

Catalytic and structural properties of ruthenium bimetallic catalysts: kinetics of hydrogenolysis of lower alkanes on variously pretreated Ru/Al₂O₃ catalysts

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Abstract

The H₂ pressure dependence of rates of hydrogenolysis of ethane, propane and n-butane on Ru/Al₂O₃ catalysts differing in dispersion and type of pretreatment has been measured at a number of temperatures, and the results interpreted in terms of a mechanism involving adsorbed partially dehydrogenated intermediates C_nH_x, and modelled by the derived rate expression. The rate-limiting step is taken as the reaction of C_nH_x with an adsorbed H atom. We thus obtain best-fit values of the rate constant k_1 , the H₂ adsorption equilibrium constant K_H , an equilibrium constant for the dehydrogenation of the alkane K_A , and of x , for each set of results. The shapes of the kinetic curves, and the constants that describe them, change markedly with dispersion, and with pretreatment: oxidation and low-temperature reduction (O/LTR), as well as causing some loss of dispersion, gives rise to other effects, ascribed to 'morphological' factors, not seen when catalysts are reduced at high temperature (753 K). What is most striking is that differences in activity seem to be determined much more by the constants K_A and K_H than by the rate constant k_1 , which when expressed per Ru surface atom varies at most three-fold. In particular K_H is much larger after the first high-temperature reduction (HTR1) than after O/LTR. The true activation energy derived from the temperature-dependence of k_1 is about the same for each alkane (≈ 60 kJ mol⁻¹), the enthalpy changes for H₂ chemisorption are small and for alkane dehydrogenation they lie between 50 and 130 kJ mol⁻¹.

The manner in which product selectivities vary with H₂ pressure also depends on dispersion and pretreatment, the dominant factor being the strength of H₂ chemisorption. Thus on a very highly dispersed catalyst for which K_H is large, intermediate product selectivities are high because the high concentration of H atoms facilitates desorption of adsorbed species, and for this reason also selectivities scarcely respond to changes in H₂ pressure. With the same catalyst after O/LTR, however, when K_H is much decreased, selectivities respond sensitively to H₂ pressure because the adsorption is weaker. It is then deduced that approximately two more H atoms are required to effect desorption of intermediates as a product alkane than to cause further C–C bond breaking.

Our results strongly suggest that structure-sensitivity in alkane hydrogenolysis is more the result of variations in chemisorption energetics, and their consequential effects on surface coverage, than of kinetic effects; this concept also accounts for dispersion-dependent differences in the temperature-dependence of product selectivities previously reported.

Keywords: Alkanes; Bimetallic catalysts; Hydrogenolysis; Kinetics; Pretreated catalysts; Ruthenium

1. Introduction

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In the preceding paper [1] we have given an account of the effects of high and low temperature reductions on the behaviour in alkane hydrogen-

olysis of various Ru/Al₂O₃ catalysts, the preparation and characterization of which had already been described [2]; this was done in terms of the rates and product selectivities they afforded in the reactions of propane and of n-butane with H₂, both under standard conditions (433 K) and as a function of temperature. A constant 10:1 alkane:H₂ ratio was used throughout. The principal conclusions were the following. (1) Following a first high-temperature reduction (HTR1), product selectivities at 433 K were quite different with the highly dispersed RuEC1 catalyst from those shown by the less well dispersed RuEC2 and RuEC3, and by RuEC1 after oxidation and low-temperature reduction (O/LTR) and after a second high-temperature reduction (HTR2). Specifically RuEC1 after HTR1 gave very high ethane selectivities S₂ which did not change quickly with temperature. (2) The O/LTR treatment applied to RuEC1 decreased its dispersion, but with all but one (RuNI1) of the catalysts examined there was, after HTR1 and O/LTR, a smooth variation of TOF with dispersion as measured by H₂ chemisorption, the TOF *increasing* as dispersion *decreased*. TOF values were in generally good agreement with those reported earlier [3]. (3) After HTR2, TOF's for a given dispersion were much lower, but product selectivities only little changed. (4) The O/LTR treatment even increased the rates shown by Ru powder; there are reports [4,5] of similar effects being observed with other metals.

The purpose of the next phase of our work was to obtain a deeper understanding of the origin of the effects summarized above. We had been struck by the marked effects obtained by varying H₂ pressure on hydrogenolysis rates obtained over Pt catalysts [6,7], and indeed had explored the consequences of changing reactant pressures on rates given by EUROPT-3 and -4 [8]. We therefore commenced a systematic study of the kinetics of hydrogenolysis of ethane, propane and n-butane on the Ru/Al₂O₃ coded RuEC1 [2] following each of the three pretreatments, and also on RuEC3 after HTR1 and O/LTR. We have subjected the rate measurements to kinetic analysis

by rate equations proposed in the literature, our search for plausible expressions based on the Langmuir–Hinshelwood formalism being greatly helped by the paper of Shang and Kenney [9] which appeared before our work started.

Our motivation for undertaking this programme was as follows. It seemed to us that to base discussions of correlations between catalytic behaviour and physical structure or chemical composition of the catalyst simply on *rates* measured under a single set of experimental conditions was to ignore the compound nature of the rate of a heterogeneously-catalysed process, namely, that it can through use of the Langmuir–Hinshelwood methodology be factorized into a *rate constant* and a term containing the *adsorption coefficients* of the reactants. By determining the kinetics (by which we mean chiefly the manner in which the rate responds to H₂ pressure variation) at a series of different temperatures, it is in theory possible to derive a *true activation energy* and the *enthalpies of adsorption* of the reactants if a simple Langmuir–Hinshelwood mechanism were obeyed. Such is not the case with alkane hydrogenolysis, which makes the task of kinetics analysis somewhat harder, but we believe our procedure, notwithstanding its limitations, allows a better appreciation of the underlying causes of particle size and surface morphology effects. To the best of our knowledge, this is the first real attempt that has been made to analyse size effects, or indeed any other means of modifying the essential catalytic properties of an element, with a view to seeing whether their origin lies in the kinetic or the thermodynamic parameters of the system. We have also measured the variation of product selectivities with H₂ pressure at various temperatures, as this gives important insights into how pretreatment affects the state of the catalyst surface, and useful correlations with the temperature effects already reported [1] are established. As before, we have interpreted changes in selectivities in terms of the Kempling–Anderson reaction scheme [10] which treats the mechanism as a 'rake' by which formation of all products is linked, rather than as independent reactions. The values of the

parameters obtained in this way also provide extremely clear and useful information about the reaction mechanism.

Preliminary accounts of certain limited aspects of this programme, which was supported by the European Union under Contracts SC1*-CT91-0681, have already been published [11–13].

2. Experimental

The preparation and physical characterization of the catalysts used have already been described [2], as have the standard pretreatments and the general *modus operandi* [1]. The following is a brief résumé. Reactions were conducted in an atmospheric-pressure flow system under micro-processor control. For studying the dependence of rates and selectivities on partial pressure of reactants, we have employed a reaction pulse method [8,11] by which for 1 min only the desired reaction mixture (H₂, alkane and N₂) was passed through the catalyst bed, at the end of which time a sample was extracted for analysis. Between reaction periods the alkane flow was stopped, and the catalyst was cleansed by passing a high concentration of H₂ in N₂ for 15 min. The H₂ and N₂ flows were then adjusted to those needed for the next reaction period, which was initiated 4 min later by switching the alkane flow into this mixture. Highly consistent results could be obtained by this technique, although it did not always succeed in maintaining a constant level of activity, but only with samples reduced at high temperature did some correction for deactivation, as described below, prove necessary. H₂ pressures were varied randomly, and checks at standard H₂:alkane ratios (either 10:1 or 2.24:1) were carried out before and after measurements at the lower H₂ pressures, where deactivation is most marked. When the H₂ pressure was varied (0.021–0.81 atm), the alkane pressure was fixed at 0.071 atm, and when the n-butane pressure was varied (0.032–0.27 atm) the H₂ pressure was kept at 0.64 atm. Rates are expressed as mol alkane reacted per g catalyst per h.

In the Kempling–Anderson treatment [10] the hydrogenolysis of n-butane is regarded as taking place through a chain of adsorbed intermediates C_j^{*} containing *j* carbon atoms (*j* = 1–4) together with a short-circuit from C₄^{*} to C₂^{*} to allow for fission of the central C–C bond. Selectivity to product C_j (*j* ≠ 4) is S_j, defined as

$$S_j = 4c_j / (c_1 + 2c_2 + 3c_3)$$

where *c_j* defines the mol fraction of the species C_j in the products. A splitting factor *F* specifies the fraction of n-butane converted directly to ethane, and the proportion of the species C_j^{*} (*j* ≠ 1) which desorbs (rather than reacting further to C_{j-1}^{*}) is given by

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

where *k_j* is the rate constant for the relevant step. Modification of this scheme to deal with variable H₂ pressure will be described below. Steady-state analysis of the reaction network provides equations which at low conversion have the form

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

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

Evidently there are more unknowns than knowns, so we assume the value of *T₂* to be that of *S₂* in the reaction of propane under the same conditions. To this latter reaction the same basic procedure is applied, but the ethane selectivity *S₂* is then the only independent variable: to avoid confusion we shall denote this *S₂* as *T₂*.

3. Results

3.1. Extents of deactivation and general remarks

As noted above, in the case of n-butane hydrogenolysis some loss of activity was often observed during determinations of the effect of H₂ pressure variation (which we will call for brevity's sake the H₂ order). Some illustrative examples are shown in Fig. 1. Not surprisingly, the extent of

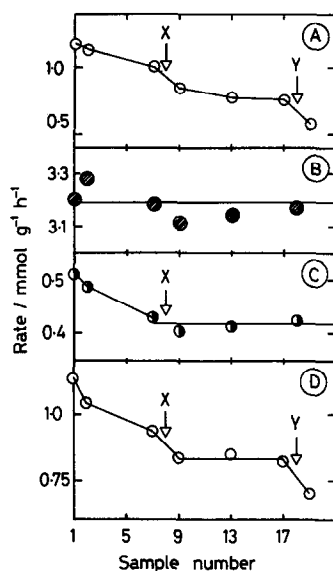


Fig. 1. Deactivation of catalysts during determination of H_2 orders for n-butane hydrogenolysis: rates obtained with standard H_2 pressures at various points. A: RuEC1, HTR1 at 397 K (BH34); B: RuEC1, O/LTR at 397 K (BH38); C: RuEC1, HTR2 at 402 K (BH39); D: RuEC3, HTR1 at 397 K (BH16); (X) sample 8, $P_{H_2}=0.040$ atm; (Y) sample 18, $P_{H_2}=0.021$ atm.

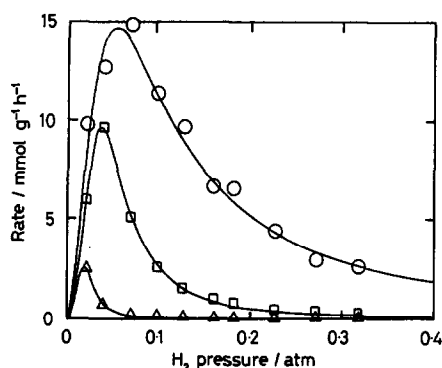


Fig. 2. Orders of reaction in H_2 for hydrogenolysis of n-butane (circles: BH35), propane (squares: PH26) and ethane (triangles: EH1a) over RuEC1 after HTR1 at 418 K.

deactivation was most marked following the use of very low H_2 pressures: the lowest value used was only 0.021 atm, corresponding to a H_2 :n-butane ratio of 0.29. This pressure was only used in the penultimate measurement, and then not always: its effect is seen in Fig. 1. Extents of deactivation found in the n-butane reaction were in a relative sense not greatly affected by temperature, but what was very noticeable was the constancy of rates found after the O/LTR treatment at all temperatures (less than $\pm 5\%$; see Fig. 1 for

an example). Reasonably constant rates were also obtained with RuEC1 after HTR2. Catalysts RuEC1 and RuEC3 lost activity to about the same extent after HTR1 (see Fig. 1), so it appears that particle size is less important than the type of pretreatment in determining catalyst stability. Similar conclusions may be drawn from the measurements made with propane and with ethane, although extent of deactivation decreased with number of carbon atoms in the reactant, so that only a few standard measurements were needed with the smaller alkanes.

Where necessary, measured rates were corrected for deactivation by assuming that the intrinsic activity (i.e. that found using the standard reactant ratio) determined the true rate for the samples taken since the *previous* standard measurement; that is to say, deactivation caused by using a low H_2 pressure was reflected in that of the *following* standard sample. This procedure, while clearly not exact, generally led to 'corrected' rates that showed minimal scatter (see for example Fig. 2). Rates were normalised to the value observed in the centre of the series (sample number 7 in the case of n-butane, see Fig. 1). It was not usually necessary to make corrections for experiments using O/LTR-pretreated catalysts.

A limited number of experiments were performed to determine orders in n-butane using RuEC1 after each pretreatment: consistent results were found after O/LTR (Fig. 3), but somewhat scattered results were found after the high-temperature treatments.

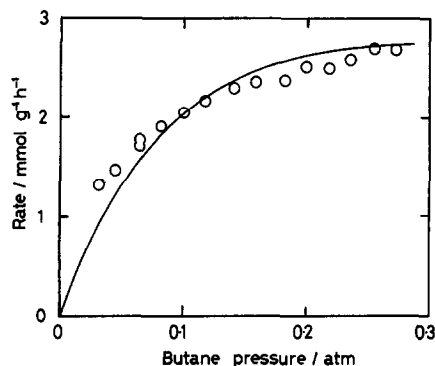


Fig. 3. Order of reaction in n-butane for hydrogenolysis on RuEC1 at 393 K after O/LTR: curve calculated using constants obtained by H_2 variation under the same conditions (BH4).

Table 1
Hydrogenolysis of ethane and of propane on RuEC1: best-fit values for the constants of equation ES5B

Pretreatment	Alkane	Code	Fig.	Temp. (K)	k_1	K_A	K_H	a	t_2
HTR1	C ₂ H ₆	EH1a	2	418	28.9	*	*	*	–
HTR1	C ₂ H ₆	EH1b	–	439	177	*	*	*	–
HTR1	C ₃ H ₈	PH2a	5	398	35.5	5.4	26.1	2.19	*
HTR1	C ₃ H ₈	PH2b	2	418	80.0	17.1	24.8	2.34	*
O/LTR	C ₂ H ₆	EH1c	–	397	29.2	2.1	19.1	1.94	–
O/LTR	C ₂ H ₆	EH1d	–	418	71.1	13.5	15.9	1.76	–
O/LTR	C ₃ H ₈	PH2c	5	398	37.8	14.2	7.0	1.36	1.67
O/LTR	C ₃ H ₈	PH2d	–	408	66.6	33.2	9.1	1.20	1.71
HTR2	C ₂ H ₆	EH1e	–	418	13.0	0.40	8.0	1.91	–
HTR2	C ₂ H ₆	EH1f	–	439	26.2	2.1	9.7	1.47	–
HTR2	C ₃ H ₈	PH1e	5	398	7.6	1.8	4.1	1.40	2.18
HTR2	C ₃ H ₈	PH1f	–	408	9.6	3.2	4.3	1.38	2.38

* Values considered unreliable.

Table 2
Hydrogenolysis of n-butane in RuEC1: best-fit values of constants of equation ES5B

Series	Pretreatment	Code	Fig.	Temp. (K)	k_1	K_A	K_H	a	t_3
I	HTR1	BH3	–	394	9.8	3.3	4.8	2.66	–
	HTR1	BH2	–	413	57.4	16.5	9.0	2.04	–
	HTR1	BH1	–	433	163	39.8	15.0	1.33	–
	O/LTR	BH4	–	393	31.3	12.4	3.1	1.42	–
	HTR2	BH5	–	393	4.2	1.5	1.7	1.93	–
II	HTR1	BH25	–	398	48.8	8.1	21.4	1.55	*
	HTR1	BH26	–	417	116	38.6	34.1	1.34	*
	O/LTR	BH27	–	398	39.5	16.0	3.4	1.25	1.06
	O/LTR	BH28	–	408	62.4	24.5	3.4	1.24	1.15
	HTR2	BH29	–	398	7.3	3.3	2.4	1.16	1.48
	HTR2	BH30	–	408	8.4	4.3	2.0	1.26	1.93
III	HTR1	BH31	4	383	27.9	4.5	21.0	1.59	–
	HTR1	BH34	–	397	47.2	11.5	26.6	1.48	*
	HTR1	BH32	4	407	78.0	23.5	28.2	1.40	–
	HTR1	BH35	–	418	111	36.7	26.9	1.38	*
	HTR1	BH33	4	428	154	47.3	23.2	1.34	–
	O/LTR	BH36	–	383	16.3	7.1	3.2	1.21	–
	O/LTR	BH38	–	397	31.1	13.0	3.2	1.28	1.02
	O/LTR	BH37	–	413	73.0	32.9	3.2	1.10	–
	HTR2	BH39	–	402	5.5	2.3	1.9	1.32	1.18
	HTR2	BH40	–	414	7.8	3.7	1.8	1.32	–
	HTR2	BH41	–	426	12.1	6.0	1.7	1.10	–

* Values considered unreliable.

3.2. Overview of experimental results

Tables 1–3 list the order determinations carried out, and provide codes for each set of results for use in cross-referencing. Three series of measure-

ments (I–III) were carried out with RuEC1: in the first series, the general form of the results was established, and in the second, the direction of the temperature effect after each pretreatment was determined. Experience taught however that with a given sample at least three temperatures had to be used to give reliable and quantitative estimates of the effect of temperature on the constants of the chosen rate expression: for this reason series III was undertaken. Only two temperatures were used after each pretreatment in the cases of propane and ethane; orders in n-butane were investigated with RuEC1 only at 393 K. Catalyst RuEC3 was fully studied using the n-butane reaction after HTR1 and O/LTR procedures, and briefly using propane

Table 3
Hydrogenolysis of n-butane on RuEC3: best-fit values for constants of equation ES5B

Pretreatment	Code	Temp. (K)	k_1	K_A	K_H	a	t_3
HTR1	BH17	373	22.7	4.6	11.9	1.30	1.17
HTR1	BH18	379	37.2	9.9	16.2	1.19	–
HTR1	BH19	388	52.6	16.4	19.3	1.06	–
HTR1	BH16	397	106	33.5	23.0	1.14	1.12
HTR1	BH20	405	105	39.2	21.7	1.04	–
O/LTR	BH21	378	29.5	11.6	5.9	1.27	–
O/LTR	BH22	386	45.8	18.0	6.5	1.29	–
O/LTR	BH23	393	65.4	25.5	6.3	1.27	–
O/LTR	BH24	400	90.7	34.5	6.2	1.27	1.22

* Values considered unreliable.

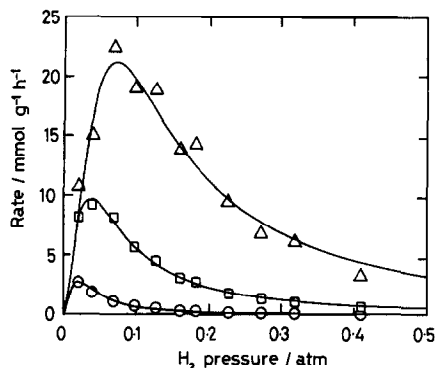


Fig. 4. Orders of reaction in H_2 for n-butane hydrogenolysis over RuEC1 after HTR1 at various temperatures: 383 K (circles: BH31), 407 K (squares: BH32), 428 K (triangles: BH33).

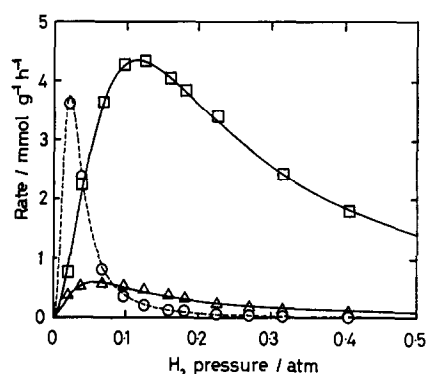


Fig. 5. Orders of reaction in H_2 for propane hydrogenolysis over RuEC1 at 393 K after various pretreatments: HTR1 (circles: PH2a), O/LTR (squares: PH2c), HTR2 (triangles: PH2e).

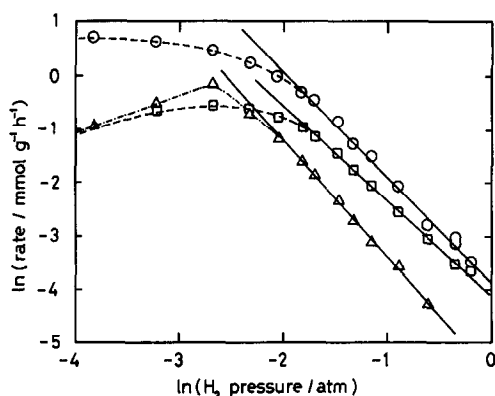


Fig. 6. Logarithmic plots of rates as a function of H_2 pressure: circles, n-butane, HTR1, 373 K; squares, propane, HTR2, 398 K; triangles, ethane, O/LTR, 397 K.

only after HTR1. The same propane results had to be used to derive true values of F and T_3 from all the n-butane series, where the same or very similar temperatures were employed. As with most research, if we had been able to start again, know-

ing what we knew at the end, we should have been able to avoid some of our mistakes; however, it should be appreciated that the work summarised in Tables 1–3 represents a very considerable investment in time and effort.

Considerations of space determine that we cannot exhibit all our results in the form of rate vs. reactant pressure plots. In Figs. 2 to 5, we show examples to illustrate some of the principal trends produced by the variable factors employed: they demonstrate (i) a comparison of the H_2 orders for the three alkanes at 418 K, using RuEC1 after HTR1 as catalyst (Fig. 2), (ii) the order in n-butane at 393 K using RuEC1 after O/LTR (Fig. 3), (iii) the effect of temperature on the H_2 order for the n-butane reaction, using RuEC1 after HTR1 (Fig. 4), and (iv) the effect of the three pretreatments on the H_2 order for the propane reaction at 398 K, using RuEC1 (Fig. 5). The sets of results used in constructing these figures are specified by the codes. In every case, the curves shown are calculated from a theoretical rate expression, the use of which will be described shortly. These figures illustrate, in a way which values of standard deviations cannot, the degree of success achieved by our mathematical modelling; they also reveal whether limited success, where it occurs, is due to experimental scatter or to systematic deviation of the points from the calculated curve in a certain range of the controlled variable (see for example Fig. 3). The other sets of results of necessity have to be represented by tabulated values of the constants of the chosen kinetic expressions that best describe them. We are willing to supply to interested persons any of the detailed experimental results that are not shown.

Some qualitative observations on the trends produced by the variables is in the order, to set the scene for the more quantitative treatment that follows. With RuEC1 after HTR1, on going from ethane to propane to n-butane the rate increases of all H_2 pressures (in contrast to the behaviour of Pt/ Al_2O_3 at higher temperature [13]) and the maximum moves to higher H_2 pressure (Fig. 2). The same happens when the temperature used for n-butane hydrogenolysis is increased (Fig. 4). By

far the most marked and dramatic changes are however produced when the pretreatment applied to RuEC1 is changed (Fig. 5; see also [11–13]). With propane as reactant, O/LTR greatly alters the form of the H_2 order curve, in the sense of broadening the sharp peak found after HTR1: in consequence, rates following O/LTR are much the faster, *but only at H_2 pressures exceeding about 0.04 atm.* Similar changes are observed with ethane and with n-butane [11]. The HTR2 treatment leads to a substantial decrease in rate, as reported before [1] and the maximum rate shifts to lower pressure: the general shape of the curve is intermediate between those found after HTR1 and after O/LTR.

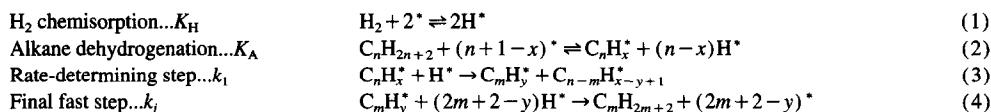
3.3. Mathematical modelling

The purpose of the exercise is to identify a plausible rate expression and then to evaluate the ‘best fit’ constants of that expression of all sets of results, with the object of using them to obtain a better understanding of the mechanism of catalytic action. Unfortunately with the present system this is no easy or straightforward task. It is desirable at the outset to agree on certain ground rules defining the criteria by which a rate expression may be judged ‘plausible’. We suggest the following. (1) It must be derivable from a plausible mechanism, i.e. one that makes chemical sense and which allows the participation of all reasonable and relevant surface processes. (2) The constants obtained must have the expected signs, and their values must be sensible; moreover derived quantities such as true activation energies and adsorption enthalpies must pass the same test. (3) The expression must not be overly complex or contain too many disposable constants, otherwise one cannot fail to obtain gratifying fits with the experimental points.

Several helpful reviews are available that survey kinetics and mechanisms of alkane hydrogenolysis [9,14], although the emphasis is generally placed on the reaction of ethane. It is unnecessary to rehearse at length the results, arguments and conclusions that have been presented, especially

since the paper by Shang and Kenney [9] is quite recent: a brief summary will suffice. There is a general consensus that the reactant alkane, after dissociative chemisorption, has to lose further H atoms before it becomes reactive in hydrogenolysis; this being accepted, one function of the analysis is to determine what this number is. One supposes that the formation of one or more multiple carbon–metal bonds adjacent to the bond to be broken is necessary in order to strain or activate it sufficiently, although this point is rarely discussed, and never quantitatively. An alternative hypothesis [15] supposes that the rate-limiting step is the initial reaction of gaseous alkane with a chemisorbed H atom, but although the consequential rate expression has been developed it does not appear to have found much favour, and we shall continue for the moment to employ an equation based on classical dehydrogenated intermediates.

Mechanisms based on such intermediates however permit a number of variations: these derive from considerations such as whether adsorption equilibrium is set up with the alkane or not, whether H_2 adsorption is competitive with the alkane or not, what form of hydrogen (atomic or molecular) is involved, whether vacant surface ‘sites’ are needed, and how many ‘sites’ are required to bond the dehydrogenated intermediate. The way in which the answers to these questions are built into the assumed mechanism then determines the form of the kinetic expression. The simplest form is of course the power rate law, which in spite of its obvious limitation of not showing a maximum as the H_2 pressure is varied still continues to be used in theoretical analyses [16]. One of the most astonishing features that we have observed in modelling alkane hydrogenolysis is close similarity between curves calculated from seemingly quite different rate expressions: this is seen in the work of Shang and Kenney [9] and is confirmed by our own experience [8]. This even extends to the power rate law, where in the region of H_2 inhibition extremely good log–log plots are obtained (Fig. 6). This means that, with the occasional exception [9], it



Scheme 1. Generalised kinetic scheme for alkane hydrogenolysis. Note: in the tables and text, the extent of dehydrogenation is defined by a , the number of molecules of H₂ evolved in step 2, so that $a = (n-x)/2$.

is impossible to eliminate a rate expression on the grounds that it does not and cannot fit the results over an extended range. Discrimination between alternatives then has to be performed with the aid of the ancillary criteria listed above.

It is also pertinent to note that although the same constants may appear in differently formulated rate expressions, their best-fit values may vary enormously: thus in Table 3 of Shang and Kenney's paper [9] the variability of K_E , the adsorption equilibrium constant for ethane, over four equations is a factor of 2×10^{10} , while even between the two quite closely similar equations, ES4 and ES5, it varies by 2×10^6 for K_E and 7×10^4 for K_H , the H₂ adsorption equilibrium constant. This great variability should however assist in the process of discrimination between alternatives.

One of the proposed criteria for acceptability was the number of disposable constants in the rate expression. We should however exclude k_1 , the rate-constant for the slow step, as this only acts as a linear scaling factor. On this basis quite the most satisfactory expression is that coded as ES2 [9], namely,

$$r = k_1 K_A P_A P_H / (K_A P_A + P_H^a) \quad (\text{ES2})$$

in which only K_A (the adsorption equilibrium constant for alkane) and a (the number of H₂ molecules lost by the alkane) are disposable. This

equation can provide good fits to experimental results [8,9]: however it fails the test of acceptability by not embracing the possibility of dissociative H₂ adsorption (there is no K_H in the equation). Having carefully considered all options, we have decided to use the equation ES5B of Shang and Kenney [9]; this had been earlier devised and used by Kristyan and Szamosi [17], and is based on the classical dehydrogenated intermediate. The formulation of the mechanism on which it is based is shown in Scheme 1, and the equation takes the form

$$r = \frac{k_1 K_A P_A (K_H P_H)^{(n-x)/2}}{[K_A P_A + (K_H P_H)^{(n-x)/2} + (K_H P_H)^{(n+1-x)/2}]^2} \quad (\text{ES5B})$$

where x is the number of H atoms remaining on the hydrocarbon species and n the number in the reactant. There are thus three disposable constants. Our results have been analysed by use of this equation, and little purpose would be served by tedious recitation of the values of constants which alternative equations produce.

It is worth being quite clear about the basic (often unspoken) assumptions underlying this and analogous rate equations. (i) It is implied that there is one and only one reactive intermediate, that is, a single value of x (or a) applies at all H₂ pressures, although of course positional isomers

Reactivity:	Zero	Small	Large	Small	Zero
Number of H atoms:	$2n+2$	$2n+1$	$2n$	$2n-1$	$2n-3$
C ₂ species	C ₂ H ₆	CH ₃ CH ₂	CH ₂ CH ₂	CHCH ₂	CHCH
C ₃ species	C ₃ H ₈	CH ₃ CH ₂ CH ₂	CH ₃ CHCH ₂	CH ₂ CHCH ₂	CHCHCH ₂
C ₄ species	n-C ₄ H ₁₀	CH ₃ CH ₂ CH ₂ CH ₂	CH ₃ CHCH ₂ CH ₂	CH ₃ CHCHCH ₂	CH ₃ CHCCH ₂
					CH ₃ CCCH ₂

Scheme 2. Reactivity in hydrogenolysis of adsorbed dehydrogenated alkanes. The position of the H atoms and of the C-metal and C=C bonds shown are purely arbitrary.

are allowed. This assumption is sometimes omitted, and different species are taken as the reactive intermediate in different zones of H_2 pressure [18], although why in this case C_2H_5 and C_2H_3 were chosen and C_2H_4 ignored is by no means clear. The assumption if valid would mean that the analysis should yield only integral values of x ($0 < x < 2n + 2$); presently we will have to cope with the significance of non-integral values. (ii) It is assumed that the same area of active surface is available under all conditions. This assumption is almost certainly invalid, except possibly for O/LTR treated catalysts, and for the others it becomes less valid as the size of the alkane is increased. The situation that one might envisage is outlined in Scheme 2.

If we suppose for the sake of argument that the *only* reactive species are C_nH_{2n-1} , then their surface concentrations are more or less adequately defined by the equilibrium shown in Scheme 1. What is not however specified is how much of the adsorbed alkane is in the form of more highly dehydrogenated species, which are assumed to be unreactive. Quantitative provision for these extra equilibria would necessitate introduction of more constants into the equation, with ensuing loss of significance. To say the simpler, the better, is good advice, but it is unrealistic when the system is inherently complex: this is the essential dilemma of mathematical modelling. Qualitatively it is clear that the more carbon atoms in the alkane, the greater are the possibilities for forming single or multiple carbon–metal bonds, and hence the more firmly anchored the species can become (Scheme 2). Clearly also there are circumstances in which it is virtually impossible to avoid forming over-dehydrogenated species, even during the short reaction period, if deactivation is due to their occurrence.

3.4. Results of mathematical modelling

Recognising the limitations of the procedure we have adopted, we nevertheless proceed to record in Tables 1 to 3 the best-fit values of the constants of the rate expression ES5B: we do not quote

standard deviations, as their values depend on the range of rates that the measurements cover, but they can be provided on request. Optimisation was performed using the Levenberg–Marquardt algorithm [19]; a more detailed account of how this was done will be submitted for publication separately. Briefly for each set of results the value of x was altered until the standard deviation was minimised; the values of all constants were then noted. One of the lessons learned at an early stage was the usefulness of having results to the left of the maximum, in addition to those on the right, where the majority lay. With some systems (e.g. C_2H_6 /RuEC1-HTR1; C_3H_8 /RuEC3-HTR1; $n-C_4H_{10}$ /RuEC1-HTR1 series I) the H_2 pressure for the maximum rate was either inaccessibly low or inadvertently not attained: constants from these sets are therefore less reliable than others, and they are either not quoted or are italicised in the Tables. They are expressed to not more than three significant figures. The most elastic of the disposable constants is undoubtedly x , the minimum in plots of standard deviation vs. x being quite shallow: changing x by ± 0.1 makes little difference to the quality of the fit. To aid further discussion, the temperature-dependence of the constants is illustrated in Figs. 7 to 9.

We may now attempt to draw some conclusions concerning the interpretation of the apparent differences in activity [1] and in the shapes of the H_2 order curves in terms of the constants of this rate expression. We begin first with the effects of pretreatment (Fig. 5). The ensuing discussion will be (it is hoped) more comprehensible if it is understood that the pretreatments following the first have two distinct effects: one, namely O/LTR, produces a change in surface morphology (for want of a better term) which in the case of RuEC1 is also accompanied by a decrease in dispersion, while the other (HTR2) changes the morphology without affecting the dispersion. These changes are shown schematically in Scheme 3.

(1) *The changes produced by the O/LTR treatment in the reaction of both propane (Fig. 5) and n-butane [11,13] are due primarily to a decrease in K_H : this is particularly*

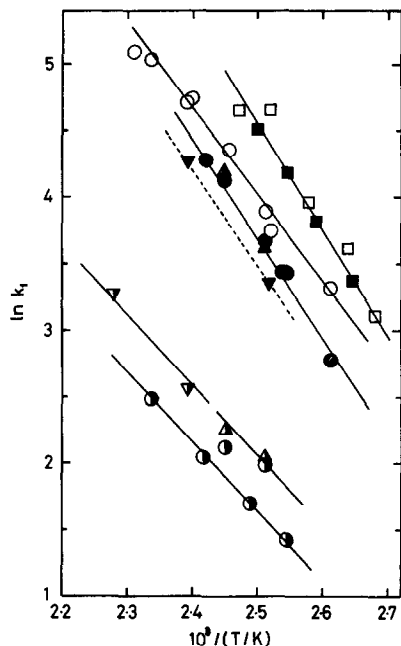


Fig. 7. Arrhenius plots of k_1 , from which true activation energies are calculated. Open points, HTR1; hatched points, O/LTR; half-filled points, HTR2. For HTR1; O, series I; \circ —, series II; \circ —, series III. Circles, n-butane; triangles, propane; inverted triangles, ethane. Squares, RuEC3; RuEC1 for all other points.

marked with n-butane on RuEC1, series II and III (Table 2 and Fig. 9), but is also seen with RuEC3 (Table 3 and Fig. 9). With RuEC1, *neither* k_1 *nor* K_A *is much altered* (Figs. 7 and 8) and with RuEC3 they are indistinguishable; nor do any significant changes occur in the values of a .

- (2) The HTR2 treatment produces a further decrease in K_H in every case (Tables 1–3, Fig. 9), the change being somewhat less marked in ethane and propane (Table 1), and very substantial decreases in k_1 (Fig. 7) and K_A (Fig. 8). Once again a is almost unaffected.
- (3) The same trends are observed with each alkane, so far as we can determine.

We now draw attention to those respects in which the behaviours of the three alkanes differ.

- (1) After HTR1, both k_1 and K_A are smaller for propane than for n-butane and this trend probably continues to ethane, but the results are not sufficiently reliable to be sure.

- (2) After O/LTR, values of k_1 for all three alkanes are similar (Fig. 7), those for ethane

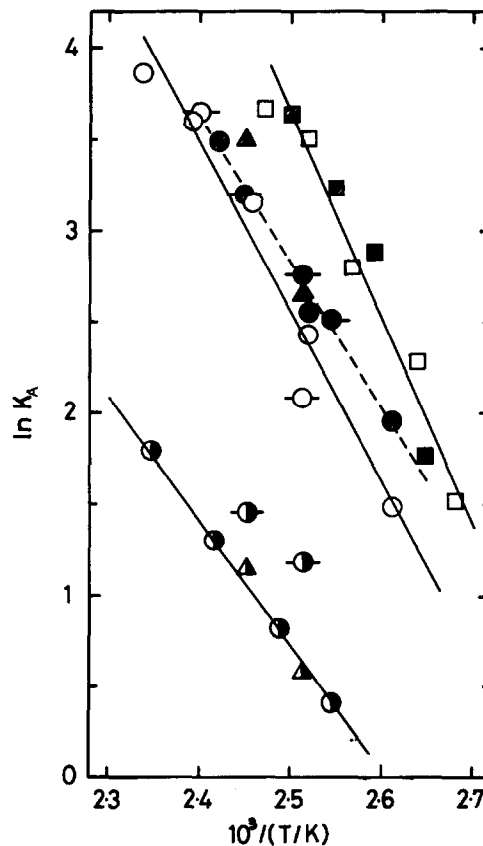


Fig. 8. Van't Hoff isochore plots for K_A (symbols as for Fig. 6). Reliable values for ethane are too few to justify showing.

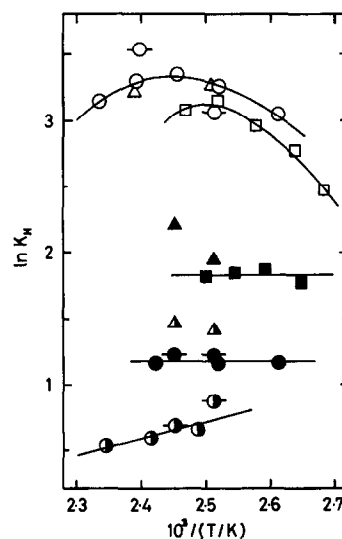


Fig. 9. Van't Hoff isochore plots for K_H (symbols as for Fig. 6). Reliable values for ethane are too few to justify showing.

being perhaps slightly smaller, while somewhat surprisingly those of K_A are about the same for propane and butane.

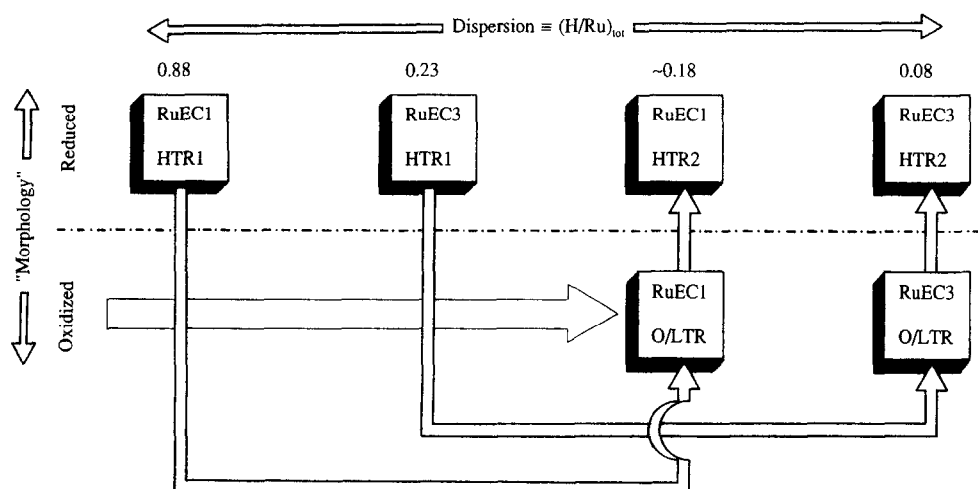
- (3) After HTR2, values of k_1 are greater for ethane and propane than for butane, but the differences are small and not highly significant; K_A is about the same for propane and butane.
- (4) One of the tests for the validity of the methodology employed is the independence of the value of K_H on the alkane used, since we are assuming the same general reaction scheme for all the alkanes, and the H_2 adsorption equilibrium should be the same in all cases. This expectation is only partially fulfilled: after HTR1 the values of K_H for propane and butane are very similar (Fig. 9), but after the other treatments the values for ethane and propane are somewhat higher than those for butane. (Compare Tables 1 and 2).

Comparison of the results in Tables 2 and 3, and in Figs. 7 to 9, show differences between the constants applicable to the two catalysts RuEC1 and RuEC3 after HTR1 and O/LTR. The values of k_1 shown in the tables and figures are those derived from rates expressed in $\text{mmol g}_{\text{cat}}^{-1} \text{h}^{-1}$, and for their better comparison they should be converted into *specific* rate constants k_{sp} ($\text{g}_{\text{Ru}}^{-1}$) and then into *atomic* rate constants k_{at} (n_s^{-1} where

Table 4
Specific and atomic rate constants for n-butane hydrogenolysis at 385 K

Catalyst	Pretreatment	k_{sp} (s^{-1})	k_{at} (s^{-1})
RuEC1	HTR1	0.83	0.095
RuEC1	O/LTR	0.54	0.29
RuEC1	HTR2	0.078	0.098
RuEC3	HTR1	0.34	0.14
RuEC3	O/LTR	0.27	0.27

n_s represents the total number of H atoms chemisorbed per g of Ru). This latter quantity might alternatively be called the *areal* rate constant or the *turnover* rate constant, but neither term exactly conveys its significance. Rather than converting all results in this way we take interpolated values of k_1 for n-butane at 385 K, and obtain the results shown in Table 4. They are quite remarkable. (i) The values of k_{sp} (excepting that for RuEC1 after HTR2) vary by less than a factor of three. (ii) Those for k_{at} are very similar for both catalysts after HTR1 and HTR2, and are about three times larger after O/LTR. Thus, in contrast to all that has been written in the past concerning particle size effects on catalytic activity, it appears that *the rate constant per surface atom is NOT significantly size-dependent*, while the effect we attribute to ‘morphology’ is the more important. The extent to which either rate constant varies is *very* much less than that of rates or turnover frequencies



Scheme 3. Representation of changes in dispersion and morphology for RuEC1 and 3 as a function of type of pretreatment.

Table 5
True activation energies and enthalpy terms for alkanes and H₂

Catalyst	Alkane	Pretreatment	E_t	ΔH_A	ΔH_A
RuEC1	C ₂ H ₆	O/LTR	61.5	127	12.4
	C ₂ H ₆	HTR2	50.9	121	14.3
	C ₃ H ₈	HTR1	55.8	79.3	-3.6
	C ₃ H ₈	O/LTR	*	*	*
	C ₃ H ₈	HTR2	31.5	76.7	7.1
	n-C ₄ H ₁₀	HTR1	54.8 ± 2.1	79.4 ± 7.9	±
	n-C ₄ H ₁₀	O/LTR	65.8 ± 4.9	66.5 ± 7.9	≈ 0
	n-C ₄ H ₁₀	HTR2	39.4 ± 9.7	51.8 ± 14.1	-6.5 ± 7.1
	RuEC3	n-C ₄ H ₁₀	HTR1	63.3 ± 8.7	84.3 ± 9.6
	n-C ₄ H ₁₀	O/LTR	62.6 ± 0.9	60.9 ± 0.9	≈ 0

E_t and enthalpy terms in kJ mol⁻¹.

* Values considered unreliable.

± Plot of ln K_H vs. 1/ T shows maximum (Fig. 8).

measured at an H₂:n-butane ratio of 10:1 [1]. Values of k_{sp} and k_{at} for the three alkanes at any selected temperature will be proportional to their k_1 values, since we have to assume that the same Ru contents and (H/Ru)_{tot} ratios apply in each case.

K_A values are similar for RuEC3 after HTR1 and O/LTR, and greater than for RuEC1 (Fig. 8); K_H values are about the same for the two catalysts after HTR1, but greater for RuEC3 after O/LTR (Fig. 9).

By the application of the Arrhenius equation to k_1 and of the Van't Hoff isochore to K_A and K_H we should be able to estimate respectively the true activation energy E_t and the enthalpy changes associated with the equilibria 1 and 2 in Scheme 1. This has been attempted, with the results shown in Table 5 and Figs. 7–9. Note that the values given in the table are derived from the results shown in the earlier tables, by the least squares method where possible, while the plots in Figs. 7–9 are for purposes of illustration only, so that the slopes of the lines may not correspond exactly to the values in the table. The following observations may be made.

(1) True activation energies E_t are considerably lower than apparent values E_{app} obtained previously [1,11] using 10:1 H₂:alkane ratios. The changing shapes of the H₂ order curves as the temperature is altered (Fig. 4)

makes it inevitable that even the apparent activation energy will be a function of H₂ pressure [13].

(2) E_t appears to be about the same for all three alkanes after HTR1 and after O/LTR (60 ± 5 kJ mol⁻¹), and possibly somewhat lower after HTR2. High precision cannot always be expected when results are obtained at only two closely similar temperatures.

(3) From the reaction scheme it appears that the rate will be maximum when the concentrations of H* and of C_nH_x* are equal: thus the maximum rates at different temperatures will correspond to equal but not necessarily constant values of their concentrations, and the activation energy derived from them may approximate to the true activation energy. From the results in Fig. 4, an activation energy based on maximum rates of about 62 kJ mol⁻¹ is obtained, close to the values in Table 5.

(4) Values of $-\Delta H_A$ are higher for ethane, but comparable for propane and n-butane, irrespective of catalyst or pretreatment. However they tend to decrease in the sequence HTR1 > O/LTR > HTR2 for n-butane. We note that since K_A increases with temperature, the process defining K_A (Scheme 1) must be endothermic, which is compatible with its not being a simple chemisorption: thus increasing temperature favours the dehydrogenation steps leading to the reactive species, and this serves to explain why apparent activation energies for hydrogenolysis are so comparatively large, and greater than true values.

(5) From Fig. 9 and Tables 1 to 3 it appears that temperature has relatively little effect on K_H , especially after O/LTR and HTR2 treatments, so the values of ΔH_H , though often small (Table 4), cannot be regarded as meaningful. We would expect ΔH_H to be negative if process 1 in Scheme 1 truly represents the way in which H₂ becomes involved, but the expected changes in K_H

would not necessarily be observed in the narrow temperature range used. Of greater significance is the difference between the high K_H values after HTR1, and the much lower values after O/LTR and HTR2: in the former case, the onset of desorption is apparent at the higher temperatures (Fig. 9). It is also reassuring that the magnitudes and temperature coefficients of K_A and of K_H are so different, in senses that correspond, at least in some degree, to physical expectations.

A further word on the values of a in Tables 1 to 3 is in order (a is the number of H_2 molecules released in forming the reactive species, i.e. $(n-x)/2$, see Scheme 1). They are a little greater for ethane and propane than for butane: with this last reactant, they are somewhat larger after HTR1 than the other treatments. There is a tendency for them to decrease with increasing temperature, especially after HTR1 (see Table 2), but the effects are generally small. It is disappointing that the values obtained do not correspond more closely to the loss of integral numbers of H atoms, but the lack of great variation suggests that the numbers found have a physical significance: moreover, as noted above, values of x or a are subject to some uncertainty.

We have paid little attention so far to the effects on the rate of varying the alkane pressure. In fact we have made only a few such measurements, as our previous experience [8] has shown that the results obtained are of little assistance. Orders in alkane are generally fractional and positive, and, although in principle it should be possible to analyse the results in terms of equation ES5B to provide values of all the constants, the form of the curve relating rate to alkane pressure does not provide sufficient constraints, as do the H_2 order curves, to enable accurate values to be obtained. We therefore show (Fig. 3) the calculated curve obtained by using the constants derived by H_2 pressure variation under equivalent conditions (set BH4). The agreement is satisfactory if not perfect, and serves to show there is no serious inconsistency between the interpretations of the two orders of reaction using this rate expression.

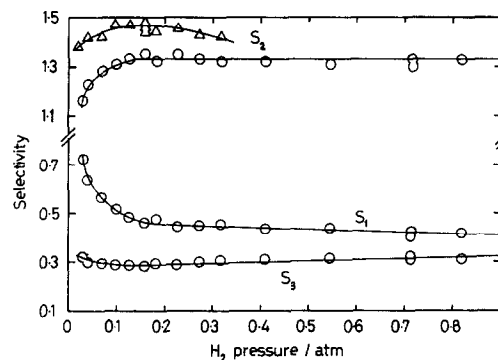


Fig. 10. n-Butane hydrogenolysis on RuEC1 after HTR1: dependence of product selectivities on H_2 pressure at 417 K (BH26) (circles) and at 383 K (BH31) (triangles).

3.5. Dependence of selectivity parameters on H_2 pressure

Thus far we have only been concerned with the dependence of rate of reactant removal on H_2 pressure; we have naturally recorded product selectivities at the same time, and consideration of how they vary with H_2 pressure at various temperatures adds new and important insights into reaction mechanisms and the state of the surface [11].

With RuEC1 following HTR1, the unusual selectivities found [1] at H_2 :n-butane ratios of 10:1 (high S_2 , low S_1 and S_3 ; $T_3 \approx 1$, $F \approx 0.7$) persist as the H_2 pressure is lowered, and at the lowest temperature used (383 K) they remain essentially unchanged down to 0.1 atm. Fig. 10 shows the selectivities obtained at 417 K, and values of S_2 at 383 K. We are only able to derive true values of F and T_3 at 397–398 K and 418 K; these indicate that the principal factor in determining the variation in selectivities (Fig. 10) is the pressure dependence of T_2 in the propane reaction, since at 417 K F is almost invariant over the whole pressure range, and T_3 (for which the points are somewhat scattered due to the form of the equations used to derive it) does not fall below 0.92 (Fig. 11). Its pressure dependence is at most slight. The effects of temperature in the range 383–428 K on the products of both reactions are also of a minor nature: S_2 decreases slightly with increasing temperature, and the H_2 pressure below which S_1 begins to rise also increases, from ≈ 0.1 to ≈ 0.2 atm. What is truly remarkable is the lack

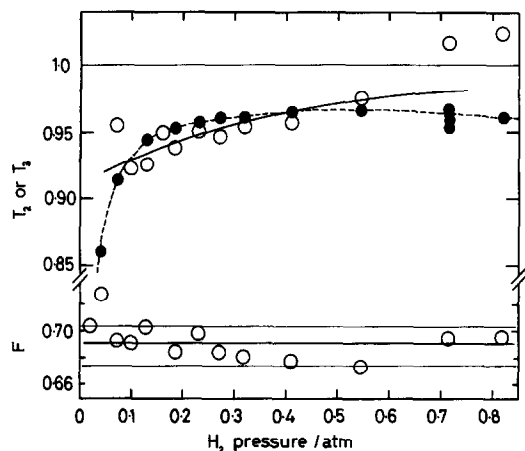


Fig. 11. Values of F and T_3 corresponding to the selectivities at 417 K shown in Fig. 9: the broken line indicates the values of T_2 from propane hydrogenolysis at the same temperature.

of any major alterations in the selectivity parameters while the rate undergoes very large changes with pressure (see Figs. 3–5); the ratio of the maximum rate to that at 0.71 atm H_2 is frequently ≈ 100 and can be as large as ≈ 500 . The obvious conclusion to draw is that *while the number of reactive centres* (that is, places capable of sustaining the transition state) *changes dramatically with H_2 pressure, the composition of these centres* (that is, the number of adsorbed H atoms and vacant sites participating, and the H:C ratio in the reactive species) *remains essentially constant*.

We must explore what circumstances might give rise to this behaviour. Reference to Scheme 1 shows that the rate of the slow step depends upon the concentrations of H atoms and of the reactive dehydrogenated intermediate $C_nH_x^*$: in the region of low H_2 pressure, the rate is a positive function of H_2 pressure because it is limited by the availability of H atoms, the concentration of which naturally rises with H_2 pressure. Above the maximum, which with RuEC1 following HTR1 is reached at a very low H_2 pressure (Fig. 2), the rate is limited by the availability of $C_nH_x^*$, the concentration of which depends on the number of vacant sites available to receive H atoms from the reactant alkane. We therefore propose that the concentration of H atoms remains high down to H_2 pressures of at most 0.05 atm, i.e. the surface

is almost fully saturated with them, and the rate is in effect controlled by a small concentration of vacant sites, which becomes even smaller as the H_2 pressure is raised. The number of vacant sites needed determines that the H_2 order above the maximum will be strongly negative. The constancy of T_3 and of T_2 above about 0.15 atm H_2 pressure implies that adequate numbers of H atoms are available to convert the fragments (e.g. C_3^*) into gaseous alkane, and that it is only when this is not so that the alternative option of bond-breaking becomes available, as this apparently needs fewer H atoms. For this reason S_1 rises and S_2 falls with both reactions (Figs. 10 and 11) as the H_2 pressure is decreased below about 0.15 atm.

Our belief that H_2 is strongly chemisorbed on the very small Ru particles contained in RuEC1 after HTR1 provides a ready explanation for the absence of rapid variation of selectivities with temperature, observed previously with this catalyst [1,11]: the adsorption of H_2 being strong, the coverage by H atoms does not decrease rapidly with increasing temperature.

Quite different results are obtained with RuEC1 following O/LTR and HTR2, and with RuEC3 after both HTR1 and O/LTR. Now, chiefly in consequence of changing to the use of much larger Ru particles, selectivities shown by n-butane change sensitively as the H_2 pressure is altered (Fig. 12), in the sense that S_1 increases, S_2 passes through a maximum and S_3 tends towards zero (or some other low limiting value) as the H_2 pressure

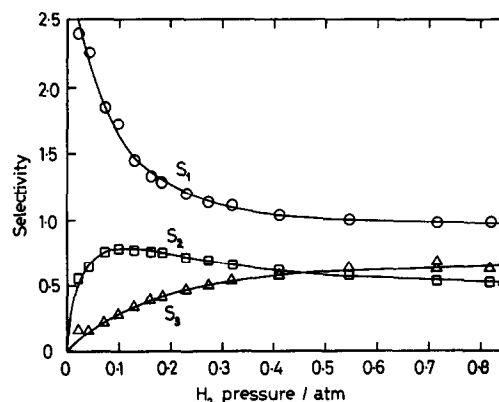


Fig. 12. Dependence of product selectivities in n-butane hydrogenolysis on H_2 pressure: RuEC1, O/LTR, 398 K (BH27).

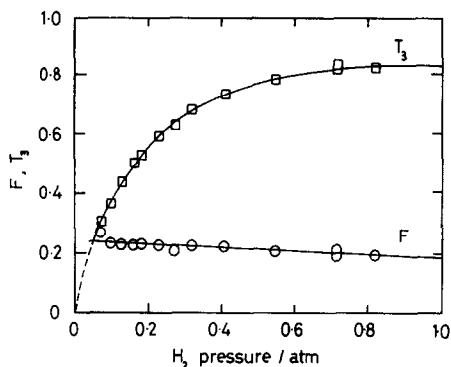


Fig. 13. Dependence of Kempling-Anderson parameters F and T_3 on H_2 pressure, corresponding to results in Fig. 12.

is decreased. In the case of RuEC1 after O/LTR, it is very clear that these changes are due entirely to T_3 and not at all to F , which remains almost unaltered (Fig. 13), but at a much lower value than before. In the other cases, F decreases slightly with increasing H_2 pressure, and escalates abruptly at very low H_2 pressures, but this may be an artifact caused by the limitations of using T_2 from the propane reaction in the calculation of F and T_3 . In all of these systems (RuEC1, O/LTR and HTR2; RuEC3, HTR1 and O/LTR) the variation in the selectivities can be traced wholly or substantially to T_3 : clearly the process leading to the formation of the intermediate products propane and ethane is favoured by higher H_2 pressures, which (since none of the steps in the proposed reaction scheme, except the first, involves molecular H_2) we must assume causes an increase in the concentration of adsorbed H atoms. On these catalysts therefore H_2 adsorption must be relatively weak, and full coverage by H atoms only achieved at H_2 pressures approaching 1 atm. For this reason the selectivities which they show change quite quickly with increasing temperature [1], in the sense that corresponds to decreasing H coverage. The fact that the equivalent changes only occur with RuEC1 after HTR1 at much lower H_2 pressures signifies how much stronger is H_2 chemisorption on this catalyst. The concept that temperature effects on product selectivities arise mainly through changes in H atoms coverages has been previously advanced by Paál [20].

Convincing independent evidence for the correctness of our interpretation of the different dependences of product selectivities on H_2 pressures following the various pretreatments comes from two sources. (1) The strength of H_2 chemisorption as measured by K_H is seen (Fig. 9, Tables 1–3) to be much greater on RuEC1 after HTR1 than after O/LTR or HTR2. The smaller changes found with RuEC3 reflect the lesser change in dispersion which O/LTR produces in this case (Scheme 3), and the effects of these smaller differences are observed in the product selectivities as a function of H_2 at various temperatures (sets BH 17–24, Table 3). (2) Dr. B. Coq (Montpellier) has reported [21] values for the isosteric enthalpies of H_2 chemisorption by application of the Clausius-Clapeyron equation to adsorption isotherms measured at various temperatures:

$$-\Delta H_H = RT^2(\delta \ln P / \delta T)_\theta$$

The results (Fig. 14) show that enthalpies given by RuEC1 are at least twice as large as those given by RuEC3: adsorption at high coverage is more rapid on the latter. The enthalpy values recorded in Table 5 relate to a more or less fully covered surface and for this reason, and because of their limited accuracy, they do not reveal this trend. It may still exist, however, but it is also possible that the entropy change contributes importantly to the value of K_H .

It may at first sight seem paradoxical that the processes requiring the greatest number of H atoms in the stoichiometric sense proceed most readily when the surface concentration of H atoms is low (Figs. 9 and 11). The problem disappears

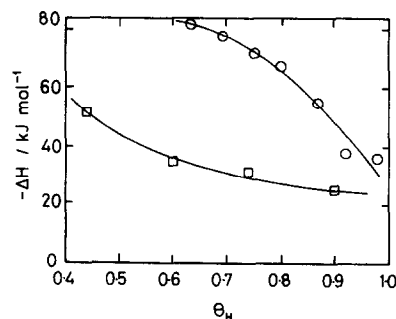


Fig. 14. Isosteric enthalpies of H_2 chemisorption as a function of coverage: circles, RuEC1; squares, RuEC3.

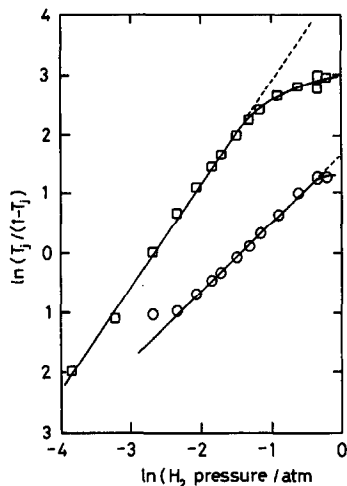


Fig. 15. Logarithmic plots of $T_j/(1-T_j)$ ($j=2$ or 3) against H_2 pressure. Circles, plot corresponding to the results in Fig. 13; squares, T_3 for the reaction of propane on RuEC1 after O/LTR, 408 K.

when it is appreciated that, because of the dehydrogenated state of the reactive intermediates (Schemes 1 and 2), more H atoms are needed to form the corresponding gaseous alkane than to effect C–C bond fission. It should be possible to quantify this difference from the dependences of T_2 and T_3 on H_2 pressure. Recalling the definition of T_3 we may write

$$T_3/(1-T_3) = k_3'/k_3^* = (\kappa_3'/\kappa_3^*) (\theta_H^a/\theta_H^b)$$

a and b being the numbers of H atoms required to convert C_3^* into respectively gaseous propane, and into C_2^* and C_1^* fragments. An analogous expression may be written for T_2 . By making certain approximations (e.g. that the rate-determining step is slower than the rate of desorption of H atoms (Scheme 1), and that $K_H P_H$ is less than unity) we are able to estimate $(a-b)$ from a plot of $\log [T_3/(1-T_3)]$ against $\log P_H$. Good to excellent linear log–log plots are indeed obtained (Fig. 15), the slope for the system RuEC1-O/LTR at 398 K being 1.06. It would therefore appear that two more H atoms are needed to effect the desorption of C_3^* as propane than to convert it to fragments. This is very direct proof of the dehydrogenated state of the reactive intermediate. Estimated values of $(a-b)$, designated t_3 for the n-butane reaction and t_2 for the propane reaction, are included in Tables 1–3. For n-butane with both

RuEC1 and RuEC3 after HTR1 and O/LTR, values of t_3 are 1.0–1.2, but after HTR2 they are significantly larger, as indeed are the values of t_2 (≈ 1.7 after O/LTR, ≈ 2.3 after HTR2). It is therefore implied that the reactive intermediate must in both cases be more dehydrogenated after HTR2, and more dehydrogenated for propane than for butane.

3.6. A synthesis of mechanistic proposals

It is now time to attempt to synthesise a coherent reaction model from the available kinetic parameters, and to explore what consistencies and what shortcomings there are in the methodology that has been adopted. We first examine the interrelations between the estimated numbers of H atoms x affixed to the reactive species (listed in the Tables as a , where $a = (n-x)/2$): the number naturally depends on the number of carbon atoms n , so we distinguish the various values by applying the subscript n . We have to remember that the x parameter is probably the least accurately obtained in the modelling, so some latitude must be allowed. Now if at a given temperature the C_3^* species formed from butane is the same as that formed by dissociative chemisorption of propane, and if the C_2^* species formed from either propane or butane equate to that formed from ethane, and if the assumption made in the kinetic model (Scheme 1) that only *one* H atom is required to break the C–C bond in all three reactive species, there should be simple numerical connections between the values of x_n , as follows.

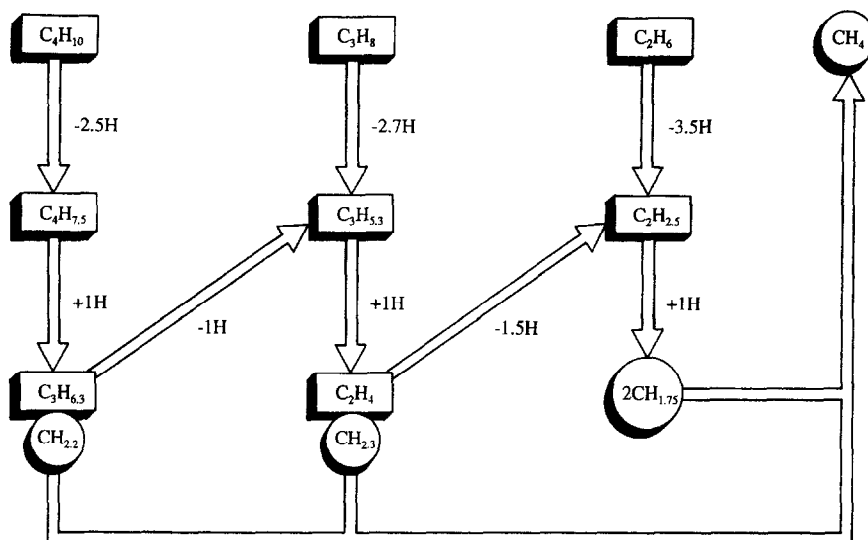
$$x_4 + 1 = x_3 + x_1 \quad (a)$$

$$x_4 + 1 = 2x_2 \quad (a')$$

$$x_3 + 1 = x_2 + x_1 \quad (b)$$

$$x_2 + 1 = 2x_1 \quad (c)$$

It is only for results obtained after the O/LTR treatment at 397–400 K that a complete set of kinetic parameters is available: taking rounded mean values from the Tables we have: $x_4 = 7.5$; $x_3 = 5.3$; $x_2 = 2.5$. It is immediately apparent that



Scheme 4. A possible description of the H content of intermediate species in the hydrogenolysis of the lower alkanes.

there is no single value of x_1 which fits all three equations in which it appears; furthermore the value of x_2 derived from equation a' (4.25) is not that observed. The most reasonable explanation of the discrepancies is that the C_3^* and C_2^* species formed by bond-splitting have to lose further H atoms in order to become the reactive species for further hydrogenolysis. A possible state of affairs is summarised in Scheme 4.

Two further tests of the methodology may be made. (1) If our analysis above of the significance of the dependence of selectivities on H_2 pressure is correct, the following relations will hold:

$$t_2 = 5 - x_2$$

$$t_3 = 7 - x_3$$

Observed mean values (Tables 1 and 2) are: $t_2 = 3.3$; $t_3 = 2.1$. Values calculated from the above values of x_n are respectively 2.5 and 1.7: the agreement, not perfect, is at least satisfactory.

(2) Some connection between values of K_A and of x or a may be expected, since both pertain to the same process, namely, the dehydrogenative chemisorption of the reactant alkane. In fact, as noted above, values of a vary remarkably little: after O/LTR, about the same values are found for propane and for butane, for RuEC1 and RuEC3 (1.2 ± 0.1 , see Tables 1–3), independent of K_A

and of the variables which cause K_A to change. After HTR1, values of a decline slightly as K_A increases, but only (with RuEC1) from 1.6 to 1.35. These observations tend to confirm the physical significance of a and of the adsorbed species it denotes. After HTR2, values of a are again 1.2 ± 0.1 , but corresponding K_A values are very small, a fact which we take to contribute to the low activity shown after this pretreatment. We are uncertain what significance should be attached to values of x that are clearly non-integral (see e.g. Scheme 4); our tentative belief is that they represent averages over several species of different reactivity (Scheme 2).

4. Conclusions

This work is an attempt to penetrate more deeply into the origins and causes of the particle-size dependence of 'catalytic activity' in alkane hydrogenolysis: it is possible that our conclusions may have more general validity. Our approach has been to select a rate expression derivable from a reaction model of the kind that has found widespread support in the literature, and, by determining the H_2 orders for ethane, propane and butane at several temperatures on Ru/ Al_2O_3 catalysts constituted and pretreated so as to show different

degrees of dispersion and different 'surface morphologies', to seek the underlying reasons for differences in behaviour in terms of the constants of the rate expression, terms which have some degree of physical significance.

The use of mathematical modelling in this context is not without its difficulties. In order to constrain the number of variables to a reasonable total, taken to be three (excluding the scaling k_1), it is necessary to devise a simple model and to include assumptions which one might prefer to avoid. These assumptions include the constancy of active area and the independence of x on H_2 pressure: moreover it may be naive to expect that the same basic mechanism will apply to all three alkanes. The rate expression ES5B provides satisfactory fits to all experimental results, but we have *not* shown, or indeed tried to show, that other expressions are less satisfactory: it was selected on the basis of the reasonableness of the mechanistic postulates. Careful inspection of the results shows however that the fit is relatively poorer at high H_2 pressures, a fact not clearly revealed in Figs. 2, 4 and 5, but very noticeable when $\log(\text{rate})$ is plotted against H_2 pressure (Fig. 6). We attempted to perform optimisation using $\log(\text{rate})$ instead of rate, but this places greater stress on the low rate measurements made at high H_2 pressure, and no *overall* improvement seemed possible. We are certain that ES5B is not the *perfect* rate expression, but we are unsure whether a better exists with no more disposable constants.

The extent to which the use of this expression is successful may be judged in terms of the rationality of the constants and their temperature-dependence. Although values of K_H are not the same for all three alkanes, their temperature coefficients are low, as may be expected. K_A varies in a manner compatible with a dehydrogenation process, and the extent of H atom loss, given by x or a , is of reasonable magnitude, being greater for ethane than for propane or butane. The near-constancy of the atomic rate constants (Table 4) and of true activation energies (Table 5) sheds a very revealing light on the origins of particle-size effects: our analysis shows that it is *the thermo-*

dynamic parameters K_H and K_A , and their consequential effects on concentrations of adsorbed intermediates, that play the dominant role in deciding reaction rates.

We believe that our conclusions are correct, at least in broad outline, but numerous problems remain to be addressed. We have not tried to understand *why* K_H and K_A are responsive to particle size and surface morphology, or *why* (in disagreement with a recent report [22]) H_2 chemisorption appears to be strong, and yet kinetically so slow, on very small Ru particles, on each of which there cannot be more than about one active centre operating at a time. Nevertheless this strength of chemisorption is clearly revealed by the lack of marked dependence of product selectivities on H_2 pressure and on temperature. In previous work with other supported Ru catalysts, especially those having a very high dispersion [3] or intentionally modified [23] or accidentally poisoned [24], we have noticed a similar behaviour in respect of temperature, but it is not yet clear whether or why the chemisorption of H_2 on these unclean surfaces should be unusually strong.

The origin of the effects we have attributed to 'surface morphology' is also unclear. Other workers have recorded similar effects after oxidative treatments [4,5], but their discussions are unsatisfactory in that they are based only on rate measurements. One possible candidate explanation is the continued existence of Ru^{x+} ions in association with the Ru^0 particles, perhaps residing between the metal and the support: their presence is clearly indicated by EXAFS measurements on RuEC1 [1] and they resist reduction even at 770 K. Greater concentrations after O/LTR are not impossible, and their effect in rendering metal particles somewhat electron-deficient is an alternative approach to that described vaguely as 'morphology'. However differences in particle shape, or in the type of exposed crystal plane, i.e. true morphological effects, cannot be eliminated.

In conclusion we believe that this work has raised a number of important questions concerning the origins of particle-size effects in catalysis, and we think that failure to attend to the additional

dimensions afforded by changing reactant pressures and temperature may be largely responsible for the unsatisfactory state of the relevant literature [25].

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