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Alkane Transformations on Supported Platinum Catalysts

5. Effects of Formation and Removal of Carbon Deposits on Alkane Hydrogenolysis Using EUROPT-1 (6.3% Platinum/Silica)

Geoffrey C. Bond and Xu Lin[1]

Department of Chemistry, Brunel University, Uxbridge UB8 3PH, United Kingdom

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The carbonaceous deposit formed during hydrogenolysis of *n*-butane on EUROPT-1 (6.3% Pt/SiO$_2$) at ∼535 K using a 10-fold excess of H$_2$ causes an increase in isomerization selectivity S_i and a decrease in the probability of central C−C bond splitting *F*, while that formed during a thermal cycle between 523 and 633 K has the opposite effect: both lead to an ∼50% loss of activity. We propose that the first kind resides mainly on sites comprising atoms of low coordination number (Type II sites) and the second kind mainly on sites in planar zones (Type I sites). Variation of H$_2$ pressure at 533 K using a short reaction-pulse technique shows that S_i decreases as H$_2$ pressure is raised; *F* also decreases, but to a lesser extent. Rates of each reaction have been fitted to a rate expression derived from a mechanism in which partially dehydrogenated intermediates enter the slow step. The intermediate for hydrogenolysis has lost two H atoms; that for isomerization, three or four. This explains the smaller value of the equilibrium constant K_A for dehydrogenation to the isomerization intermediate, and also the much higher apparent activation energy for this reaction.

INTRODUCTION

In Part 1 of this series (1) there was reported a detailed study of the reactions of *n*-alkanes containing two to four carbon atoms with H$_2$ on the reference catalyst EUROPT-1 (6.3% Pt/SiO$_2$), with particular attention to the effect of temperature on rates obtained using a 10 : 1 H$_2$: alkane ratio. This extended our earlier work (2) in which the thermal stability of this catalyst and the effects of various pretreatments were investigated. The principal features of the more recent work (1) are as follows: (i) highly reproducible initial rates; (ii) with *n*-butane, a substantial deactivation following the first thermal cycle (525–655 K), *followed by stability with respect to rates and product selectivites,* unaffected by further thermal cycles; and (iii) a marked tendency for skeletal isomerization to increase with temperature. It is however clear from the extensive work of Paál, Sárkány, and their associates on reactions of higher alkanes and cycloalkanes with H$_2$ on Pt catalysts (3–6) that product selectivites as well as rates respond sensitively to changes in H$_2$: alkane ratios, and for this reason we have recently turned our attention to the effects of varying reactant concentrations on the reactions of the simpler alkanes. We have already reported what we have found with EUROPT-3 (0.3% Pt/Al$_2$O$_3$) and EUROPT-4 (0.3% Pt–0.3% Re/Al$_2$O$_3$) in both clean and partially carbided states (7), and with Ru/Al$_2$O$_3$ catalysts (8, 9). We now describe the results of a study of the kinetics of transformations of propane and of *n*-butane in the presence of H$_2$ over EUROPT-1.

The background of this work is as follows. There is now a clear appreciation that the reaction pathways adopted by higher *n*-alkanes (3, 4), branched alkanes (3, 5), and cycloalkanes (3, 6) in their reactions with H$_2$ over EUROPT-1 and other monofunctional Pt catalysts depend critically on the state of the surface, as defined by the amount and composition of the "carbonaceous residues" residing on it. Three conditions of the surface have been recognized (4), and have been denoted as Pt−H (essentially clean), Pt−C−H, and Pt−C to represent the change in composition of the residues with severity of pretreatment or reaction conditions. From our own work (1, 7, 8–10) it appears that in the low-temperature regime ($T < 600$ K) the residues are principally dehydrogenated forms of the reactant alkane, bound to the surface by multiple Pt−C bonds, and that the extent of dehydrogenation increases as the temperature is raised or as the H$_2$: alkane ratio is decreased. Above 600 K there is a growing tendency to form polymeric carbonaceous species, and ultimately graphite (11). The origin of the effects which these "residues" have on reaction pathways is uncertain: it may lie in the mean size of the active center, or in the class of Pt surface atoms that remain unobstructed (11), or the residue may itself in some way participate in the reaction. Active centers to which the neighboring ions of the support contribute may also come into play under certain conditions (12).

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[1] On leave of absence from Department of Chemistry, Guizhou University, Guiyang, Guizhou 550025, China.

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Such is the complexity of the products formed from alkanes containing six or more carbon atoms that no quantitative model has yet been proposed to describe the effects of reactant concentrations and temperature. Our philosophy is to employ simpler alkanes, having up to four carbon atoms, in the expectation that the more limited range of reaction possibilities and of intermediate structures may allow a better analysis of the relevant factors, including surface composition (7); such work may ultimately provide a basis for modeling the behavior of more complex systems.

There are three variables that affect the extent and type of carbon deposits formed from a given alkane: (i) time-on-stream at constant temperature and fixed reactant ratio; (ii) temperature, studied by a constant short reaction time at each temperature, and with a fixed reactant ratio; and (iii) H_2/alkane ratio at constant temperature, using some procedure that controls the reaction time at each point. These variables may be examined in any sequence, and depending on the prior amount of carbon deposited may lead to its decrease as well as to its increase. Each variable has previously been investigated using EUROPT-3, and, in a more limited way, EUROPT-4 (7, 10), but with EUROPT-1 we have so far only reported the results obtained by temperature variation (1). In the work to be described, we compare and contrast the effect of each variable, alone and in combination.

A particular feature of the present work is the fitting of the results obtained by varying H_2 pressure to a rate expression previously employed (8), and hence deriving true rate constants, and equilibrium constants for the chemisorption of H_2 and of alkane. This analysis allows us to see to what extent these quantities are affected by partial carbonaceous layers.

EXPERIMENTAL

Catalyst Pretreatment

The preparation and characterization of EUROPT-1 has been described (see (3) and references therein): portions of about 0.2 g were used. In most cases, after the reactor was purged with N_2, the sample was given an initial high-temperature reduction (HTR): it was heated to 750 K at 5 K min^{-1} in pure H_2 (40 cm^3 min^{-1}), and after 13 h it was cooled at the same rate to reaction temperature.

Reaction Procedures

Thermal cycles were performed to try to bring the catalyst to a stable partially deactivated state: one of three methods was used. Most often there was a *continuous reactant flow* ($H_2 : \text{alkane} : N_2 = 100 : 10 : 30$ cm^3 min^{-1} for *n*-butane, and (because of its lower reactivity) 55 : 5.5 : 16.5 cm^3 min^{-1} for propane). Temperature was increased in steps of about 10 K from 523 to 633 K, and 2 min before the end of each isothermal period a sample was taken for analysis: this is referred to as *stage 1*. The same procedure was used as the temperature was returned to its initial value, this constituting *stage 2*. The whole is called a *thermal cycle* (TC). Alternatively the cycle was made using the *short reaction-pulse* (SRP) method (7): at each temperature the $H_2 : N_2$ mixture was passed for 19 min, and then the alkane flow was introduced for 1 min, using the same flow rates, at the end of which time a sample was extracted for analysis. This procedure was used in order to minimize formation of carbonaceous deposits. With the same intention, a third procedure was used: this had 40-min isothermal steps, in the first half of which the $H_2 : N_2$ mixture only was passed, and then the alkane flow was brought in, and the sample for analysis taken 19 min later. This is the *interrupted-flow* (IF) method.

Prolonged isothermal experiments (PIR) were carried out with the standard reactant flow at 523 K in order to investigate (i) the stability of the carbonaceous deposits formed during a thermal cycle and (ii) the formation of such deposits on freshly reduced catalyst. Samples were analyzed every 20 min. *H_2 orders* were measured, after a specified pretreatment, usually by the short reaction-pulse method at 533 K: after a cleaning period of 15 min with the 100 : 30 $H_2 : N_2$ flow, the H_2 flow was changed to that required for the next reaction pulse, and after its completion the $H_2 : N_2$ flow was again used. Reaction pulses 1, 2, 6, 8, 11, 14, 17, and 20 employed the standard mixture, normally containing an H_2 pressure of 0.714 atm (i.e., 100/140) but on occasion 0.16 atm; rates given by H_2 pressures less than 0.1 atm were normalized to the rate of standard pulse 11 by assuming that the corresponding standard rate was that of the *following* pulse, and for H_2 pressures greater than 0.1 atm the corresponding standard rates were obtained by interpolation.

Correction for Propane Impurity in n-Butane

The desirability of sometimes working at low conversion means that very great care must be exercised over correcting measured rates and selectivities for impurities present in the reactant alkane. Two different cylinders of *n*-butane (British Oxygen Co.) were used: levels of the principal impurities are given in Table 1. Using the second cylinder it

TABLE 1

Levels of Hydrocarbon Impurities in *n*-Butane Cylinders

Cylinder No.	Date	C_3H_8/%	${}^iC_4H_{10}$/%
1	—	0	0.050
2	22 Feb 94	0.303	0.0310
	28 Feb 94	0.284	0.0329
	6 Mar 94	0.255	0.0335
	9 Mar 94	0.235	0.0324
	22 Mar 94	0.197	0.0323

was necessary when carrying out lengthy experiments (thermal cycles or isothermal runs) to measure these levels before and after each experiment, and to apply a correction based on the average value, as the level of the more volatile propane decreased with time, while that of isobutane remained about constant (Table 1). Impurity levels in the propane were too small to necessitate any correction.

Treatment of Results

The methods used to treat the results have been described on numberous occasions (1, 7–10), so a short summary will suffice. The isomerization selectivity S_i is the fraction of *n*-butane converted to isobutane, and the selectivities of the hydrogenolysis products are defined by

$$S_1 + 2S_2 = 3 \qquad \text{for propane,}$$

$$S_1 + 2S_2 + 3S_3 = 4 \qquad \text{for } n\text{-butane.}$$

Rates of hydrogenolysis r_h, of isomerization r_i, and their sum r_t are in mmol g_{cat}^{-1} h^{-1}; the same subscripts are used to identify other kinetic parameters.

The parameters F, T_2, and T_3 are derived from the mechanistic analysis of the *n*-butane reaction due originally to Kempling and Anderson (13), and which has also been fully described before (1, 7–10). Briefly F is the fractional chance of an adsorbed C_4 species breaking at the central C—C bond, the T_j of an adsorbed C_j intermediate vacating the surface as alkane rather than suffering a further C—C bond fission. From a steady-state analysis of this reaction scheme (13), equations are derived which at low conversion simplify to

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

and

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

Since T_2 also equates to the ethane selectivity S_2' in the hydrogenolysis of propane, the assumption that the same value applies to C_2 intermediates in the reaction of *n*-butane has been used, and is usually satisfactory. Since S_2' is normally very close to unity, this value of T_2 is used in solving the above equations.

We have also previously shown (7–9) how the variation of rate with H_2 pressure may be described by the rate expression ES5B:

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

This equation is derived from a mechanism (see Scheme I of Ref. 7) by which the alkane C_nH_m is changed into its reactive form C_nH_{m-x} by loss of xH atoms, and is then converted by reaction with a single H atom into products by the breaking of either a central or a terminal C—C bond. The rate constant for this step is k_1; K_A is the equilibrium constant defining the dehydrogenation of the alkane and K_H that for H_2 chemisorption. P_A and P_H are respectively the pressures of alkane and of H_2. Since as will appear below S_i decreases markedly with increasing H_2 pressure, we shall apply this expression to the rates of both hydrogenolysis and isomerization. Optimum values of the constants were obtained using the Levenburg–Marquardt algorithm (14) by altering the value of x until values of the other constants were found to minimize the standard deviation.

It is necessary to stress the assumptions implicit in this mechanism. It is supposed that for each reaction there is but a single reactive intermediate C_nH_{m-x} throughout the entire range of H_2 pressure used, and that it occupies only a single "site." The sites occupied by this intermediate and by H atoms are taken to be the same. Further elaboration of the mechanism to take account of these and other limitations of the currently used mechanism is possible but only at the expense of the comparative simplicity of what we have done before; the introduction of further constants into the equation would exacerbate the problem of finding optimum values and would also limit their significance. For further discussion of the choice of rate expression, see (7).

RESULTS AND DISCUSSION

Carbon Deposition Immediately Following a First High-Temperature Reduction

(i) Thermal cycles. In attempting to make precise measurements on standard catalysts, it is essential to show that reproducible behavior can be obtained over long periods of time when fixed operating procedures are used. Table 2 shows the results obtained for two thermal cycles performed with n-C_4H_{10} in the range 523–623 K immediately after an initial HTR; rates and selectivities are those found in 573 K. They are compared with one of the sets of results obtained previously (1), and the agreement is generally excellent. The present results are in one respect superior to those given earlier (1), when we experienced difficulty in measuring Arrhenius parameters in stage 1. We now see that E_h and E_i are both consistently about 30% higher in stage 2 than in stage 1, presumably because progressive deactivation occurs during heating. We had previously (1) detected systematic changes in the slopes of Arrhenius plots at about 600 K, but in what we now report the numbers of points above this temperature are too few to reveal the effect clearly: we generally therefore quote only one activation energy.

Table 2 also includes results for two other thermal cycles, using different procedures as described under Experimental. The use of the short reaction-pulse technique leads to slightly faster rates and to selectivities that are broadly similar to those which the continuous flow method afforded. The loss of activity is however somewhat less, and the value of S_i hardly changes. Arrhenius plots for both reactions show clear breaks at about 573 K, the tabulated values

TABLE 2

Arrhenius Parameters, and Rates and Product Selectivities at 573 K, for *n*-Butane Hydrogenolysis Obtained by Various Types of Thermal Cycles on Freshly Reduced EUROPT-1

Expt./cyclinder No.	Method[a]	Stage	E_h/kJ mol^{-1}	ln A_h[b]	r_h[b]	S_2	S_3	F	T_3	S_i	E_i/kJ mol^{-1}	Note
2202/2	TC	1	101 ± 2	21.59	1.52	0.607	0.685	0.296	0.973	0.174	154 ± 11	[c]
2202/2	TC	2	131 ± 1	27.28	0.84	0.678	0.649	0.331	0.970	0.128	202 ± 18	
2502/2	TC	1	97 ± 4	20.50	1.04	0.604	0.685	0.292	0.968	0.169	157 ± 5	[c]
2502/2	TC	2	135 ± 3	27.69	0.56	0.671	0.652	0.327	0.970	0.121	207 ± 15	
	TC	1	—	—	1.22	0.628	0.674	0.306	0.971	0.197	—	[d]
	TC	2	118 ± 3	24.1	0.52	0.708	0.632	0.346	0.966	0.108	232	
1203/2	SRP	1	133 ± 9	28.61	2.06	0.642	0.671	0.317	0.983	0.168	137 ± 9	[e]
1203/2	SRP	2	145 ± 4	30.79	1.46	0.655	0.663	0.323	0.980	0.160	158 ± 20	
2801/1	IF	1	96 ± 2	21.65	4.74	0.640	0.666	0.311	0.966	0.172	163 ± 26	[c]
2801/1	IF	2	115 ± 4	25.28	3.89	0.702	0.633	0.340	0.959	0.164	189 ± 35	

[a] TC, thermal cycle; SRP, short reaction pulse; IF, interrupted flow.
[b] A_h and r_h in mmol g_{cat}^{-1} h^{-1}.
[c] Temperature range 523–633 K.
[d] From Part 1, Table 2, sample II; temperature range, 524–603 K.
[e] Temperature range 543–623 K.

being those found below this temperature; the higher values found above 573 K are thought to be less reliable. Table 2 also contains results obtained by use of the interrupted-flow method; this produced faster rates, and less deactivation, but other parameters fall within the range observed with the other methods. As with the pulse method, the value of S_i scarcely changes.

These experiments lead to the following conclusions. (i) The quite closely reproducible rates (viz., r_h) found in stage 1 of the thermal cycle at 573 K must refer to a somewhat poisoned surface, because the other methods give faster rates. This conclusion is not surprising, since as remarked above the lower values of E_h and of E_i in stage 1 betoken the occurrence of deactivation. (ii) The use of the pulse method does not however eliminate deactivation, although it lessens it somewhat, and the interrupted-flow method decreases it even further but does not quite abolish it. It appears that a loss of hydrogenolysis activity approaching 50% is needed before the selective deactivation of isomerization is apparent.

(ii) Prolonged isothermal runs. Changes in catalytic behavior during prolonged isothermal use under continuous flow at 533 K are illustrated in Fig. 1. This shows results for three periods of 100 min each in a run lasting about 20 h: during the first 2 h the rate (r_h) falls by 50% and thereafter remains perfectly stable. There is a slight initial decrease in S_2 and hence in F, and perhaps a small increase in S_i from ~0.02 to ~0.045, but S_3 and T_3 show no variation. Results obtained after 20 h are close to those found after 13 h. A similar run was performed with another sample, and the results of the first and last (25 h) analyses are shown as shaded points in Fig. 1: they follow closely the results of the first run.

There is a clear difference between the effect of carbon deposited in a thermal cycle and in an isothermal run. Although deactivation in the former was only slightly greater (−70%), F did not decrease as shown in Fig. 1, but on the contrary rose a little (see Table 1 and Fig. 2 of Part 1) (1)).

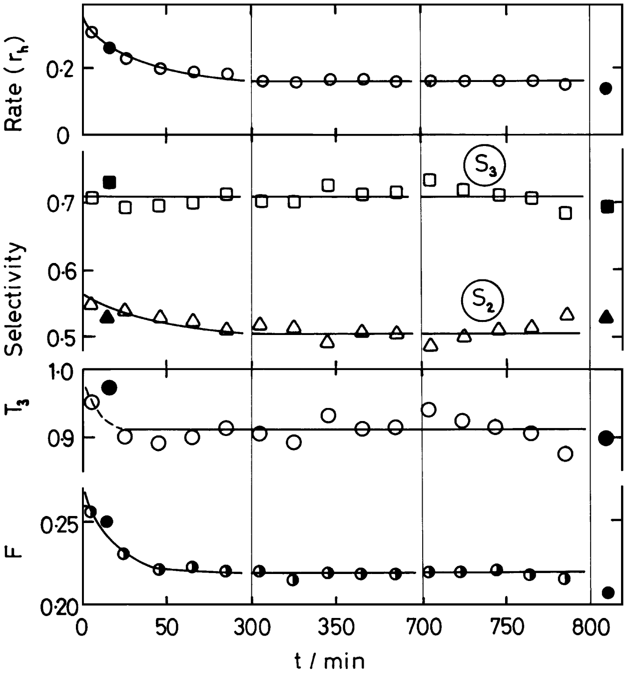


FIG. 1. Hydrogenolysis of *n*-butane on EUROPT-1: prolonged isothermal run (PIR) at 533 K, $H_2/n\text{-}C_4H_{10}$ (experiment 0303). The figure shows results obtained in the periods 0–100, 300–400, and 700–800 min. Filled points are selected from results of a duplicate experiment, the last being at 25 h time-on-stream.

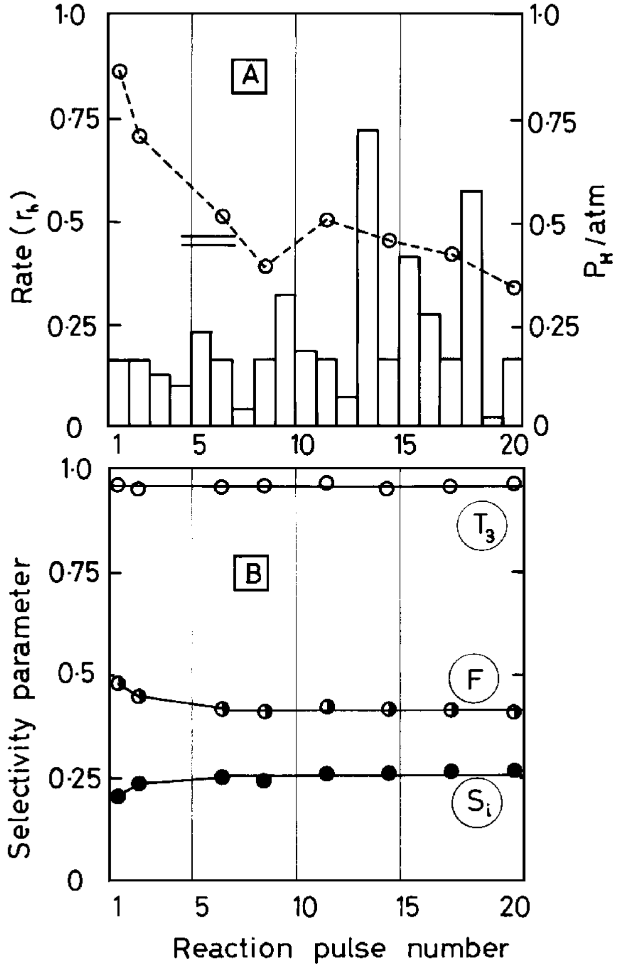


FIG. 2. Dependence of the rate of *n*-butane hydrogenolysis on H_2 pressure at 533 K (experiment 0102). (A) Variation of rate under standard conditions ($P_H = 0.16$ atm) with pulse number (left-hand scale) and values of P_H used in intervening samples (right-hand scale). (B) Variation of selectivity parameters under standard conditions with pulse number.

(iii) Variation of H_2 pressure. The effect of varying H_2 pressure, as described under Experimental, on the behavior of *n*-butane hydrogenolysis at 533 K is illustrated in Figs. 2 and 3. Figure 2A shows that the hydrogenolysis rate r_h under standard conditions (here $P_H = 0.16$ atm) decreased considerably to start with, but thereafter the variation was comparatively small. The changes between the standard measurements are qualitatively understood by supposing that using a low H_2 pressure suppresses the following rate (compare rates for pulses 6 and 8, and 17 and 20), while a high value tends to remove a previously formed carbon deposit (compare rates for pulses 8 and 11). The correction procedure described above satisfactorily reduces the scatter in the rates of the reactions of *n*-butane (see Figs. 3A and 3B for examples), and in the rate of reaction of propane (Fig. 3C): these corrected rates were used to obtain optimum values of the constants of equation ES5B (see below), used to calculate the curves drawn through the points in these figures.

Figure 2B shows that the initial loss of activity is accompanied by a decrease in *F* and an increase in S_i as was seen in the continuous isothermal run (Fig. 1). Once this phase is complete, there is no further change, and in particular the use of very low H_2 pressures in pulses 7 and 19 does not affect the following standards. Values of T_3 are constant throughout.

Does HTR Completely Restore a Previously Used Catalyst?

To expedite the work, it would be convenient if carbonaceous material could be completely removed by HTR, and the virgin state of the sample restored. A series of experiments was performed to explore this possibility: first, thermal cycles were carried out on catalysts that had earlier been used for (a) an H_2 pressure variation series (experiment 0202) and (b) a prolonged isothermal run and a thermal cycle (experiment 0703). The results are summarised in Table 3; comparison with Table 2 suggests that the second HTR effectively restores initial behavior; specifically the changes in *F* and in S_i between stages 1 and 2 are well reproduced, suggesting that little if any carbon remains after the HTR.

An H_2 pressure variation experiment (0302) was then performed on a catalyst which had earlier been used for a similar experiment (0102) and for a thermal cycle, before receiving a further HTR. Apart from the fact that the initial rate was somewhat lower (0.33 mmol g^{-1} h^{-1}) and the early deactivation a little greater, the results were generally very similar to those in Figs. 2 and 3. Mean values of selectivity parameters under standard conditions for runs 0102 and 0302 are given in Table 4.

The Effect of Carbon Deposits Formed in Standard Thermal Cycles

It appeared from our previous work (1, 10) that the first thermal cycle following HTR brought the catalyst to a stable partially deactivated state that was not altered by a further cycle. The purpose of the experiments to be described was to examine the stability of the carbon deposit so formed by performing (i) a prolonged isothermal run and (ii) an H_2 pressure variation experiment in which we hoped there would be less of a problem with deactivation than before (see Fig. 2A).

The results for the prolonged isothermal run are shown in Fig. 4. Contrary to our expectations, the rate at 536 K increased steadily with time-on-stream, rising by almost 50% in 4 h, although not achieving the value found at the start of a thermal cycle ($\simeq$0.14 mmol g^{-1} h^{-1}). Product selectivities also changed substantially during this period: S_1 and S_2 decreased and S_3 rose, and at the end, when

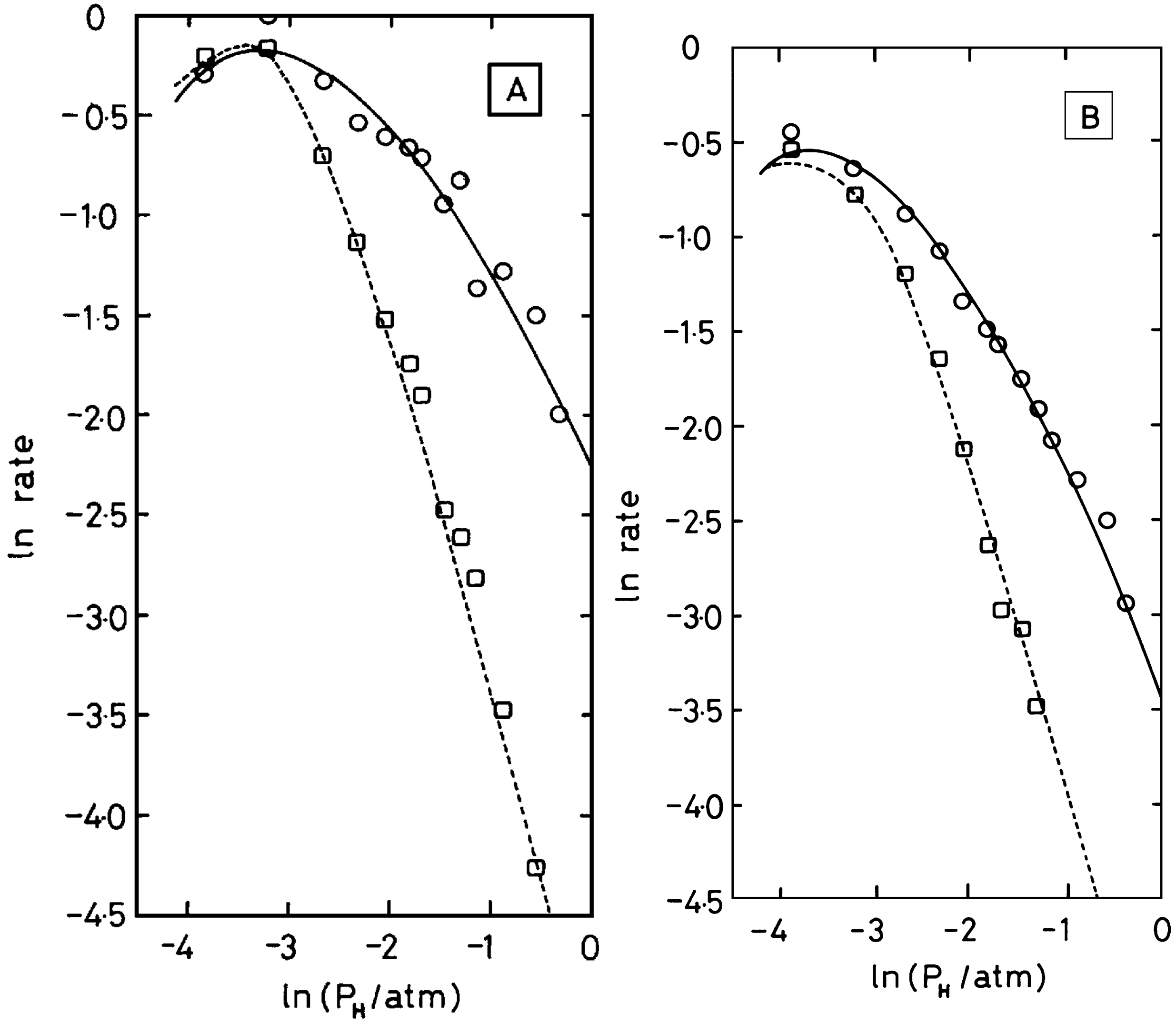


FIG. 3. Dependence of rates of hydrogenolysis (○) and of isomerization (□) on H_2 pressure at 533 K. (A) Experiment 0102 (immediately after first HTR). (B) Experiment 0803 (following TC and PIR; see Table 4). (C) Experiment 2703 (reaction of propane following TC, PIR, and a second TC). Curves are calculated using equation ES5B and the constants given in Table 5.

$S_1 \simeq S_3$, values corresponded closely to those seen at the beginning of a cycle. The reason for the changes in selectivities is almost certainly the formation of methane from the carbon deposit, of which perhaps 15–20% is removable in 4 h. The fact that selectivities were then about those expected for the hydrogenolysis reaction alone suggests that no further methane was being or would be formed.

Performing an H_2 pressure variation experimental immediately after a thermal cycle afforded average values for selectivities and derived parameters at the standard H_2 pressure (0.714 atm) that were within the normal range (experiment 2302; see Table 4); there was no obvious excess methane formation.

The Effect of Carbon Deposits Formed in Isothermal Runs

The results for a thermal cycle carried out after a 20-h isothermal experiment are shown in Table 3 (experiment 0403): they are very similar to those found in cycles performed immediately after an HTR (see Table 2, experiments 2202 and 2502; Table 3, experiments 2020 and 0703), especially with respect to r_h, E_h, and E_i, and the changes in F and S_i between stages 1 and 2. It appears that the carbon deposition that causes the slight changes occurring at the start of an isothermal run (Fig. 1) does not prevent further deposition occurring during a thermal cycle.

Two H_2 pressure experiments were performed following isothermal runs (Table 4, experiments 0203 and 2402); the

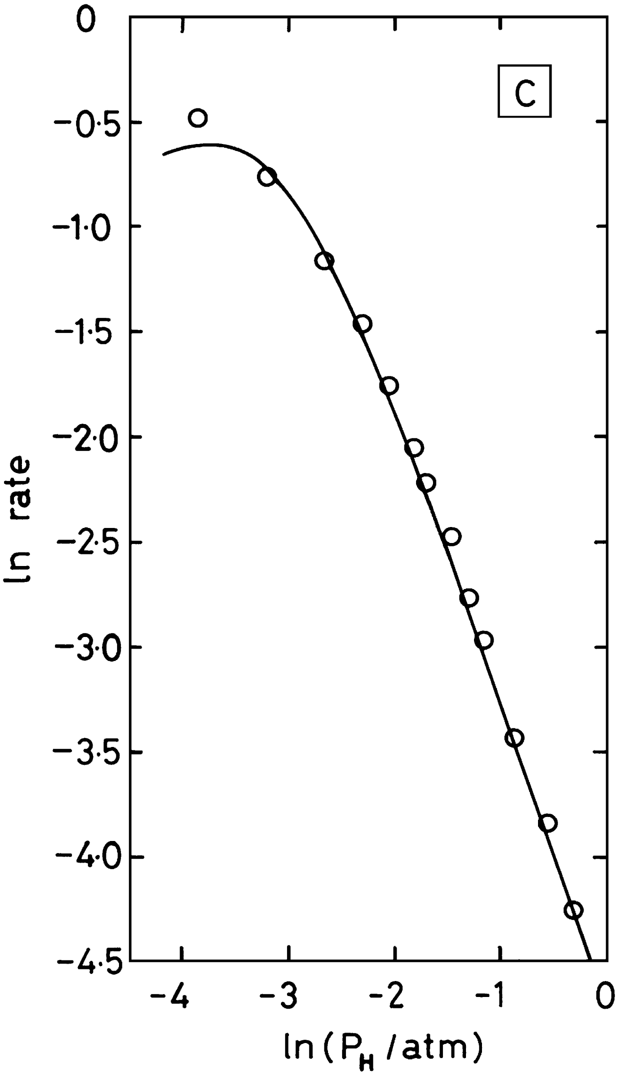


FIG. 3—*Continued*

results are much in line with other results, except for low values of T_3, which are attributed to uncertainty in the correction to be made for the propane impurity. The value of S_3, and hence of T_3, is extraordinarily sensitive to the assumed impurity level, because of the use of low conversions; thus, for example, in a typical case changing the assumed level from 0.30 to 0.31% alters T_3 from 0.90 to 0.75. We therefore discount all recorded T_3 values of less than 0.95; in experiments with very pure *n*-butane (2801, Table 2; 0202 and 0402, Table 3; and 0102 and 0302, Table 4), they were 0.95–0.99 at 533 K and 0.96–0.98 at 573 K. The activity changes occurring in these experiments where H_2 pressure was varied are hardly affected by the previous isothermal aging.

The further H_2 pressure variation experiments were performed immediately following *both* a thermal cycle *and* an isothermal run (experiments 1103 and 0803, Table 4). Values of T_3 are again low, probably for the reason suggested above, but F and S_i values under standard conditions are similar to those found earlier.

The Dependence of Rates and Selectivity Parameters on H_2 Pressure

It is convenient now to review the further information that stems from the experiments in which H_2 pressure was randomly varied (see Table 4). (i) Averaged selectivity parameters measured under the standard H_2 pressure of 0.714 atm at 533 K, omitting where necessary early values as shown in Fig. 2B, are remarkably constant; viz., $S_i \simeq 0.03 \pm 0.01$; $F \simeq 0.25 \pm 0.02$; $T_3 \simeq 0.96 \pm 0.01$. Comparison of these values with those at 573 K taken from the thermal cycles (Table 2) confirm the sense of their temperature dependences seen previously (see Fig. 2 of Ref. 7). The absence of an HTR immediately before the experiment, as in the last five entries in Table 4, has no apparent effect on F, or (as far as the accuracy of the measurements allows us to see) on S_i. (ii) Table 4 also shows the rates shown in the fifth standard measurement (r_{11}; see Fig. 2A); where HTR has immediately preceded the experiment, rates are 0.12–0.14 mmol g_{cat}^{-1} h^{-1}, and are only marginally slower after a prolonged isothermal run (experiment 0203; compare Fig. 1), but they are distinctly lower ($\sim$0.07 mmol g_{cat}^{-1} h^{-1}) where the HTR has *not* been performed. (iii) The extent of deactivation during the experiment is, as might be expected, somewhat lower in those cases where the initial rate is low.

We come now to consider the values of the constants of equation ES5B as derived for the two reactions (Table 5). The algorithm used to obtain best-fit values is not perfect, and the results depend slighly on the initially selected

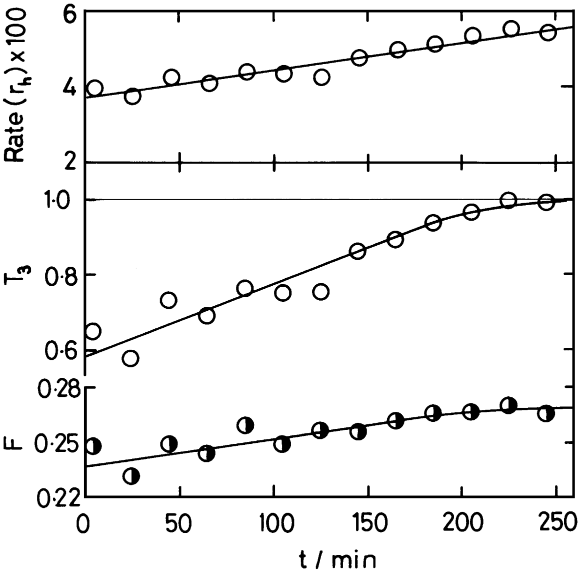


FIG. 4. Variation in rate of hydrogenolysis of *n*-butane at 536 K with time-on-stream (prolonged isothermal experiment) following a TC experiment 0703: selectivity parameters are also shown ($H_2 : n\text{-}C_4H_{10} = 10$).

TABLE 3

Arrhenius Parameters, and Rates and Product Selectivities at 573 K, for *n*-Butane Hydrogenolysis Obtained by Thermal Cycles: Effect of HTR Following Prior Use

Expt./cyclinder No.	Stage	Prior use[a]	E_h/kJ mol^{-1}	ln A_h	r_h	S_2	S_3	F	T_3	S_i	E_i/kJ mol^{-1}
0202/1	1	HV, HTR	102 ± 2	21.47	1.16	0.640	0.667	0.311	0.969	0.194	170 ± 9
0202/1	2		133 ± 3	27.49	0.60	0.711	0.632	0.348	0.969	0.146	230 ± 16
1003/2	1	HV	105 ± 2	21.91	0.91	0.647	0.700	0.287	0.981	0.164	156 ± 7
1003/2	2		131 ± 2	26.75	0.47	0.681	0.637	0.317	0.933	0.114	211 ± 9
0703/2	1	PIR, TC, HTR	106 ± 3	23.03	0.80	0.600	0.679	0.283	0.972	0.205	152 ± 6
0703/2	2		136 ± 1	23.06	0.40	0.650	0.663	0.317	0.984	0.136	223 ± 19
0403/2	1	PIR	103 ± 3	21.42	0.90	0.591	0.686	0.276	0.946	0.172	152 ± 6
0403/2	2		133 ± 3	27.07	0.48	0.680	0.630	0.310	0.913	0.108	207 ± 18

[a] Excluding initial HTRs : HV, H_2 variation; PIR, prolonged isothermal run; TC, thermal cycle.

numbers; for this reason, small differences are not considered important. However, careful inspection of Table 5 shows that values of k_1, K_A, and K_H for those experiments in which the catalyst was *not* reduced just before the start are generally *less* than the average values, this being the case for both reactions. There is with each reaction a positive correlation between k_1 and K_A, which we had noted in our work (7) on EUROPT-3, so that it is impossible to say whether the lesser activity shown after prior use is due to a decrease in k_1 or in K_A, since either will depress the rate.

Comparison of the constants' values for the two reactions leads to unexpected conclusions. The greater dependence of r_i on H_2 pressure (Fig. 3) is *not* attributable to a greater K_H, as might have been expected, but to significantly smaller values of K_A and $(m - x)$. Thus the intermediate form of the alkane for isomerization is *more* dehydrogenated, having lost about 3.4 H atoms, than that for hydrogenolysis, which has lost only 1.8 H atoms. As a direct consequence of this, K_A for isomerization is smaller than that for hydrogenolysis, and the marked decrease in the rate of the former as H_2 pressure (and hence θ_H) is increased is due to the rehydrogenation of the critical intermediate to unreactive forms. Alternatively, but equivalently, it may be seen as caused by the increased difficulty of finding vacant sites to accept H atoms from the alkane, since their concentration will fall with rising H_2 pressure. It is a reassuring validation of the usefulness of the ES5B equation that the average values of K_H are almost exactly the same for the two reactions; this is of course as it should be if in the chemisorption step there is no awareness of the future use to which the atoms will be put.

Apart from the trends in the values of the constants with the prior use of the catalyst sample, noted above, there is remarkably little variation about the mean values. The greatest divergence is seen with K_A, which for each reaction varies about twofold. It is also found that the values of each of the constants for the two reactions show an approximate

TABLE 4

Effect of Varying H_2 Pressure on the Reactions of *n*-Butane: Averaged Kinetic Parameters under Standard Conditions[a] (P_H = 0.714 atm), Median Rates, and Deactivation

Expt./cylinder No.	Prior use[b]	S_i	F	T_3[c]	r_{11}[d]	$100(r_2 - r_{20})/r_2$[e]
1012/1	—	0	0.244	0.953	0.12	52
1003/2	—	0.041	0.233	0.936	0.14	70
0302/1	HV, TC, HTR	0.016	0.247	0.973	0.13	74
2302/2	TC	0.038	0.275	*	0.08	33
0203/2	PIR	0.050	0.217	*	0.11	53
2402/2	TC, HV, PIR	0.038	0.264	*	0.065	31
1103/2	HV, TC, PIR	0.033	0.265	*	0.07	40
0803/2	TC, PIR	0.031	0.263	*	0.055	36

[a] Ignoring first two analyses because of trends as shown in Fig. 2A.

[b] Excluding initial HTR; for acronyms, see footnote to Table 3.

[c] Asterisks denote values considered inaccurate due to difficulty of fixing propane impurity level (see text).

[d] Standard hydrogenolysis rate (mmol g_{cat}^{-1} h^{-1}) for reaction pulse 11, to which other rates were normalized.

[e] Percentage deactivation during the experiment (r_2 = rate for pulse 2; r_{20} = rate for pulse 20).

TABLE 5

Constants of Equation ES5B for the Hydrogenolysis and Isomerization of *n*-Butane and for the Hydrogenolysis of Propane at 533 K

	Hydrogenation					Isomerization				
Expt.	k_1	K_A	K_H	$m - x$	sd[a]	k_1	K_A	K_H	$m - x$	sd[a]
0102	11.2	3.14	6.17	8.26	0.023	11.7	0.91	6.98	6.51	0.005
1003	11.5	2.96	7.01	8.65	0.015	12.3	0.91	7.56	6.78	0.006
0302	13.5	2.79	8.51	8.36	0.010	13.8	1.00	8.29	6.75	0.004
2302	10.2	2.11	5.80	7.81	0.010	9.2	0.57	5.64	6.19	0.004
0203	10.0	2.67	5.58	8.20	0.018	11.4	0.87	6.75	6.16	0.008
2402	10.9	1.82	6.90	8.22	0.008	9.2	0.78	5.65	7.15	0.034
1103	9.4	1.66	5.81	8.15	0.007	8.0	0.37	5.16	6.42	0.005
0803	9.3	1.48	5.96	8.02	0.006	8.6	0.45	5.47	6.58	0.005
Average	10.7	2.33	6.47	8.21	—	10.5	0.73	6.44	6.57	—
2703[b]	8.6	0.70	5.42	5.17	0.007	—	—	—	—	—

[a] sd, standard deviation.

[b] Values for propane.

proportionality, slopes of the relevant plots being close to unity for k_1 and K_H, but respectively about 0.3 and 0.8 for K_A and x. It is not however clear whether these correlations have fundamental significance, or whether they result from inherent limitations to the experimental and computational methods.

The mean values of the constants for hydrogenolysis (Table 5) may be compared with those found for the same reaction on EUROPT-3 (0.3% Pt/Al_2O_3 at 547 K (7)): allowing for their probable temperature dependences, k_1 and x are somewhat higher, K_H is about four times larger, while K_A has about the expected value.

We may also compare the values of the constants of equation ES5B derived from the single experiment with propane (Fig. 3C and Table 5), which followed the performance in sequence of an STC, a PIR, and a second STC, with those for *n*-butane after similar pretreatments. The values of k_1 and K_H are a little smaller, while K_A is considerably smaller, while the value of $(m - x)$ corresponds to the loss of about 1.4 H atoms, compared to about 0.9 for *n*-butane. These differences agree qualitatively with those found with EUROPT-3 (7) and reflect the greater thermochemical reluctance of propane to undergo dehydrogenation.

The decrease in S_i with increasing H_2 pressure (Figs. 3 and 5) harmonizes with its increase with temperature, which will cause a decrease in θ_H and an increase in vacant site concentration; i.e., it is equivalent to decreasing H_2 pressure. This correspondence enables us to rationalize the much higher apparent activation energies observed here and elsewhere (10) for isomerization. The concentration of the more dehydrogenated intermediate will rise more quickly with temperature than that of the less dehydrogenated intermediate for hydrogenolysis, because its formation is more endothermic, and this effect augments the apparent activation energy. A similar argument has been used to account for the different values shown by ethane, propane, and *n*-butane (16, 17). Since our kinetic measurements have been made at only one temperature, we cannot report values for the true activation energies.

Raising the H_2 pressure also produces changes in the hydrogenolysis selectivity parameters (Fig. 5). The decreases in S_2 and in the S_1/S_3 ratio imply a decrease in F and an increase in T_3; in fact the former passes through a somewhat flat maximum at H_2 pressures between 0.05 and 0.15 atm, while the latter becomes constant at 0.975 above about 0.25 atm. Similar behavior was shown by EUROPT-3 (16), but only below about 600 K, and by Rh/SiO_2 (18), but not by Rh on other supports. The effect while distinct is quite small, and does not necessarily mean that the intermediate for central bond splitting is less dehydrogenated than that for terminal splitting: were this so, one would not expect to see a temperature variation. It may be, for example, that the species undergoing central bond splitting needs an additional vacant site in order to form, by reason of its geometry; this would explain why F does not fall with increasing H_2 pressure above 600 K (16), as progressive decrease in θ_H with rising temperature would create more free sites.

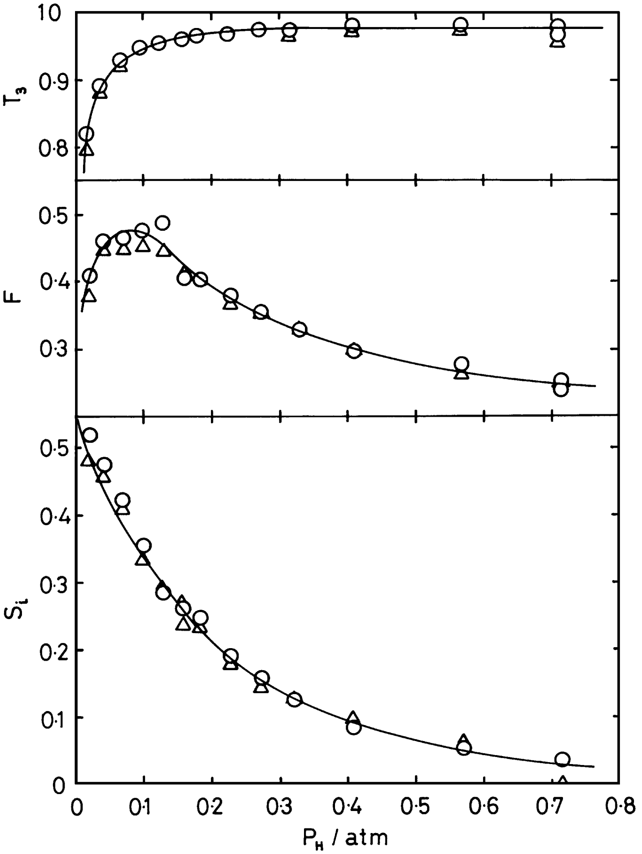


FIG. 5. Dependence of selectivity parameters F, T_3, and S_i on H_2 pressure. This figure also shows the degree of reproducibility attainable in two independent experiments (see Table 4; experiment 0102, △; experiment 0302, ○). Values of T_3 for experiment 0102 in the middle range of H_2 pressure are not shown.

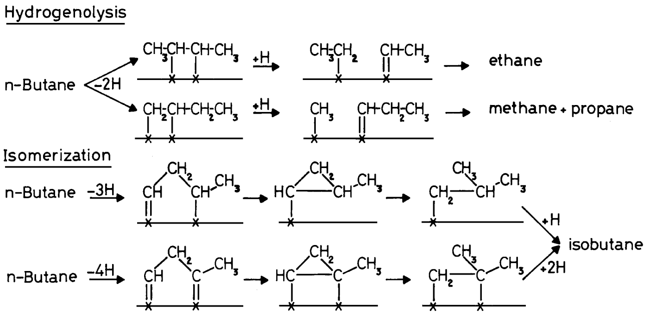
SUMMARY AND CONCLUSIONS

The study of the formation and reactivity of carbonaceous deposits derived from alkanes has potential practical as well as theoretical interest; the attention recently given by several groups of workers to the possibility of converting methane into C_2 and higher products via dehydrogenated intermediates (19–21) highlights the relevance of this work. What we report above assists our understanding of the nature and probable location of those species formed in particular from *n*-butane.

The deposit that is formed in the first hour or so of time-on-stream using a continuous reactant flow (H_2 : *n*-$C_4H_{10} = 10$) at 535 K results in a 50% loss of activity, a decrease in F (Fig. 1), and a slight increase in S_i. That formed in the early stages of an H_2 pressure variation experiment results in a 50–70% deactivation, and in the same changes to F and S_i (Table 4 and Fig. 2B). Deposits formed under these conditions are therefore similar, and resemble the "Pt–C–H" state described by Sárkány in his work with *n*-hexane (22). They differ from those formed in thermal cycles (Tables 2–4) in that the latter cause an *increase* in F and a *decrease* in S_i, as observed earlier (1), with a similar loss of activity. We have argued previously (1, 23) that this type of deposit, which is comparable to Sárkány's "Pt–C" state (22), shows some degree of preference for sites on low Miller index planes, comprising Pt atoms of high coordination number (our Type II sites). Since the deposits formed isothermally have opposite effects on selectivity parameters, we take it as a working hypothesis that they have preference for the Type I sites which comprise edges and corners, or at least embrace low coordination number atoms. The higher values of the constants k_1 and K_A for both reactions (see the first three entries in Table 5) may therefore apply more to the Type II sites, and the lower values (entries five to eight of Table 5) to Type I sites. A clear distinction between two classes of sites is not to be expected, but their probable existence is supported by the further deactivation, increase in F, and decrease in S_i that occur when a thermal cycle is performed after isothermal use without an intervening HTR (Table 3). Similar samples on which an H_2 pressure variation experiment is performed after a cycle without intervening HTR still lose 30–40% of their activity (Table 4).

The deposit formed at low temperature when short pulses of low H_2/C_4H_{10} reaction mixture are used is sometimes partially removed by the $H_2:N_2$ flow at the same temperature (Fig. 2A). It is therefore a "nonselective" poison, presumably affecting Types I and II sites indifferently. The high-temperature deposit is also slowly removed at 536 K (Fig. 4), methane being the chief product. HTR seems to remove all carbon deposits (Table 3), in contrast to statements made in the literature concerning the difficulty of eliminating deposits created by higher alkanes, except by oxidation (15).

It remains to offer some interpretation of the computed best-fit constants for the ES5B equation, and in particular to discuss the clearly exposed greater degree of dehydrogenation of the intermediate leading to isomerization. It appears that the intermediate for hydrogenolysis has to lose two H atoms (Table 5); similar values were found with EUROPT-3 between 547 and 625 K (16), tending to somewhat higher values at the bottom end of this range. At a much lower temperature (433 K), Ru/Al_2O_3 catalysts give values of $(m - x)$ in the region of 7(8). The critical intermediate for isomerization needs to have lost three or four H atoms (Table 5), and the additional difficulty that this causes is reflected in the lower value of K_A and in the higher value of the apparent activation energy (Tables 2 and 3). If our methodology is correct, the two reaction paths cannot occur through the same intermediate (e.g., a metallacyclobutane) reacting in different ways. It has never been clear what extraneous factors might determine the mode of reaction of such a species; it now appears necessary to accommodate two quite different intermediates. Some possible processes are shown in Scheme 1.



SCHEME 1

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REFERENCES

1. Bond, G. C., and Lou, Hui, *J. Catal.* **137**, 462 (1992).
2. Bond, G. C., and Xu, Yide, *J. Chem. Soc. Faraday Trans.* **80**, 969 (1984).
3. Bond, G. C., and Paál, Z., *Appl. Catal. A: Gen.* **86**, 1 (1992).
4. Paál, Z., Groeneweg, H., and Paál-Lukács, J., *J. Chem. Soc. Faraday Trans.* **86**, 3159 (1990).
5. Paál, Z., and Zimmer, H., *J. Catal.* **41**, 648 (1993).
6. Paál, Z., and Zimmer, H., *J. Mol. Catal.* **51**, 261 (1989).
7. Bond, G. C., and Cunningham, R. H., *J. Catal.* **166**, 172 (1997).
8. Bond, G. C., and Slaa, J. C., *J. Mol. Catal. A: Chem.* **98**, 81 (1995).
9. Bond, G. C., and Slaa, J. C., *J. Chem. Technol. Biotechnol.* **65**, 15 (1996).
10. Bond, G. C., and Gelsthorpe, M. R., *J. Chem. Soc. Faraday Trans. I* **85**, 3767 (1989).
11. Bond, G. C., *Appl. Catal. A: Gen.* **149**, 3 (1997).
12. Kramer, R., and Zuegg, H., *J. Catal.* **85**, 530 (1984).
13. Kempling, J. C., and Anderson, R. B., *Ind. Eng. Chem. Process Des. Dev.* **11**, 146 (1962).
14. Twizell, E. H., "Numerical Methods with Applications in the Biomedical Sciences." Ellis Horwood, Chichester, 1988.
15. Fülöp, E., Gnutzmann, V., Paál, Z., and Vogel, W., *Appl. Catal.* **66**, 319 (1990).
16. Bond, G. C., and Cunningham, R. H., *J. Catal.* **163**, 327 (1996).
17. Bond, G. C., Hooper, A. D., Slaa, J. C., and Taylor, A. O., *J. Catal.* **163**, 319 (1996).
18. Bond, G. C., Calhoun, J., and Hooper, A. D., *J. Chem. Soc. Faraday Trans.* **92**, 5117 (1996).
19. Guzci, L., van Santen, R. A., and Sarma, K. V., *Catal. Rev.-Sci. Eng.* **38**, 249 (1996) and references therein.
20. Solymosi, F., *Catal. Today* **28**, 191 (1996).
21. Yang, Zifeng, Xue, Jinghen, Shen, Shikang, and Wang, Hongli, *Chin. J. Catal.* **17**, 249 (1996).
22. Sárkány, A., *Catal. Today* **5**, 173 (1989); *J. Chem. Soc. Faraday Trans. 1* **84**, 2267 (1988).
23. Bond, G. C., and Lou, Hui, *J. Catal.* **142**, 512 (1993).