization of linear alkanes, by suppressing alkene formation and, hence, carbon deposition. © 1997 Academic Press

INTRODUCTION

Platinum-containing KL zeolite is renowned for its ability to effect the aromatization of linear alkanes containing six or more carbon atoms, and notorious for its sensitivity to poisoning by sulfur. These interesting characteristics have generated much research on this and cognate materials, and numerous and varied explanations have been offered to account for them (1). These may be grouped into (i) models assigning importance to the linear channels in the zeolite, and (ii) models attributing activity and selectivity to some modification of the electronic structure of the metal, either in consequence of its small particle size (<1 nm) or of an interaction with the zeolite framework, or the K^+ ions. However, for every piece of evidence favoring one interpretation there are two against it, and after more than "a decade of research, . . . the function of these materials in alkane aromatization is still unclear" (1). While it may be simplistic to seek a single explanation, the relative contributions of all factors require evaluation.

In previous papers in this series, we have examined the hydrogenolysis of small linear alkanes on both Pt/Al_2O_3 (EUROPT-3) (2, 3) and Pt/SiO_2 (EUROPT-1) (4, 5) and have modelled the dependences of rates on H_2 pressure by means of a rate expression derived from a reaction mechanism in which the alkane is activated by the loss of several H atoms before suffering C–C bond breaking by the attack of a single H atom (3, 5). This rate equation, coded ES5B, allows us to estimate a true rate constant (*k*), an adsorption coefficient for H_2 (K_H), an equilibrium constant for the dehydrogenative activation of the alkane (K_A) and the number of H atoms removed in the activation (*x*). With Pt/Al_2O_3, where kinetic measurements were made at several temperatures (3), we could derive a true activation energy from *k* and an enthalpy of adsorption from K_A. We have made a brief study of the hydrogenolysis of propane and of *n*-butane on Pt/KL in the expectation that by varying the H_2 pressure and using our previous methodology we might obtain values of these constants which could be compared with those given by the other Pt catalysts. We hoped that these results might assist our understanding of the causes of the unique behaviour of the Pt/KL catalyst.

EXPERIMENTAL

The Pt/KL catalyst (1 wt% Pt) was kindly provided by Professor V. Ponec (Leiden University); its preparation has been described (6). It was activated in the following way: about 0.2g were heated (5 K min^{-1}) in N_2 (30 cm^3 min^{-1}) to 573 K, and then treated with air (3 h, 40 cm^3 min^{-1}) for 3 h (LTO). After purging with N_2 (1 h), the temperature was raised to 863 K under H_2 and remained there for either zero (HTRO), 1 (HTR1), or 4 h (HTR4); it was then lowered to the initial reaction temperature.

Reactions were carried out in a continuous-flow atmospheric pressure system, standard gas flows being H_2: *n*-C_4H_{10}: N_2 = 100:10:30 cm^3 min^{-1} and H_2: C_3H_8: N_2 = 55:5.5:16.5 cm^3 min^{-1}. Thermal cycles (TC) were performed as described previously (2–5), the results being recorded at about 10 K intervals over a range of between ~40 and 115 K, each isothermal period lasting 20 min. Quite generally we attempted to bring the catalyst to a steady state (SS) by

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running isothermally, usually at 523 K, for at least 2 h before starting a systematic variation of an operating variable; the results were not, however, recorded in these periods. Because only a limited amount of catalyst was available, samples were on occasion reactivated by performing a second sequence designated LTO*-HTR. The dependence of rate on H_2 pressure (HV) was studied at 573 K by changing the H_2 and N_2 flows sympathetically, each condition being maintained for 20 min. The short reaction pulse method, used earlier to minimise coking, could not be employed here because every pulse was totally absorbed and retained by the catalyst. Results were corrected for propane and isobutane impurities in the n-butane as described before (5).

Rates of reactant removal are expressed in mmol $g_{cat}^{-1}\ h^{-1}$. Product selectivities are defined such that for n-butane

$$S_1 + 2S_2 + 3S_3 = 4$$

and for propane

$$S_1 + 2S_2 = 3,$$

where the subscript numeral defines the number of carbon atoms. Variations of rate with H_2 pressure were modelled by a rate expression denoted as ES5B (3, 5, 7). Selectivity parameters are defined following the methodology of Kempling and Anderson (8): F is the probability of breaking the central C−C bond in n-butane, and T_j is the probability of an intermediate in either reaction containing j carbon atoms returning to the gas phase as the corresponding alkane rather than suffering further cracking ($j = 2, 3$

for n-C_4H_{10}; 2 for C_3H_8). In the reaction of n-butane, these quantities are derived from the following relations, applicable at low conversion (8):

$$(S_2/T_2) + S_3 = 1 + F$$
$$S_3/(1 - F) = T_3.$$

These equations can only be solved by assuming a value for T_2, which is here set equal to unity, the resulting values of F and T_3 being indicated by primes: T_2 equates to S_2 in the reaction of propane. S_i is defined as the fraction of n-butane converted to isobutane. Further information on procedures and computation will be found in our earlier papers (3, 5, 7).

RESULTS

Thermal Cycling Experiments

The performance of a thermal cycle allows comparison of the parameters describing a catalyst's behaviour at a standard temperature (623 K) in the increasing and decreasing temperature modes (stages 1 and 2, respectively), and so to evaluate the extent of deactivation and changes in selectivities that the excursion to high temperature causes. At the same time the effects of varying the temperature on rates and selectivities in each stage are obtained. Arrhenius parameters, as well as rates and selectivities at 623 K, for hydrogenolysis of propane and of n-butane are given in Table 1.

TABLE 1

Hydrogenolysis of n-Butane and of Propane on Pt/KL: Arrhenius Parameters, and Rates and Product Selectivities at 623 K

Exp. no.	Alkane	Pretreatment[a]	Temp. range/K[b]	E_H/kJ mol^{-1}	$\ln A_h{}^c$	$r_h{}^c$	S_2	S_3	F'	T'_3	S_i
1503	n-C_4H_{10}	HTR0	586–627	176	37.36	31.5	0.795	0.636	0.431	1.12	0.445
			626–532	179	38.09	37.4	0.741	0.669	0.410	1.13	0.378
1603	n-C_4H_{10}	HTR0-SS	567–609	208	43.57	25.1	0.813	0.623	0.436	1.10	0.506
			639–535	190	39.58	20.9	0.658	0.724	0.382	1.17	0.474
2303	n-C_4H_{10}	HTR0-SS	599–619	248	48.86	2.7	0.986	0.510	0.495	1.01	0.758
			639–577	248	48.39	1.9	0.954	0.524	0.478	1.01	0.763
1903	n-C_4H_{10}	HTR1-SS	555–618	252	49.38	1.7	0.955	0.519	0.475	0.988	0.699
			638–575	273	52.89	1.2	0.908	0.543	0.451	0.987	0.668
2203	n-C_4H_{10}	HTR1-SS-HV-SS	587–638	271	51.07	0.32	0.702	0.640	0.341	0.972	0.422
			638–586	227	42.83	0.35	0.729	0.628	0.357	0.977	0.474
2503	C_3H_8	HTR0	617–637	202	37.83	0.34	0.615	—	—	—	—
			637–616	236	44.46	0.28	0.746	—	—	—	—
2803	C_3H_8	HTR0-SS	598–639	242	44.50	0.10	0.976	—	—	—	—
			639–597	244	44.46	0.11	0.985	—	—	—	—

[a] Pretreatment and prior use. All the pretreatments listed in column 3 were preceded by a low-temperature oxidation (LTO); in the case of Experiments 1603, 2303, and 2503, the catalyst sample had been used before. All stabilizations (SS) were performed at 523 K for 2 h, *except* for Experiment 2303, where there was an extra 2 h at 533 K, and Experiment 2203, where the second stabilization lasted 9 h.

[b] The range over which the Arrhenius plot was taken to be linear.

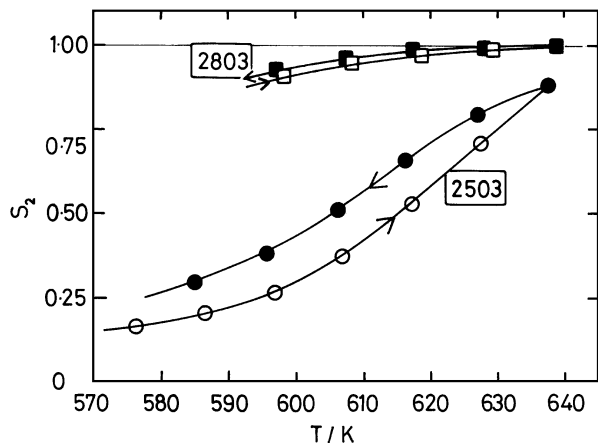[c] A_h and r_h in mmol $g_{cat}^{-1}\ h^{-1}$.

FIG. 1. Hydrogenolysis of propane on Pt/KL catalyst; dependence of ethane selectivity S_2 on temperature for Experiments 2503 and 2803 (see Table 1 for pretreatments). Open points, stage 1; filled points, stage 2.

We consider first the results for propane. A previously used sample after reactivation was active above 575 K, but the slopes of the Arrhenius plots in each stage increased with temperature, and the quoted activation energies, which are only approximate, apply to the top end of the temperature range (Experiment 2503). This behaviour is associated with an unusual *increase* in S_2 with temperature, which is reversed in stage 2 (Fig. 1); normally the change is in the opposite sense (2, 4). A fresh sample after activation and being brought to a steady state at 523 K showed a lower

activity, but improved Arrhenius plots, although S_2 increased with temperature as before (Experiment 2803, Fig. 1). S_2 became equal to S_1, i.e. multiple hydrogenolysis ceased, at about 640 K. Activities in stages 1 and 2 were the same (Table 1).

Thermal cycling experiments with n-butane also produced some unexpected results. An activated and reduced (HTR0) sample, not previously used, gave rates of hydrogenolysis and of isomerization that were 100-fold greater than the corresponding rate for propane (Experiment 1503, Table 1), but reduction for 1 h (HTR1) led to lower activities (Experiments 1903 and 2203) and for 4 h (HTR4) to no activity at all. Presumably the longer reduction times resulted in sintering of the Pt particles. All samples, irrespective of their prior use, if any, showed extensive multiple hydrogenolysis at the start of stage 1, but this effect terminated at about 600 K, after which the hydrogenolysis selectivites showed only slight temperature dependence (Fig. 2A); however, unlike the behaviour of propane (Fig. 1), n-butane gave no multiple hydrogenolysis towards the end of stage 2, so selectivities maintained their minimal temperature variation over the whole range (Fig. 2B). In the temperature range where multiple hydrogenolysis was experienced, the Arrhenius plot was deformed (Fig. 3) and the quoted activation energies for stage 1 refer to the upper end of the range (see Fig. 3) and are of limited accuracy. Stage 2 plots showed much better linearity (Fig. 3). A further disturbing feature shown by the most active sample (Experiments 1503 and 1603) was that,
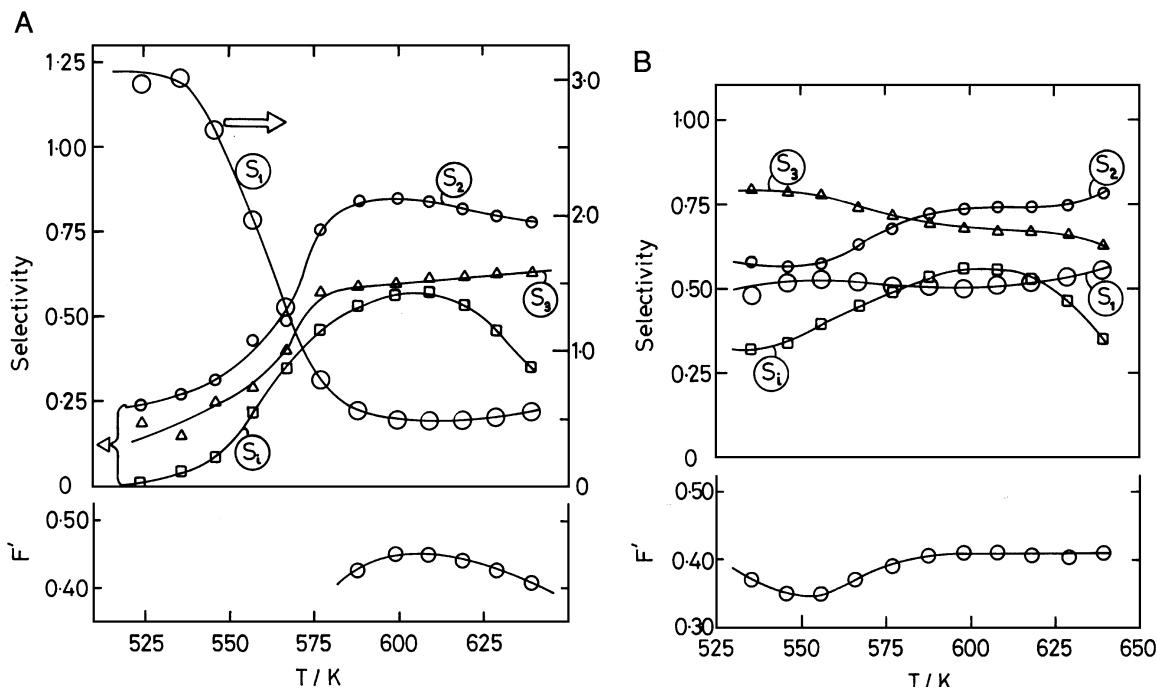

FIG. 2. Reaction of n-butane with H_2 on Pt/KL catalyst; dependence of selectivities and of F' on temperature for Experiment 1603 (see Table 1 for pretreatment): A, stage 1; B, stage 2.
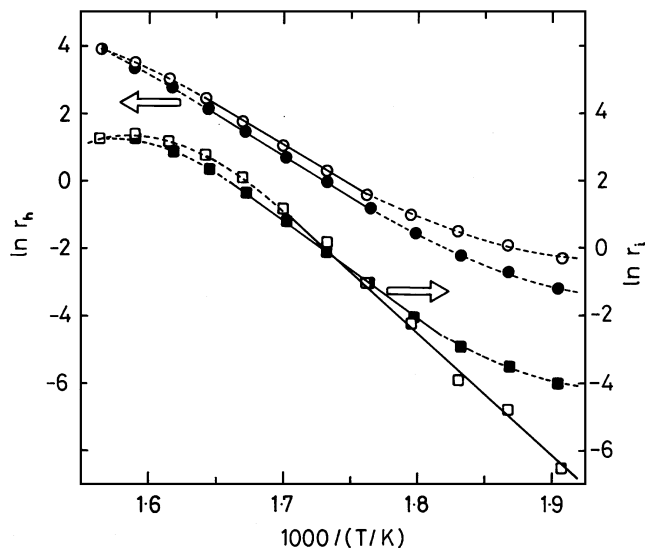
FIG. 3. Arrhenius plots for the hydrogenolysis ○ and isomerization □ of *n*-butane on Pt/KL catalyst, Experiment 1603: open points, stage 1; filled points, stage 2.

wherever multiple hydrogenolysis did *not* occur, S_3 exceeded S_1 (Fig. 2); for the samples of lower activity, S_3 was always equal to or less than S_1.

Activation energies for hydrogenolysis E_h vary quite widely (Table 1), although—bearing in mind the foregoing comment on the reliability in stage 1—the differences between stage 1 and stage 2 values are often not large. The lowest values are found with the most active catalysts, and *vice versa*. Values of F' at 623 K (Table 1) are between about 0.35 and 0.50 and are also similar in both stages. Where multiple hydrogenolysis is not a problem, F' shows very slight temperature dependence (Fig. 2). For the more active catalysts, values of T_3 exceed unity by 10–20% (Table 1): when seen before (5), this was attributed to failure to use the appropriate value of T_2 in solving the defining equations. As stated above, we have taken T_2 to be unity to obtain T_3, but, if the value of T_2 relevant to the *n*-butane reaction is reflected in T_2 for the propane reaction, it will be considerably less than unity at 623 K (Table 1 and Fig. 1). We have shown (5) that T_3 depends sensitively on the assumed value of T_2; for the samples of lower activity, taking T_2 as unity is evidently more justified ($T_3 = 0.97$–1.01).

At 623 K quite high values of S_i ($\sim$0.4–0.75) were shown under all conditions (Table 1); the highest values were shown by the samples having moderate activity (Experiments 1903–2303), and in general, there were no major differences between values in stage 1 and stage 2. S_i initially increased with temperature (Figs. 2A and B), so that the activation energy E_i was substantially higher than that for hydrogenolysis E_h, being 310 ± 10 kJ mol^{-1} in stage 1 (Table 2). However, the slope of the Arrhenius plot began to decrease before the maximum temperature was reached (Fig. 3), and in consequence, values of S_i pass through a

maximum (Fig. 2A). They are larger at low temperatures in stage 2 than in stage 1 (Figs. 2A and B), and as a result E_i has a lower value (Table 2 and Fig. 3).

Variation of H$_2$ Pressure

The dependence of the rates of reaction of both alkanes on H$_2$ pressure was studied by using 20 reaction periods, each of 20 min duration, in which the H$_2$ pressure was randomly altered by simultaneous change of the H$_2$ and N$_2$ flow rates; periods 1, 2, 6, 11, 14, 17, and 20 used the standard H$_2$ pressure of 0.16 atm. in order to assess what deactivation was occurring (Fig. 4). In fact this was substantial for both alkanes, but the method of correction for this, described in detail previously for the reactions on EUROPT-1 (6% Pt/SiO$_2$) (5), proved satisfactory, and smooth decreases of corrected rate with increasing H$_2$ pressures were obtained (Fig. 5). However, conversions obtained with H$_2$ pressures greater than 0.309 atm. were too small to be accurately measurable. The largest decreases in rate were seen during the first few reaction periods and, especially, after using very low H$_2$ pressures (0.04 atm. or less) (Fig. 4); in this respect the Pt/KL catalyst behaved very similarly to EUROPT-1 (5). It is noteworthy that this deactivation occurs notwithstanding a prior stabilization period at the lower temperature of 523 K in the case of *n*-butane and with propane a thermal cycle, as well (Experiment 2803).

The variations of the corrected rates with H$_2$ pressure are successfully described by the rate expression ES5B used previously (3, 5, 7), based on the mechanism referred to in the Introduction. The expression takes the form

$$r = \frac{k_1 K_A P_A (K_H P_H)^{(m+1-x)/2}}{\left[K_A P_A + (K_H P_H)^{(m-x)/2} + (K_H P_H)^{(m+1-x)/2} \right]^2},$$

where $m = 8$ for propane and 10 for *n*-butane, P_A and P_H being respectively the pressures of alkane and of H$_2$: the

TABLE 2

Isomerization of *n*-Butane on Pt/KL: Arrhenius Parameters and Rates at 623 K

Exp. no.	Temp. range/K	E/kJ mol^{-1}	$\ln A_i$	r_i
1503	545–586	313	65.37	24.7
	607–545	221	46.63	22.2
1603	524–588	319	66.39	25.0
	618–535	223	46.41	20.4
2303	556–619	303	60.70	8.4
	639–577	277	55.21	6.1
1903	555–607	309	61.50	4.0
	638–554	273	53.43	2.4
2203	587–638	300	56.50	0.24
	636–586	277	52.22	0.32

Note. Conditions of pretreatment are given in Table 1; see also the footnotes to Table 1.
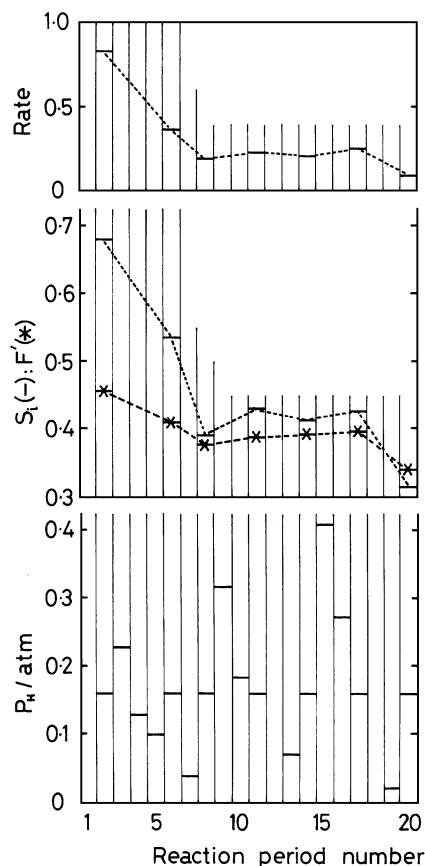
FIG. 4. Variation of isomerization selectivity S_i and of F' on reaction period number in the determination of the effect of varying H_2 pressure. The points shown were obtained with $P_H = 0.16$ atm; the pressures used for the intervening periods are also shown.

other terms have been defined above. The curves drawn in Fig. 5 are calculated by substituting the values of the best-fit constants (Table 3) into this equation. This figure shows the results as semilogarithmic plots in a deliberate attempt to magnify the differences between observed and calculated rates, which are not visible in normal plots. Rates differed by a factor of about 100 with n-butane and about 200 with propane. At the highest H_2 pressure the difference between

TABLE 3

Values of the Best-Fit Constants for the Rate Expression ES5B

Catalyst	Alkane	T/K	k	K_A	K_H	a[a]	Reference
6% Pt/SiO$_2$	C$_3$H$_8$	533	9.0	0.70	5.4	1.41	5
(EUROPT-1)	n-C$_4$H$_{10}$	533	~11	2.3	~6.5	~0.90	5
0.3% Pt/Al$_2$O$_3$	C$_3$H$_8$	573	17.3	5.5	4.7	2.22	3
(EUROPT-3)	n-C$_4$H$_8$	578	18.8	7.9	1.6	1.43	3
Pt/KL	C$_3$H$_8$	573	23.5	0.88	17.5	2.35	This work
	n-C$_4$H$_{10}$	573	55.9	8.72	37.8	1.83	This work

[a] The number of H_2 molecules released in the dehydrogenative chemisorption of the alkane.
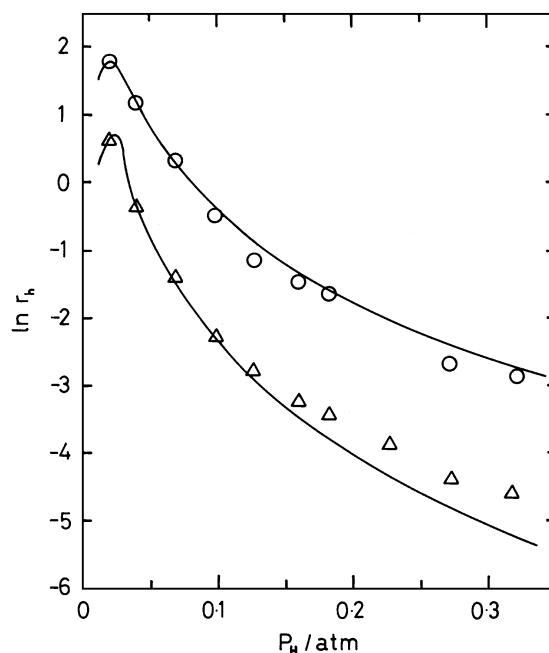

FIG. 5. Semilogarithmic plots of the rates of reaction of propane ($\triangle$) and n-butane ($\bigcirc$) as a function of H_2 pressure. The curves are calculated using expression ES5B (see text) and the best-fit constants given in Table 3.

the observed and calculated rates for the propane reaction is less than a factor of 2, while for n-butane it is only 20%.

For the reaction of n-butane the total rate of reactant removal was used. It was impractical to evaluate the effect of H_2 pressure separately on rates of hydrogenolysis and of isomerization because the latter was selectively deactivated, S_i falling from an initial value of 0.68 to a final value of 0.31 at the standard H_2 pressure of 0.16 atm. (Fig. 4). However, after the initial fall and before using the lowest H_2 pressure, S_i remained approximately constant, and in this range showed no marked dependence on H_2 pressure (0.35–0.43). Values of F' were also affected by deactivation, varying in the same way as S_i (Fig. 4), suggesting a casual connection between central C–C bond breaking and isomerization. Values in the stable region were 0.33–0.39, passing through a slight maximum, corresponding to the maximum in S_i; neither S_1 nor S_3 changed greatly, and the ratio S_1/S_3 was generally close to unity (Fig. 6). T_3 however appeared to decrease at H_2 pressures less than 0.1 atm., and to be about 0.99 above it.

DISCUSSION

Thermal Cycling Experiments

The results of the thermal cycling experiments present some unusual and puzzling features that are not easily explained. In the reaction of propane, the ethane selectivity S_2 increases with temperature and decreases when the direction of temperature change is reversed (Fig. 1). This is
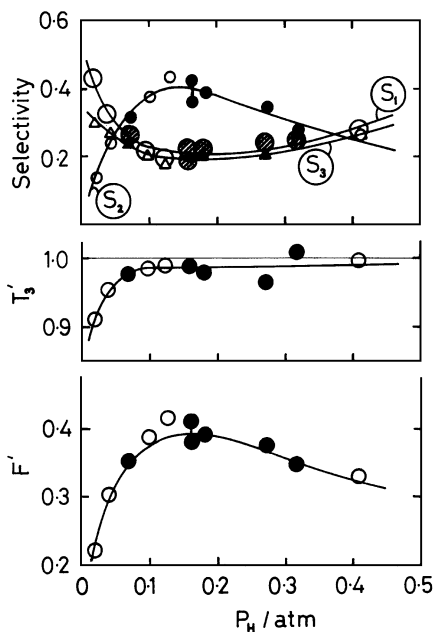
FIG. 6. Hydrogenolysis of n-butane: dependence of product selectivites S_1, S_2, and S_3, and of F' and T'_3, on H_2 pressure. Filled points are those least affected by the deactivation shown in Fig. 5.

deep hydrogenolysis. Less may be held back at higher temperatures, when the reaction follows a more normal course.

A further unusual finding is that, with the more active catalysts only, the ratio of $S_3 : S_1$ exceeds unity after multiple hydrogenolysis has died down, viz., at the end of stage 1 and in stage 2 (Figs. 2A and B). Normally this should not happen. We suspect it may be linked with the excessive multiple hydrogenolysis discussed above: possibly C_3 species *are* formed at the same time as methane in the first part of stage 1 but are only released slowly during the ensuing period of the experiment, thus creating an artificially high S_3. We are perhaps witnessing problems associated with the carrying out of reactions in a highly porous support. Alternatively, C_1 species may be selectively incorporated into a "carbonaceous residue," rather than being returned to the gas phase as methane (9).

Except for S_i, which passes through a maximum as temperature is raised, for reasons discussed above, the hydrogenolysis product selectivities show somewhat small variations with temperature when multiple hydrogenolysis does not obscure the picture (Figs. 2A and B). Valid values of T_3 are close to unity over much of the temperature range investigated, and F' also shows only a minor effect of temperature.

The results in Table 1 deserve a few further comments: (A) Values of E_h tend to increase as the activity of the samples decreases. They probably reflect changes in the concentration of H atoms or of vacant sites on the Pt particles (10), but in the absence of more detailed kinetic information (e.g., on how E_h varies with H_2 pressure) further speculation is unwarranted. (B) Values of r_h vary widely. While stabilization at 523 K has only a slight depressing effect (compare Experiments 1503 and 1603), a further stabilization period at 533 K lowers the rate tenfold (compare Experiments 1603 and 2303). The longer 1 h reduction time also lowers the rate sharply (compare Experiments 1503 and 1903), perhaps because the Pt particles sinter. The lowest rates are shown in Experiment 2203, where the prior use, especially for H_2 pressure variation, is doubtless responsible. (C) There is no clear trend of isomerization selectivity S_i with r_h, highest values being shown by samples having intermediate activity. There is, however, a positive correlation between the central bond splitting factor F' and S_i.

Effect of Varying H_2 Pressure

The rates of hydrogenolysis of propane and of n-butane at 573 K are severely suppressed by increasing the H_2 pressure (Fig. 5), much more so than was the case with either Pt/Al$_2$O$_3$ (EUROPT-3) (2) or Pt/SiO$_2$ (EUROPT-1) (5) at roughly corresponding temperatures (Fig. 7). With the Pt/KL catalyst, rate maxima occur at inaccessibly low H_2 pressures, although the solution to the ES5B equation using best-fit constants suggests that these may occur at 0.02–0.03 atm pressure. Turning to the values of these constants,
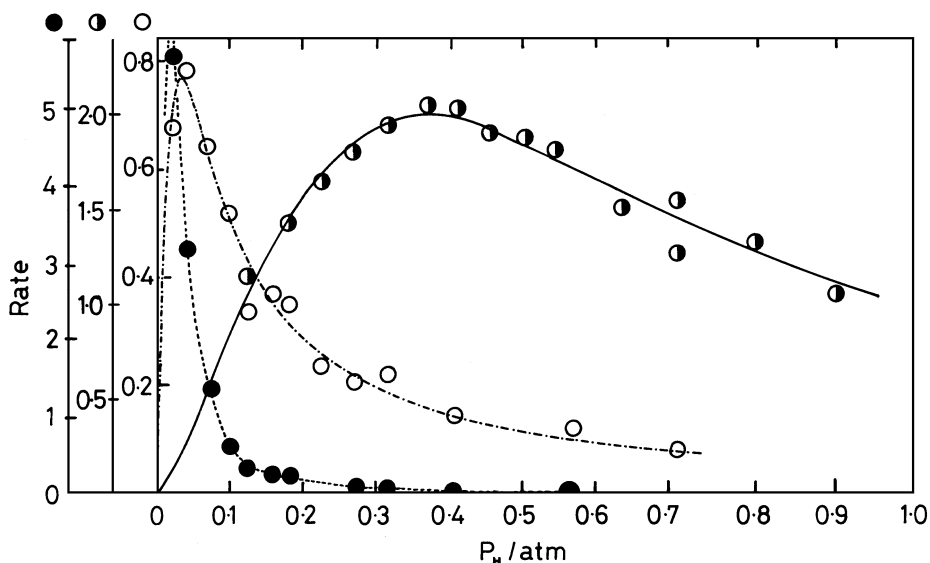
contrary to what is generally observed (2, 4), although on EUROPT-3 (0.3% Pt/Al$_2$O$_3$) and its analogue with 0.6% Pt a reversible increase has been seen at low temperatures (see Fig. 4 of Ref. (2)). It may be that in this region (<580 K), and below about 640 K in the present work (Fig. 1), the activation energy for converting the adsorbed C_2 species to ethane is greater than that for its bond-breaking, and that with other Pt catalysts a further mechanism for methane formation starts to operate at high temperatures (>620 K for the Pt/Al$_2$O$_3$ catalysts).

The reversibility of this change of S_2 with temperature in the case of propane suggests that it is an intrinsic feature of the reaction and is not due to any artifact. The high values of methane selectivity S_1, found invariably at the beginning of the reaction of n-butane, are not, however, seen at the end of stage 2 (see Fig. 2B), so they cannot be explained in the same way. The effect is observed in four cases (Experiments 1603, 2303, 1903, and 2203; Table 1) in which the sample has first been stabilized, as well as where (as in Experiment 1503) there had been no prior use. The stabilization was, however, performed at 523 K (and at 533 K, as well, in one case), which is well below the starting temperature for stage 1 of the less active catalysts, and the rate at the beginning of stage 1 is greater than that predicted from the Arrhenius plot at higher temperatures (Fig. 3). Deactivation of multiple hydrogenolysis by a carbon deposit is therefore the most likely explanation. An alternative possibility is that at the start of stage 1 the catalyst absorbs and retains much of the n-butane feed and that this creates a high local concentration at the metal particles, favoring

FIG. 7. Dependence of rates of reaction of *n*-butane on H_2 pressure: $\bigcirc$, 6% Pt/SiO_2 (EUROPT-1) at 533 K (5); ◑, 0.3% Pt/Al_2O_3 (EUROPT-3) at 578 K (3); ●, Pt/KL catalyst at 573 K.

shown in Table 3 for all three catalysts, we may make allowance for the lower temperature used in the work on Pt/SiO_2 (EUROPT-1) (5) by employing the Van't Hoff isochore on K_A. With *n*-butane the values for Pt/KL and for EUROPT-1 fit well with those found with EUROPT-3, where temperature was varied (Fig. 8). This suggests that the enthalpy change for its dehydrogenative chemisorption may be much the same ($\sim$78 kJ mol^{-1}) on all three catalysts. However, the values of K_A recorded for propane (Table 1) are considerably lower for Pt/KL and for EUROPT-1 (5) than would be expected from the Van't Hoff plot for EUROPT-3 (3).

The differences in the shapes of the plots of rate against H_2 pressure (Fig. 7) are great. The plot for EUROPT-1 at 533 K would, if determined at $\sim$573 K, have shown less strong inhibition by H_2 and a maximum rate at higher pressure, if the trends shown (3) for EUROPT-3 apply. Our first reaction was to attribute the shape of the curve for Pt/KL to a very strong adsorption of H_2 on this catalyst; this is indeed borne out by the values of K_H shown in Table 3, which are at least three times larger than for any other catalyst. K_H values do not show a large temperature dependence on EUROPT-3, so we feel that comparison of the values in Table 3 is valid. We have noted before (3) that uncertainties connected with the curve-fitting routine imply that too much significance should not be given to differences of less than a factor of 2; however, the K_H values for the Pt/KL catalyst are clearly egregious.

While there does not appear to have been any systematic study of the kinetics of the aromatization of linear alkanes, the detailed study by Vaarkamp *et al.* of the reaction of MCP on Pt/KL and other Pt catalysts (11) provides confirmation

of the greater strength of H_2 chemisorption on the alkaline catalyst. They analyse their kinetic results by means of a mechanism similar to that which we use, but their use of a multiatom rate-limiting step in which three to six H atoms
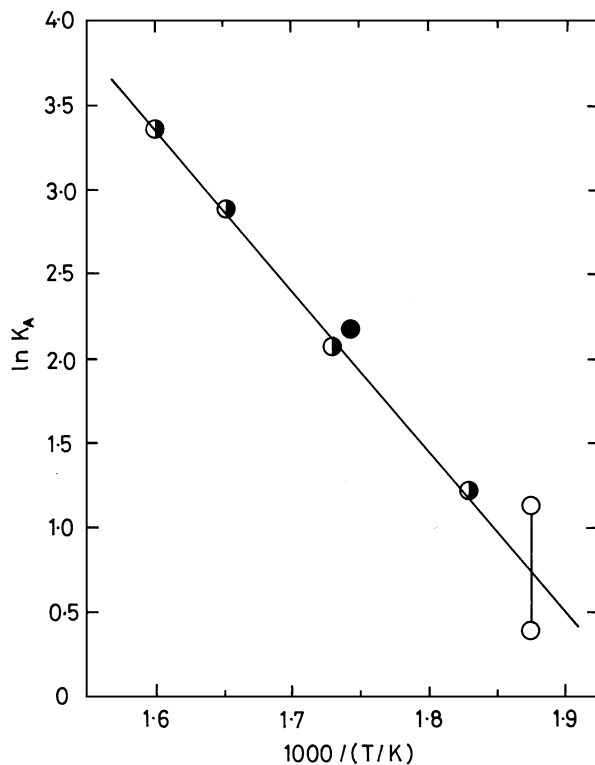

FIG. 8. Van't Hoff isochore plot of K_A for *n*-butane: symbols as in Fig. 7. For EUROPT-1, the largest and smallest values recorded (5) are shown.

participate leads to a somewhat intractable rate expression and to values of the constants of the expression that are not comparable with ours. Recent calorimetic measurements of the chemisorption of H_2 and of CO on a number of alkaline Pt catalysts, as well as neutral or acidic catalysts, also show that both molecules are more strongly chemisorbed on the former (12).

There are other clear indications that the adsorption of H_2 on Pt/KL may be unusually strong: these are (i) the comparatively small variations in product selectivities in both reactions above 0.1 atm H_2 pressure, such that for n-butane both F' and T_3 are almost independent of H_2 pressure in this region (Fig. 6), and (ii) the similarly small changes in these parameters when temperature is altered (Figs. 2A and B) outside the region of multiple hydrogenolysis. Precisely the same behaviour has been seen with a very highly dispersed Ru/Al_2O_3 catalyst (7), and assigned to very strong H_2 adsorption, the argument being that surface coverage by H atoms will not change rapidly with either H_2 pressure or temperature when this is high. The behaviour of the Pt/KL catalyst contrasts with those of Pt/Al_2O_3 (EUROPT-3 and its 0.6% Pt analogue) (2, 13) and of Pt/SiO_2 (EUROPT-1) (4), where the decrease of T_3 and the increase of F with temperature may be associated with the weaker H_2 chemisorption in these cases (Table 3).

It now remains to consider whether it is possible to use the hypothesis of strong H_2 chemisorption to understand better the peculiar abilities of the Pt/KL catalyst in the aromatization of linear alkanes. It has been shown (1, 14) that in the reaction of n-hexane there are no alkenes formed when a Pt/SSZ-94 (a microporous zeolite) is used, whereas under the same conditions they account for 48% of the products over Pt/SiO_2. The formation of carbonaceous deposits would certainly be hindered on Pt/KL, and its activity preserved, if a high surface concentration of H atoms limited the formation of alkenes. It is not, however, firmly established that the unusually strong chemisorption of H_2 found on Pt/KL is due simply to a very small metal particle size; indeed Sharma *et al.* (12) show that Pt/SiO_2 catalysts having dispersions of 51 and 76% dispersion show the same adsorption enthalpies over the whole range of coverage, although they do not attribute the specific characteristics of Pt/KL to the stronger chemisorption that it shows. It seems likely that the small particle size, the presence of K^+ cations, and the electric field gradient within the zeolite cavities all contribute to a stronger form of chemisorption. Pt and Pd supported on MgO or $MgO–Al_2O_3$ are very good catalysts for alkane aromatization (15, 16), and Pt/MgO shows quite high isomerization selectivites (17); cations clearly play an important role in both reactions, which must share some mechanistic features. In the case of the Ru/Al_2O_3 catalysts referred to above, EXAFS measurements have shown that the average particle contained about 12 atoms (18). This suggests that a very small metal cluster
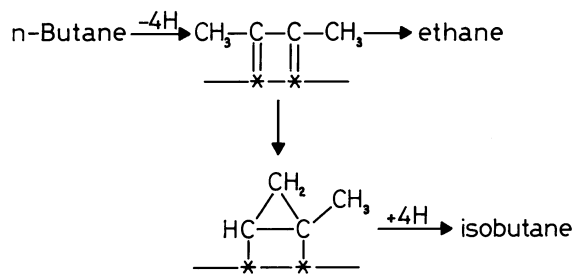
SCHEME 1

size may be a contributory factor to exceptionally strong H_2 chemisorption.

We cannot draw any definite conclusion concerning the dependence of S_i or r_i on H_2 pressure, because the latter is selectively deactivated by the carbon deposit formed especially when low H_2 pressure is used (Fig. 4). We note that, as with EUROPT-1 (5), further carbon is formed during the variation of H_2 pressure, over and above that deposited during prior stabilization and/or thermal cycles; in the reaction of n-hexane on EUROPT-1, this also led to a decrease in S_i (19). However, S is *larger* at the end than at the beginning of a thermal cycle (Fig. 2); there must be, therefore, at least two distinct forms of carbon, having different effects on S_i (5). One of these may be formed predominantly from C_1 precursors, as suggested above. On EUROPT-1, S_i decreased with increasing H_2 pressure, and it was concluded (5) that the intermediate species must have lost one or two more H atoms than was needed for hydrogenolysis; this was held to account for the larger activation energy for isomerization. While the effect of temperature on S_i is quite clear (Fig. 2), we cannot in this case be sure whether the intermediates for the two processes are the same or not. The obvious connection between isomerization and central C–C bond fission suggests some common feature in their mechanisms (see Scheme 1), but if the Pt particles are in fact as small as is claimed (1) it is difficult to assign different reaction paths to different types of site, as we have sought to do previously (5, 9). It may be that the presence of carbonaceous material on or near the metal acts to disfavour the formation of 2,3-diadsorbed butane, but in the absence of more extensive kinetic measurements further speculation has little value.

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