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Alkane Transformations on Supported Platinum Catalysts

Part 2: Reactions of Propane and of *n*-Butane on EUROPT-1 Modified by Titania and by Alumina

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EUROPT-1 (6.3% Pt/SiO_2) has been modified by adding various amounts of TiO_2 and of Al_2O_3; H_2 chemisorption isotherms, and rates for hydrogenolysis of propane and of *n*-butane, and of isomerization of the latter, over a range of temperatures, have been measured. Two types of pretreatment have been used: high-temperature reduction (750 K), and then oxidation followed by low-temperature reduction (520 K). Addition of TiO_2 decreases the rates of all reactions, but with butane the isomerization is selectively poisoned; rates decrease more quickly than the H/Pt ratio, catalysts having 9 wt% TiO_2 being of low activity but still giving H/Pt ≅ 0.75. Adding Al_2O_3 also causes the H/Pt ratio to decrease, but rates of the alkane reactions fall only slowly until a high Al_2O_3 loading (~18 wt% Al_2O_3) is attained; the isomerization rates in general fall more slowly than those of hydrogenolysis. After a first high-temperature excursion to ~660 K, the rates of all catalysts fall but then attain a very stable activity, not affected by further thermal cycling. This initial deactivation always causes the isomerization selectivity to decrease, very markedly in some cases; activation energies for hydrogenolysis, which sometimes show two distinct linear parts, rise after the initial loss of activity and then stabilise. Careful control of pretreatment and reaction conditions allows activation energies to be measured very precisely and reproducibly. Results are interpreted by a simple site-blocking model, in which both TiO_x and carbonaceous residues occupy one class of high coordination number sites; the extent to which catalyst activity is diminished by the latter is inversely related to the extent of deactivation by the former. AlO_x species behave similarly to TiO_x, but tend to occupy selectively sites comprising low-coordination-number Pt atoms.

INTRODUCTION

In Part 1 of this series (*1*), the case was presented for studying the nature of active centres on supported metal catalysts by modifying the surface of the particles with oxidic species such as TiO_2 and Al_2O_3; these formulae for the oxides are used without implication as to the actual identity of the species formed in practice. Work of this kind should, it was argued, contribute not only to our understanding of the Strong Metal–Support Interaction (SMSI) (*2, 3*) but also to the definition of active centres if the modifiers were able selectively to eliminate a certain class (or classes) of surface atoms. It is now well established that certain of the Group IVB elements (especially Sn and Pb (*4, 5*)) act with some degree of selectivity in blocking specific surface sites, while the presence of more common poisons such as "coke" and sulphur can also change product selectivities as well as activities (*6*).

The logic of adding the modifier to a preformed supported metal was also explained in Part 1 (*1*), the principal advantage being that the size of the metallic particles might perhaps remain constant, so that positive statements about the extent of coverage of the metal by the modifier could then become

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possible. Furthermore, total encapsulation of the metal might be avoided and the effects of low modifier concentrations examined; the nuisance of extensive retention of Cl^- should also be evaded. This paper therefore reports on the effects brought about by adding TiO_2 and Al_2O_3 in various amounts to EUROPT-1, a 6.3% Pt/SiO_2 reference catalyst, the properties of which are well known (*7*, *8*). H_2 isotherms have been measured, and detailed results are given for the reactions of propane and of *n*-butane with H_2 on the modified catalysts. Corresponding results for the unmodified catalyst were given in Part 1 (*1*). Once again considerable emphasis is placed on the accurate measurement of kinetic parameters, and on the effect of pretreatment on the precise state of the surface. Only in this way can reliable conclusions be drawn as to the effect that the modifiers have on the behaviour of the metal particles.

EXPERIMENTAL

Catalyst Preparation

The Al_2O_3-modified EUROPT-1 catalysts were prepared by applying aqueous solutions of $Al(NO_3)_3$ to the as-received EUROPT-1 by the incipient wetness method. After drying (first on a steam-bath, then overnight in air at 393 K), the products were calcined in air at 573 K for 1 h.

The TiO_2-modified catalysts were prepared analogously, using solutions of titanium isopropoxide in isopropanol; calcination was performed at 748 K for 3 h. Nominal weight percentages of the modifiers expressed as the oxides, and the corresponding atomic ratios of the modifier cation to surface Pt atoms (Pt_s) (assuming $Pt_s = 2 \times 10^{20}$ g_{cat}^{-1} (*7*)), are given in Table 1. The latter ratio is used to identify catalysts in the subsequent tables.

Characterisation

For measurement of H_2 chemisorption isotherms, the sample (~0.3 g) was placed in a through-flow reactor to permit *in situ* pretreatments exactly as performed before rate measurements (see below). Samples were finally outgassed at 750 K for 30 min before being cooled to room temperature, where isotherms were recorded up to equilibrium pressures of ~80–160 Torr.

Rate Measurements

Each catalyst sample was pretreated in two ways: (i) high-temperature reduction (HTR; 2 h at 750 K) and then (ii) low-temperature oxidation and reduction (LTO/R; air, 1 h at 620 K; H_2, 2 h at 520 K). Fuller details of the pretreatment conditions were given in Part 1 (*1*). Rates and product yields were measured in the range 520–660 K in a continuous-flow system at atmospheric pressure, using 10 : 1 H_2 : alkane mixtures. Temperature was increased in steps of 10 K and samples extracted for analysis after 18 min; the following step and thermal equilibration were effected while the previous sample was being analysed. This constituted stage 1 of the reaction, and the procedure was repeated as the temperature was lowered to its starting value (stage 2). Usually the cycle was repeated to give stages 3 and 4; further cycles following the LTO/R treatment then gave stages 5 to 8. Part 1 should be consulted for further details, where the treatment of the results is also described. Briefly the isomerization selectivity S_i is the fraction of *n*-butane converted to isobutane, and the *n*-butane hydrogenolysis selectivities S_j (j = 1–3) are defined by the equation

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

Rates (symbolised as *r* in the tables) are for hydrogenolysis only, although for *n*-butane isomerization rates are readily calculated either from the corresponding value of S_i or from the Arrhenius parameters for isomerization given in Table 8. Rates and selectivities are given for 603 K and rates and preexponential factors (A) are in mmol g_{cat}^{-1} h^{-1}. Values of the rates quoted in the tables will not in general equate exactly to those which may be calculated from the given Arrhenius parameters, because their

TABLE 1

Composition and Results obtained from H_2 Chemisorption Measurements

Modifier	wt% as oxide	M/Pt$_s$[a]	Pretreatment	V_{H_2} (μmol g_{cat}^{-1})	H/Pt
—	0	0	HTR	170.7	1.06
			LTO/R	188.3	1.17
Al_2O_3	0.5	0.5	HTR	142.1[b]	0.880
			LTO/R	157.2	0.974
	1.9	2.0	HTR	135.5	0.845
			LTO/R	133.8	0.830
	17.8	18	HTR	134.2	0.831
			LTO/R	125.2	0.775
TiO_2	0.78	0.5	HTR	147.4	0.919
			LTO/R	155.7	0.971
	3.0	2.0	HTR	141.0	0.879
			LTO/R	143.9	0.897
	9.1	6.2	HTR	118.3	0.737
			LTO/R	123.1	0.768

[a] Atomic ratio of modifier cation to surface Pt atoms.

[b] Mean of two determinations (see text).

values are rounded to three significant figures. The quoted rates, however, are in almost every case obtained by solving the relevant Arrhenius equation for the rate at 603 K using precise values of the activation energy and of ln A obtained by linear regression analysis. For this purpose some discretion was exercised in eliminating points where either the rate was too low for analysis to be reliable or at high temperature where the catalyst was suffering deactivation. Quoted activation energies are then thought to be extremely accurate (see Part 1). In a number of cases, however, the Arrhenius plot seemed to consist of two linear portions, with a change of slope at 600 ± 20 K. If activation energies derived from the two parts differed by more than the sum of the standard deviations, then the two values are quoted (e.g., if $E_1 = 120 \pm 2$ kJ mol^{-1} and $E_2 = 131 \pm 3$ kJ mol^{-1}, $11 > 4 + 6$). To simplify tabular presentation, the low-temperature range is coded A, and the high-temperature range as C. Where the nonlinearity is not statistically significant, a single activation energy is given for the whole temperature range (coded B).

The parameters F and T_3 quoted in the tables derive from a mechanistic analysis, due originally to Kempling and Anderson (*9*), and described in Part 1 (*1*) and elsewhere (*10*). Briefly F is the fractional chance of the n-butane molecule breaking first at the central C–C bond, and T_3 is the fractional chance that an adsorbed C_3 intermediate will appear as propane. At low conversion these parameters are derived from the observed selectivities by the equations

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

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

T_2 (defined analogously to T_3) is taken to be the value of S_2 in the reaction of propane under corresponding conditions.

RESULTS

H_2 *Chemisorption Isotherms*

Plots of the results according to the linearized form of the Langmuir equation assuming dissociative adsorption afforded excellently straight lines, from the slopes of which monolayer volumes were obtained with high accuracy (Table 1). Although the slopes of the isotherms were generally small above about 30–50 Torr equilibrium pressure, values of monolayer volumes derived from the linear plots were greater by as much as 10% from those estimated by extrapolating the volumes in the high-pressure region to zero pressure. The higher (and probably more accurate) values are used throughout. Duplicate measurements on the catalyst containing 0.5% Al_2O_3 gave monolayer volumes of 141.7 and 142.6 μmol g_{cat}^{-1} (H/Pt = 0.878 and 0.883), and we therefore feel justified in quoting H/Pt ratios to three significant figures, recognising that the accuracy with which the Pt content of the sample is known may be the limiting factor.

Values of the H/Pt ratio (Table 1) are in most cases higher after the LTO/R treatment than after HTR (but not for the higher Al_2O_3 contents). Values decrease progressively as the concentration of the modifier is raised, but in both cases it is the first increment that produces the largest effect; thereafter the ratio declines only slowly. It is quite clear from these results only a small fraction of the modifier is actually in contact with the metal particles. At the lowest concentration, where the atomic Al/Pt_s or Ti/Pt_s ratio is 0.5, the number of Pt atoms available to chemisorb H_2 has declined by only about 15%. At higher modifier concentrations, an even smaller fraction is engaged with the metal. Nevertheless, as we shall see, these somewhat small extents of coverage of the metal produce some highly significant changes in catalytic behaviour. We do not feel inclined to use the measured H/Pt ratios to calculate turnover frequencies, as quite evidently these will not be constant quantities. However, we shall explore how rates vary with the extent of free surface as revealed by the H/Pt ratio.

*Hydrogenolysis of Propane on Al_2O_3-Modified EUROPT-*1

Arrhenius plots for this reaction on unmodified EUROPT-1 (*1*) showed a tendency to be composed of two linear parts, the break occurring at about 600 K; however, it was concluded that the effect was hardly statistically significant, and only mean activation energies for the whole temperature range were cited. We have carefully examined the corresponding plots for the modified catalysts, and conclude that, after HTR1, the Al_2O_3-modified EUROPT-1 samples show distinct breaks in the Arrhenius plots only in stage 1; above about 623 K, activation energies are some 50 kJ mol^{-1} *lower* than in the low temperature range (see Fig. 1 for an example). In later stages (Table 2), excellent linear plots are obtained over the whole range (523–663 K, see also Fig. 1). The changes in slope in stage 1 probably betoken the onset of coking, since the rates at 603 K are lower in stage 2; the deactivation is not, however, progressive, rates and activation energies remaining sensibly constant in stages 2–4 (Table 2). However, the original behaviour is restored by the LTO/R treatment, confirming that it is characteristic of a clean surface. Coking then occurs again at the end of stage 5, to about the same extent as before, and constant kinetic parameters are again found thereafter. In Table 3, which summarises all the kinetic parameters, it is therefore only necessary

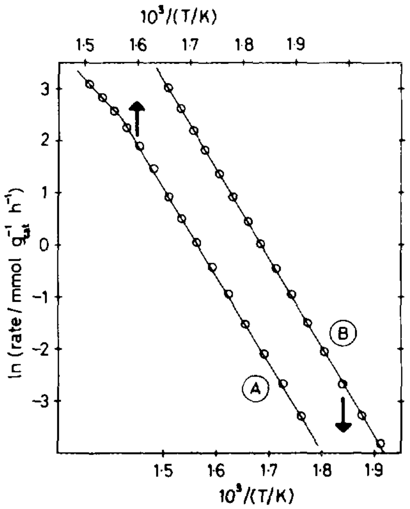

FIG. 1. Arrhenius plots for propane hydrogenolysis on Al_2O_3-modified EUROPT-1 (Al/Pt_s = 0.5): (A) stage 1 and (B) stage 4.

TABLE 2

Kinetic Parameters for the Hydrogenolysis of Propane on Al_2O_3-Modified EUROPT-1 (Al/Pt$_s$ = 0.5)

Pretreatment	Stage	Temp. range[a]	E (kJ mol^{-1})	ln A	r
HTR	1	A	140.0 ± 1.7	28.9	2.60
	2	B	143.7 ± 1.4	29.2	1.67
	3	B	144.5 ± 2.6	29.4	1.76
	4	B	141.1 ± 1.2	28.6	1.45
LTO/R	5	A	155.1 ± 5.5	32.1	3.06
	6	B	144.5 ± 2.1	29.3	1.54
	7	B	148.8 ± 2.3	30.2	1.72
	8	B	142.3 ± 1.3	28.8	1.45

[a] For an explanation of the symbols A and B, see text.

to quote the average of their values found in stages 2–4 or in stages 6–8. The value of S_2 is always between 0.990 and 0.995.

It is now necessary to analyse the results in Table 3, to distinguish the separate effects of pretreatment, age, and Al/Pt$_s$ ratio on the kinetic parameters. The rates at 603 K always decrease progressively as the Al/Pt$_s$ ratio increases, in a way which will be considered further below; extents of deactivation caused by the first high-temperature excursion following either pretreatment decrease as the inhibiting effect of the Al_2O_3 increases. Rates after LTO/R are slightly higher than after HTR (ratio 1.14 ± 0.04). After HTR, activation energies do not vary

TABLE 3

Kinetic Parameters for the Hydrogenolysis of Propane on EUROPT-1 Modified with Various Amounts of Al_2O_3

Pretreatment	Stage	Al/Pt$_s$	Temp. range[a]	E (kJ mol^{-1})	ln A	r
HTR	1	0	A/C	149/117	31.0/24.8	3.41
		0.5	A/C	140/103	28.9/21.7	2.59
		2	A/C	146/95	29.9/20.2	2.12
		18	A/C	181/128	35.9/25.5	0.79
HTR	2–4	0	B	153	31.2	1.91
		0.5	B	143	29.0	1.70
		2	B	148	29.9	1.43
		18	B	168	32.7	0.43
LTO/R	5	0	A/C	177/131	36.6/27.5	3.64
		0.5	A/C	155/95	32.1/20.2	3.13
		2	A/C	155/89	31.9/19.1	2.72
		18	A/C	179/110	35.6/22.2	0.92
LTO/R	6–8	0	B	159	33.5	4.10
		0.5	B	145	29.4	1.65
		2	B	149	30.0	1.26
		18	B	172	33.4	0.39

[a] For an explanation of the symbols A, B, C, see text.

TABLE 4

Kinetic Parameters for the Hydrogenolysis of Propane on EUROPT-1 Modified with Various Amounts of TiO_2

Pretreatment	Stage	Ti/Pt_s	Temp. range	E (kJ mol^{-1})	ln A	r
HTR	1	0	A/C	149/117	31.0/24.8	3.41
		0.5	A/C	135/115	27.3/23.3	1.35
		2.0	A/C	132/115	26.4/22.9	1.09
		6.2	A/C	132/119	25.6/23.1	0.46
HTR	2	0	B	153	31.2	1.91
		0.5	A/C	141/127	28.1/25.4	1.05
		2.0	A/C	139/126	27.6/24.8	0.87
		6.2	A/C	139/131	26.7/25.2	0.36
LTO/R	3	0	A/C	177/131	36.6/27.5	3.64
		0.5	A/C	156/103	31.9/21.2	2.08
		2.0	A/C	163/116	32.9/23.1	1.43
		6.2	A/C	145/115	28.3/21.9	0.41
LTO/R	4	0	B	159	33.5	4.10
		0.5	A/C	145/127	29.1/25.5	1.11
		2.0	A/C	143/127	28.4/25.0	0.72
		6.2	B	128	24.2	0.27

significantly with stage number, except at the highest Al/Pt_s ratio, where values are significantly higher than for the lower ratios. LTO/R causes activation energies to increase (again the material having the highest Al/Pt_s ratio is exceptional), but when stabilised all show values very similar to those found in stages 2–4 after HTR.

Hydrogenolysis of Propane on TiO_2-Modified EUROPT-1

Slightly different procedures were adopted with the TiO_2-modified catalysts. Only two stages were carried out after HTR, and two after LTO/R (Table 4); however, nonlinear Arrhenius plots were frequently encountered (Fig. 2), and in such cases the activation energies for both the low- and high-temperature regions are recorded. The high-temperature activation energies show some regularities. After HTR1, for all four catalysts, values are 117 ± 2 kJ mol^{-1}; for the three modified catalysts, they are 128 ± 3 kJ mol^{-1} in stage 2, and in stage 3 (after LTO/R) they are 109 ± 6 kJ mol^{-1}. In the low-temperature region (<600 K; entries coded A in Table 3), activation energies are similar in stages 1 and 2 after HTR, and as with Al_2O_3-modified catalysts are raised by the LTO/R treatment; in stage 4, however, their values agree quite closely with those

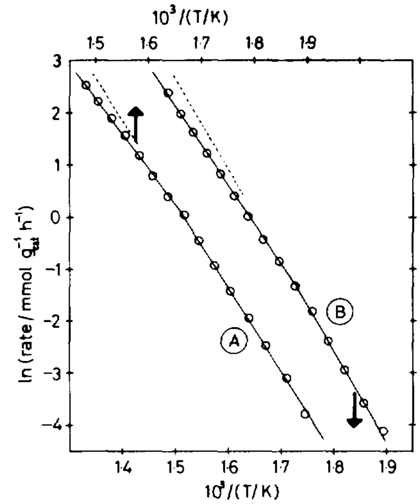

FIG. 2. Arrhenius plots for the hydrogenolysis of propane on EUROPT-1 modified by TiO_2 (Ti/Pt_s = 2): (A) stage 1 and (B) stage 4.

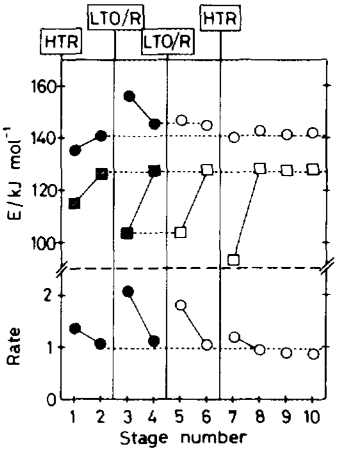

FIG. 3. Effects of HTR and of LTO/R pretreatments on activation energy and rate for propane + H_2 at 603 K on TiO_2-modified EUROPT-1 ($Ti/Pt_s = 0.5$). Squares, high-temperature activation energy; circles, low-temperature activation energy. Dotted lines connect points at which the kinetic parameters have similar values; full lines highlight changes between stages 1 and 2. Shaded points are those quoted in Table 4.

in stage 2. It appears that the breaks in the Arrhenius plots may have a kinetic origin, as they appear during the cooling stages (2 and 4) as well as in the heating stages (1 and 3), and they occur at somewhat lower temperatures than with the Al_2O_3-containing samples. Rates at 603 K decrease with increasing Ti/Pt_s, in a manner which will be discussed further below; the changes, however, are clearly associated with the ln *A* term rather than with activation energy.

Additional experiments were performed with the TiO_2-modified catalysts to establish the reproducibility of the effects created by the different pretreatments (Table 4); these are most clearly seen in the various activation energies shown in stages 1 and 3. The results of these experiments are shown in Figs. 3 and 4. With the catalyst having a Ti/Pt_s ratio of 0.5, we repeated the LTO/R treatment after stage 4, and the HTR treatment after stage 6 (Fig. 3). The high-temperature activation energy in the second (i.e., cooling) and subsequent stages after each treatment is very closely reproducible (127.5 ± 1.0 kJ mol^{-1}); the first stage values are more variable, but are almost the same after the LTO/R treatments (~104 kJ mol^{-1}). Most of the high-temperature values after HTR are close to 141 kJ mol^{-1}, those following LTO/R being slightly higher. Rates at 603 K also show marked regularities. In the second and later stages, rates are 0.95 ± 0.15 mmol g_{cat}^{-1} h^{-1}; in the first stages, rates are somewhat higher after LTO/R than after HTR (Table 3 and Fig. 3).

With the catalyst having $Ti/Pt_s = 2$, the HTR and LTO/R treatments were alternated (Fig. 4); again very clear regularities are visible. High-temperature activation energies in each stage are almost constant (117 ± 3 kJ mol^{-1} in the first stages, 126 ± 1 kJ mol^{-1} in the second stages), and the low-temperature values are comparably steady after the first cycle. Rates are also constant after the first cycle (1.45 mmol g_{cat}^{-1} h^{-1} in the first stages, 0.65 ± 0.05 mmol g_{cat}^{-1} h^{-1} in the second stages). With neither of these catalysts, therefore, does the type of preatreatment have a marked effect on surface structure.

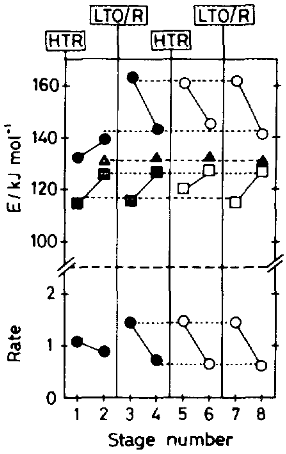

FIG. 4. Effects of HTR and LTO/R on activation energy and rate for propane + H_2 at 603 K on TiO_2-modified EUROPT-1 ($Ti/Pt_s = 2.0$). Symbols as in Fig. 3; triangles, mean activation energy. Shaded points are those quoted in Table 4.

TABLE 5

Kinetic Parameters for the Hydrogenolysis of *n*-Butane on Al_2O_3-Modified EUROPT-1 (Al/Pt$_s$ = 18)

Pretreatment	Stage	Temp. range	E (kJ mol^{-1})	ln A	r	S_i	S_2	S_3	F	T_3
HTR	1	B	109	22.0	1.13	0.423	0.765	0.607	0.378	0.975
	2	A/C	122/160	23.3/31.1	0.43	0.370	0.794	0.591	0.391	0.971
	3	A/C	126/160	24.2/31.3	0.48	0.390	0.801	0.588	0.394	0.971
	4	A/C	121/163	23.0/31.6	0.36	0.370	0.794	0.589	0.394	0.972
LTO/R	5	B	117	23.6	1.17	0.546	0.751	0.612	0.368	0.968
	6	A/C	121/123	24.4/24.7	0.46	0.521	0.782	0.597	0.385	0.971
	7	A/C	120/167	22.8/32.6	0.51	0.529	0.795	0.591	0.391	0.970
	8	A/C	122/169	23.1/32.7	0.37	0.501	0.785	0.593	0.387	0.969

Reactions of n-Butane with H_2: Introductory Comments

Study of this reaction enables us to judge how the modifiers affect the rates of both isomerization and hydrogenolysis, and the fine structure of the latter as judged by the selectivities for the individual products. Some information on the kinetic parameters for isomerization is also obtained. Some of the effects of the modifiers (e.g., on hydrogenolysis selectivities) are surprisingly small, but the high precision with which they can be measured, and their reproducibility, makes discussion of their effects worthwhile. The quality of the results is demonstrated in Table 5; after the first stage of each pretreatment, the catalyst (Al/Pt$_s$ = 18) settles to a constant behaviour in respect of activation energy (in both low- and high-temperature regimes), rate at 603 K, and product selectivity parameters. There is very little to choose between any of the analogous quantities in stages 2–4 and 6–8, except for the isomerization selectivity, which is quite significantly increased by the LTO/R treatment. The initial deactivations, at the end of stages 1 and 5, operate on hydrogenolysis selectivities only through the splitting parameter F; T_3 lies in the range 0.950 ± 0.005. Similar behaviour was found with TiO_2-modified EUROPT-1. It is therefore only necessary in the subsequent tables to quote results for stages 1 and 5, and the *averages* of those found in the following stages.

Reactions of n-Butane with H_2 on Al_2O_3-Modified EUROPT-1

Reactions of n-butane with H_2 were studied on the three Al_2O_3-modified EUROPT-1 samples, and the results are given in Table 6 (see also Fig. 5). There are important differences in the Arrhenius plots from those shown by propane (Table 3). Here the breaks in the plots, which when they appear are very marked, occur only *after* the first stage following either pretreatment (Fig. 5). The tendency to show a two-part Arrhenius plot in the first stages, which is clear with

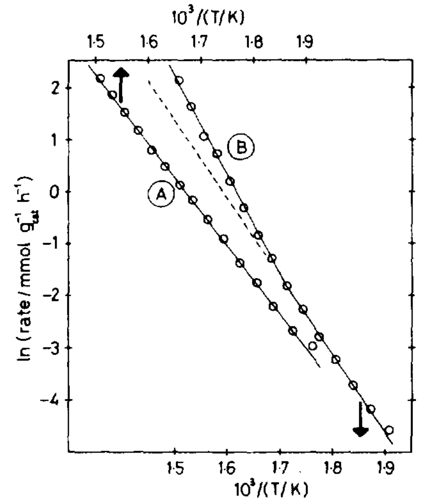

FIG. 5. Arrhenius plots for the hydrogenolysis of *n*-butane on Al_2O_3-modified EUROPT-1 (Al/Pt$_s$ = 18): (A) stage 1 and (B) stage 2.

TABLE 6

Kinetic Parameters for the Hydrogenolysis of *n*-Butane on EUROPT-1 Modified by Various Amounts of Al_2O_3

Pretreatment	Stage	Al/Pt_s	Temp. range	E (kJ mol^{-1})	ln A	r	S_i	S_2	S_3	F	T_3
HTR	1	0	A/C	95/117	20.0/24.6	3.25	0.335	0.788	0.586	0.380	0.945
		0.5	B	99	20.8	2.83	0.421	0.830	0.563	0.399	0.938
		2	B	101	24.1	2.56	0.423	0.784	0.591	0.381	0.954
		18	B	109	22.0	1.14	0.423	0.675	0.607	0.378	0.975
	2–4	0	A/C	122/144	25.0/29.3	1.84	0.255	0.834	0.561	0.400	0.934
		0.5	A/C	116/136	23.5/27.4	1.40	0.188	0.848	0.551	0.405	0.926
		2	A/C	119/144	23.7/28.8	1.06	0.273	0.828	0.565	0.401	0.942
		18	A/C	123/161	23.5/31.3	0.43	0.376	0.796	0.589	0.393	0.971
LTO/R	5	0	A/C	99/120	21.0/25.0	3.32	0.430	0.780	0.582	0.364	0.915
		0.5	B	98	20.5	2.64	0.465	0.823	0.566	0.396	0.937
		2	B	99	20.7	2.50	0.484	0.785	0.588	0.381	0.950
		18	B	117	23.6	1.26	0.751	0.751	0.612	0.368	0.968
	6–8	0	A/C	122/152	24.9/30.9	1.57	0.360	0.830	0.558	0.393	0.919
		0.5	A/C	118/139	23.8/27.5	1.23	0.246	0.848	0.549	0.406	0.923
		2	A/C	120/148	23.9/29.4	0.96	0.362	0.822	0.567	0.396	0.939
		18	A/C	120/168	22.8/32.6	0.46	0.517	0.787	0.594	0.388	0.970

the unmodified EUROPT-1 (*1*), is removed by the presence of Al_2O_3. Mean activation energies in stages 1 and 5 are low (~100–120 kJ mol^{-1}), but in later stages the low-temperature values are close to 120 kJ mol^{-1} after both pretreatments, those in the high-temperature regime being more variable. Once again, as with propane (Table 3), very high values (160–170 kJ mol^{-1}) are shown by the catalyst having Al/Pt_s = 18, but only in the high-temperature region.

The addition of Al_2O_3 to an Al/Pt_s ratio of 18 removes 60–80% of the hydrogenolysis activity at 603 K. Changes in S_2 and S_3 with Al_2O_3 content are described by (i) an initial increase in F, followed by a decrease, and (ii) an initial decrease in T_3, followed by an increase. The effects, although small, are remarkably consistent, the results shown by the modified catalyst after stages 2–4 and 6–8 being especially close. The parameter showing the most complex behaviour is the isomerization selectivity S_i: its value at 603 K is (i) increased in stage 1 by the presence of Al_2O_3 to an extent that does not depend on the Al/Pt_s ratio; (ii) decreased after stage 1 to an extent which is greatest at Al/Pt_s = 0.5 and least when Al/Pt_s = 18; (iii) increased in each case by the LTO/R treatment to an extent which is also a positive function of the Al/Pt_s ratio; and (iv) decreased after stage 5 but to a smaller extent than after stage 1. S_i correlates positively with T_3 and (in a more satisfactory way) inversely with F.

The measurement of isomerization rates is in general less accurate than that of hydrogenolysis rates, the former being usually slower, and the derived kinetic parameters are therefore somewhat less precise. However, it is quite evident that activation energies for isomerization are always higher than for hydrogenolysis, as is generally observed (*6*), and values of S_i accordingly increase with rising temperature (Fig. 6). Arrhenius plots of isomerization rate are sometimes linear over only a somewhat restricted temperature range, due to limited accuracy of measurement at low temperatures and a tendency to deactivation at high temperatures.

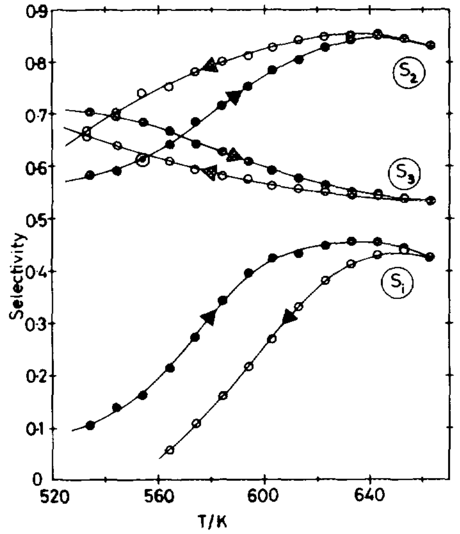

FIG. 6. Dependence of product selectivities on temperature for *n*-butane hydrogenolysis on Al_2O_3-modified EUROPT-1 ($Al/Pt_s = 2$): stages 1 and 2.

Nevertheless, the Arrhenius parameters recorded in Table 8 are not without interest. For the Al_2O_3-modified catalysts, activation energy is increased by the initial deactivation but the increase is not progressive: in the steady state its value is about 225 ± 10 kJ mol^{-1}, independent of Al_2O_3 content.

Reactions of n-Butane with H_2 on TiO_2-Modified EUROPT-1

The results obtained with the TiO_2-modified catalysts are in Table 7; there are substantial differences from those for the Al_2O_3-modified catalysts. To start with, none show significant breaks in the Arrhenius plots: activation energies are again low in stages 1 and 5 (~90–105 kJ mol^{-1}) and almost constant (117 ± 5 kJ mol^{-1}) in both stages 2–4 and 6–8. These latter values clearly correspond to the low-temperature values for the unmodified EUROPT-1 and the Al_2O_3-modified materials. Hydrogenolysis rates are lowered by ~85–90% by the addition of TiO_2 to a Ti/Pt_s ratio of 6.2. There are only very slight changes in hydrogenolysis product selectivities, and when they occur (e.g., in stage 5) they are more closely associated with F than with T_3. However, what does change far more dramatically is the value of S_i: it rapidly decreases as the Ti/Pt_s ratio is

TABLE 7

Kinetic Parameters for the Hydrogenolysis of *n*-Butane on EUROPT-1 Modified by Various Amounts of TiO_2

Pretreatment	Stage	Ti/Pt_s	Temp. range	E (kJ mol^{-1})	ln A	r	S_i	S_2	S_3	F	T_3
HTR	1	0	A	95	20.0	3.25	0.335	0.788	0.586	0.380	0.945
		0.5	B	103	21.3	2.44	0.270	0.792	0.582	0.379	0.939
		2.0	B	98	19.7	1.09	0.140	0.832	0.560	0.394	0.923
		6.2	B	105	19.8	0.30	0.035	0.835	0.555	0.396	0.914
	2–4	0	A	122	25.0	1.84	0.255	0.834	0.561	0.400	0.934
		0.5	B	117	24.0	1.84	0.102	0.834	0.558	0.399	0.927
		2.0	B	114	22.4	0.72	0.063	0.842	0.547	0.397	0.911
		6.2	B	114	22.5	0.29	0.020	0.828	0.558	0.392	0.916
LTO/R	5	0	A	99	21.0	3.32	0.430	0.780	0.582	0.364	0.915
		0.5	B	88	18.1	1.58	0.417	0.870	0.535	0.418	0.918
		2.0	B	92	18.4	0.98	0.218	0.822	0.558	0.394	0.910
		6.2	B	90	17.0	0.40	0.055	0.792	0.577	0.374	0.923
	6–8	0	A	122	24.9	1.57	0.360	0.830	0.558	0.393	0.919
		0.5	B	119	23.5	0.84	0.082	0.855	0.550	0.399	0.914
		2.0	B	114	22.3	0.59	0.057	0.830	0.554	0.391	0.909
		6.2	B	112	21.0	0.15	0.023	0.810	0.565	0.376	0.908

TABLE 8

Kinetic Parameters for the Isomerization of *n*-Butane on EUROPT-1 Modified by Various Amounts of Al_2O_3 and of TiO_2

Pretreatment	Stage	Al/Pt_s	E (kJ mol^{-1})	ln A	Pretreatment	Stage	Ti/Pt_s	E (kJ mol^{-1})	ln A
HTR	1	0	167	33.8	HTR	1	0	167	33.8
		0.5	174	35.5			0.5	242	48.3
		2	175	35.6			2.0	143	26.8
		18	146	28.8			6.2	139	24.2
	2–4	0	237	47.0		2–4	0	237	47.0
		0.5	220	42.8			0.5	259	50.1
		2	235	46.0			2.0	185	33.7
		18	238	46.2			6.2	152	26.7
LTO/R	5	0	259	32.6	LTO/R	5	0	159	32.6
		0.5	173	35.4			0.5	210	42.4
		2	171	35.0			2.0	170	32.7
		18	145	29.3			6.2	116	20.2
	6–8	0	234	46.6		6–8	0	234	46.6
		0.5	216	42.3			0.5	211	39.5
		2	221	43.4			2.0	199	36.2
		18	234	46.0			6.2	159	27.8

raised, in a way that is quite unconnected with any other kinetic parameter.

Kinetic parameters for isomerization on the TiO_2-modified catalysts are given in Table 8. As with Al_2O_3-modification, activation energy is raised, but not progressively, by the initial deactivation, but it tends to decrease as the TiO_2 content is increased. Paradoxically the catalysts having least activity for isomerization also have the lower activation energies.

Hydrogenolysis of n-Hexane

Measurements were made on this reaction, using EUROPT-1 and the modified catalysts having the highest loadings of Al and of Ti, in the laboratory of Professor R. Burch, Reading University. We hope to publish a fuller account of this work in due course, so for the moment we merely note that the addition of Al ($Al/Pt_s = 18$) lowers the activity by a factor of about two, without significantly altering the product distribution. At 603 K, the chief reaction is isomerization (~75%), followed by hydrogenolysis (~20%) and cyclization (~5%). The addition of Ti ($Ti/Pt_2 = 6$) reduces activity even further, but markedly increases hydrogenolysis selectivity (76% at 523 K, 52% at 603 K). TiO_2 thus acts as a selective inhibitor of isomerization, as found with *n*-butane (Table 7).

DISCUSSION

Prologue

This study has generated a large number of experimental results, by no means all of which have been described above; for example, we have not discussed in detail the temperature dependences of the product selectivities (Fig. 6 is a single illustrative example) and of the Kempling–Anderson parameters. Of the results given above, only those which bear directly on the construction of a simple model to account for what we find can receive attention. We have, however, encountered a number of systematic trends which will also be noted in what follows, although not all will find a logical explanation.

We have to consider the effects upon rates, activation energies and product selectivities of three variables: (1) the pretreatment of the sample, (2) the number of stages it has experienced, and (3) its composition. The HTR pretreatment was originally instituted in the knowledge that reduction at 750 K would not lead to sintering (*11*), but would produce a thermally annealed surface, as the Hüttig temperature for 1.8 nm Pt particles would probably be less than 750 K (*12*). The LTO/R treatment was designed to remove carbonaceous residues formed in the prior use, and to produce by O_2 chemisorption a roughened surface which might resist annealing during reduction at 520 K. In the case of the TiO_2-modified catalysts, however, the HTR treatment might be expected to generate an SMSI, while the LTO/R treatment might avoid it. No reduction of Al^{3+} is of course expected below 750 K, although the different pretreatments might affect the extent to which the ions associate with the metal. On the basis of the H_2 chemisorption results (Table 1), it does not appear that such changes are very significant, and even with TiO_2-containing materials there is no marked loss of H_2 adsorption capacity. H/Pt ratios after LTO/R are only a little higher than after HTR in either case, except for catalysts having Al/Pt_s ratios of 2 and 18.

It is a remarkable characteristic of EUROPT-1 that, when used for the reactions of propane and of *n*-butane with H_2, it loses a fraction of its activity *and then remains perfectly stable:* there are similarly no further changes in activation energy or in product selectivities (*1*). The obvious interpretation is that the formation of strongly-adsorbed dehydrogenated forms of the reactant alkane (which in shorthand we can refer to as "carbon" or "coke") cover a part of the available surface (Type-I sites), while another part of the surface (Type-II sites) remains unaffected: the fact that this initial deactivation does not completely eliminate either isomerization or hydrogenolysis (*1*) shows that both kinds of site can catalyse both reactions. EUROPT-1 therefore differs significantly from the Pt/Al_2O_3 catalyst EUROPT-3 (*10*), where two kinds of site could only be recognized from distinct changes in product selectivities with age; *the rate declined continuously.* With EUROPT-1, the fraction of surface initially deactivated may not be constant, and may increase with (i) the maximum temperature attained in thermal cycling, (ii) the alkane/H_2 ratio, and (iii) the number of carbon atoms in the alkane. The thermochemistry of the dehydrogenation of the reactant alkane into strongly adsorbed species that effectively block the surface is clearly the relevant factor. We must therefore envisage a family of sites showing a continuous degree of reactivity towards alkanes, the dividing line between deactivation and maintenance of activity being dependent on the abovenamed variables. It will be of interest to see how this dividing line is moved by the presence of the modifiers. Finally, we will need to consider how each modifier and each level of modification alter the kinetic parameters and whether the observed differences depend on the pretreatment and age of the sample. These considerations should then lead us to some working model for the role of the modifiers.

Variation of Rates with Pretreatment, Age, and Modifier Concentration

Comprehension of the results requires us to look separately at (i) how rates in the first stage after each pretreatment vary with modifier concentration, and (ii) how the decrease in rate effected by the first high-temperature excursion depends on the deactivation brought about by the modifier.

The best measure we have of the extent to which the modifiers occupy the surface of the Pt particles is the H/Pt ratio (Table 1); this seems to show that the first addition both of TiO_2 and of Al_2O_3 produces the largest effect. However, the observed H/Pt

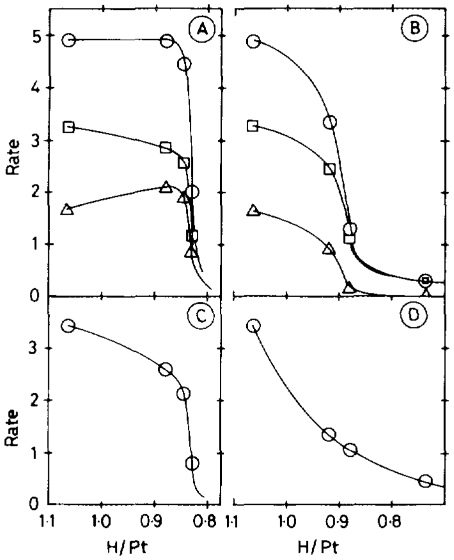

FIG. 7. Variation of rates of reaction of *n*-butane (A and B) and of propane (C and D) with modifier concentration as measured by H/Pt ratio; HTR pretreatment. (A) and (C), Al_2O_3-modified EUROPT-1. (B) and (D), TiO_2-modified EUROPT-1. Circles, total rate; squares, hydrogenolysis; triangles, isomerization.

ratio is not necessarily a true indicator of the amount of free surface, as all values exceed that expected for particles of mean size 1.8 nm, viz. ~0.6 for a 1 : 1 H/Pt_s stoichiometry. The discrepancy has been considered at length (*13*), and it has been concluded that not all the H_2 taken up is utilised in forming H–Pt bonds at the surface; some may be employed in breaking Pt–O–Si bonds at the interface with the support. It might therefore be more appropriate to subtract the measured decrease in H/Pt from 0.6 rather than from the values we find for EUROPT-1, to give truer estimates of free surface. This will not affect the shapes of the curves depicting the variation of rates with H_2 titre, and so the measured H/Pt values are employed unchanged in Figs. 7 and 8. These show that the addition of Al_2O_3 brings about, with either alkane, decreases in rate which are initially only slow, but the rates then decline precipitately when the H/Pt ratio falls below 0.8 to 0.85. Type of pretreatment has little effect on the shapes of the curves (compare Figs. 7 and 8). After HTR the isomerization rate actually increases, suggesting that Al_2O_3 creates new isomerization sites, either on or at the periphery of the metal particles. With TiO_2, on the other hand, the rates of both reactions are diminished from the outset, and the selective deactivation of isomerization is clearly seen.

It is evident from Tables 6 and 7 that the extent to which catalysts are deactivated by "carbon" deposition decreases as the modifier concentration is increased. Figures 9 and 10 show how the changes in rate correlate, and there are (all things considered) satisfactory inverse linear relations between the rate changes. This suggests a connection between the sites at which "carbon" deposition occurs and those to which the modifying species are attached.

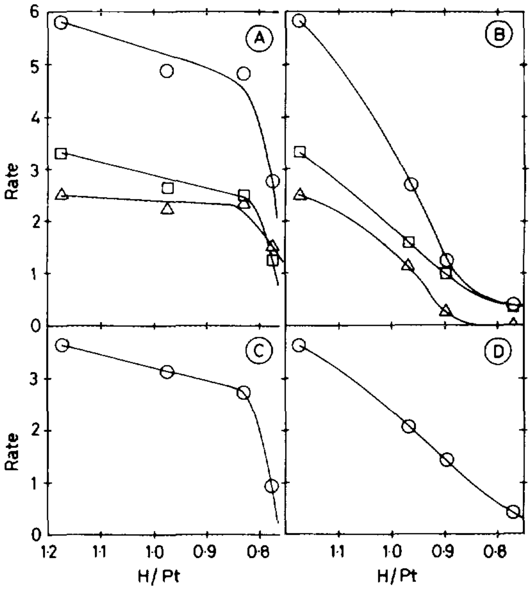

FIG. 8. Variation of rates of reaction of *n*-butane (A and B) and of propane (C and D) with modifier concentration as measured by H/Pt ratio; LTO/R pretreatment. (A) and (C), Al_2O_3-modified EUROPT-1. (B) and (D), TiO_2-modified EUROPT-1. Symbols as in Fig. 7.

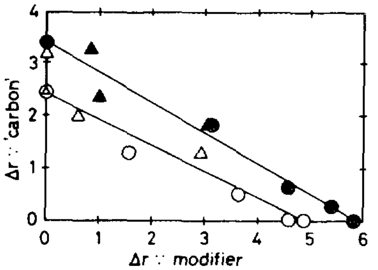

FIG. 9. Correlation between decrease in total rate of reaction of butane due to the modifier and the decrease due to "carbon" deposition. Open symbols, HTR; filled symbols, LTO/R. Circles, TiO_2; triangles, Al_2O_3.

Effects of the Variables on Selectivity Parameters

The initial deactivation experienced by all catalysts effects changes to other kinetic parameters, namely, to the incidence of two-part Arrhenius plots (Tables 3–7, Figs. 2 and 5), to the values of the activation energies and to product selectivities at 603 K. We consider the product selectivities first. As Fig. 6 shows, the initial deactivation leads to changes in S_2 and S_3 that are much greater at lower temperature (550–560 K) than at 603 K, but the latter is chosen as the standard temperature for comparison, partly for historic reasons (*10*) and partly because the value of S_1 after stage 1 is often immeasurably low below 560 K (see Fig. 6). The small but very consistent changes in product selectivities and the derived parameters F and T_3 can be summarised as follows. (i) As with rates, the changes are not progressive (Table 5). (ii) The changes are attributable solely to variations in the splitting parameter F, values of T_3 in various stages generally being within experimental error (Tables 5–7); the same was found with EUROPT-3 (*10*). (iii) With EUROPT-1 and the Al_2O_3-modified derivatives, F increases with stage number by ~3–5% (Table 6); with the TiO_2-modified catalysts, there is little change in F at the higher TiO_2 loadings (Table 7). The Type-I hydrogenolysis sites therefore have slightly *lower* values of F (but the same values of T_3) as those resistant to deactivation (Type-II): the opposite was found with EUROPT-3, where the effect was greater (*10*).

Effects of the Variables on the Linearity of the Arrhenius Plots

The occurrence of the "two-part" Arrhenius plot (Figs. 2 and 5) is dependent on stage number, and also on the presence of a modifier and on the alkane used, but *not* on the type of pretreatment or the concentration of the modifier (Tables 2–7). Thus with Al_2O_3-modified catalysts and propane (Table 3), the "two-part" effect is *only* shown in stage 1, while with TiO_2-modified catalysts it is seen in all stages (Table 4). Conversely, with the butane reaction, the effect is only seen *after* stage 1 with Al_2O_3-containing catalysts (Table 6), whereas with TiO_2-containing catalysts it is not seen at any time (Table 7). This apparently haphazard incidence of the occurrence of the "two-part" Arrhenius plot automatically eliminates the possibilities that it is either associated with the initial deactivation or due to some kind of diffusional limitation. This conclusion is strengthened by the fact that with butane the activation energies are consistently *higher* in the high-temperature range (Fig. 5 and Table 6). We are therefore left with the probability that these changes reflect a change in the composition of the adsorbed species and/or in the rate-determining step, but doubt whether further progress can be

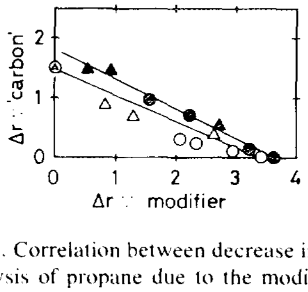

FIG. 10. Correlation between decrease in rate of hydrogenolysis of propane due to the modifier and the decrease due to "carbon" deposition. Symbols as in Fig. 9.

made without a full kinetic analysis (e.g., determination of orders of reaction above and below 600 K). Differences in activation energies shown between the unmodified and modified catalysts (e.g., Table 3) therefore need to be approached with caution, as they may arise from differences in surface coverages by the two reactants.

Effects of the Variables on Activation Energies

It is now necessary to analyse the extensive results (Tables 3, 4, 6, and 7) on activation energies for hydrogenolysis, to see what light they throw on changes in surface structure. A few preliminary comments are in order. First, the values quoted are in every case highly reliable (see Table 2) and differences of 5 kJ mol^{-1} or greater are certainly significant. Second, we may suppose that the value of the activation energy (although it is only an "apparent" value) carries valuable information concerning the energetics of the transition state for the rate-determining step, and hence the electronic state of the active centre.

Tables 3, 4, 6, and 7 record more than 85 values of activation energy for hydrogenolysis, and Table 8 a further 24 values for isomerization: many more were in fact recorded, but are not reported as we found it possible to average the values for stages 2 to 4. There are some quite remarkable consistencies with only a very few catalysts or individual measurements falling out of line. Let us deal with the principal exception first. The catalyst having the highest Al_2O_3 content ($Al/Pt_s = 18$) shows significantly higher activation energies than those with lower loadings, for both propane (Table 3) and butane (Table 6), in the case of the former (but not the latter) after both HTR and LTO/R. With this sole exception, general statements can be made which apply to all modifier contents.

(1) Activation energies for the reaction of propane are without exception higher than corresponding values for butane; for stabilised catalysts having either modifier, the ratio of the low-temperature values is close to 1.22, while for EUROPT-1 itself it is 1.25–1.30.

(2) Where a high-temperature activation energy can be identified, it is without exception lower than the low-temperature value with propane, but higher for butane.

(3) With propane, the low-temperature values for stages 2–4 are usually either the same as or less than those for stage 1; with butane they are consistently higher (by 10 to 20%).

(4) Values for butane show somewhat greater regularity than those for propane. For example, with butane, all low-temperature values for stage 1 (including those for EUROPT-1) are between 88 and 105 kJ mol^{-1}; all the low-temperature values for stages 2–4 are 117 ± 6 kJ mol^{-1}. With propane, the corresponding value is 144 ± 5 kJ mol^{-1} (i.e., 1.23 times greater).

Because of the greater regularity of the activation energies recorded for butane hydrogenolysis, discussion will focus first on these. They lead to the surprising conclusion that neither the form of pretreatment nor the presence, identity or concentration of modifier (with the single exception mentioned above) appears to affect activation energy, so *the rate changes must be chiefly a consequence of a reduction in the number of active centres.* Neither of the modifiers therefore causes any detectable change in the electronic composition of the Pt particles, such as might be reflected in activation energies. The only effect of any size is that associated with the initial deactivation, which causes the low-temperature activation energy for butane to increase to ~117 kJ $mole^{-1}$. This consistent increase in activation energy implies that it is more difficult to form the transition state from the reactive intermediate derived from the alkane in the presence of the "carbon" deposit than in its absence. The increase might be a result of the elimination of Type-I sites, or it might have its origin in a decrease in availability of bonding electrons at the free Pt atoms, occasioned by the withdrawal of electrons to form the multiple C–Pt bonds between the carbonaceous species and the surface. With propane the corresponding change is usually either small or in the opposite sense, perhaps because the extent of initial deactivation is less than with butane.

Kinetics of Skeletal Isomerization

It is with isomerization kinetics that the most dramatic effects are seen, and where the effects of stage number, pretreatment and of modifier are most clearly differentiated. Inspection of Tables 6–8 shows the following.

(1) In every case the isomerization selectivity S_i is lower in the second and subsequent stages than in the first; the decrease is most marked with TiO_2-containing catalysts after LTO/R. "Carbon" deposition therefore selectively blocks isomerization sites.

(2) LTO/R treatment always leads to an increase in S_i.

(3) Addition of Al_2O_3 leads in stage 1 to an increase in S_i which is either independent of Al_2O_3 concentration (after HTR) or increases slightly with it (after LTO/R).

(4) Addition of TiO_2 leads in stage 1 to a steady decrease in S_i following HTR or to a more rapid decrease after LTO/R.

(5) The different effects of Al_2O_3 and of TiO_2 on S_i at 603 K are associated with systematic changes in activation energy (Table 8): with Al_2O_3 values are 145 ± 15 kJ mol^{-1} in stage 1, rising to 230 ± 10 kJ $mole^{-1}$ in stages 2 to 4, while with TiO_2 they always decrease from a maximum, usually at the lowest TiO_2 loading, to values lower than those for EUROPT-1.

Construction of a Structural Model

It is our task now to try to devise a model to account for the principal features of the experimental results; this requires us to deduce the probable locations of the modifiers under the various conditions employed.

Some of the trends in performance shown by the modified catalysts (e.g., with pretreatment and with age) are qualitatively similar to those shown by EUROPT-1, and so we may begin by considering the behaviour of the parent material. The principal effect is that produced by the initial deactivation, which causes increases in activation energies for both processes, and a decrease in S_i. We suppose that heavily dehydrogenated and unreactive forms of the reactant alkanes, formed in the first high-temperature excursion, block the Type-I sites which consist mainly of high coordination number Pt atoms (*10*), which are the preferred locations for skeletal isomerization. It must be stressed that these Type-I sites are a very distinct subset of the whole under the conditions of our experimentation, but their proportion is determined by the nature of the alkane, the alkane/H_2 ratio and the maximum temperature attained. The resistant Type-II sites chiefly comprise atoms of lower coordination number, and here (because of a different electronic environment) the transition states are less easily formed and the activation energies for both processes are higher.

There is now a great deal of evidence in support of the view that distinctly different roles can be assigned to high- and low-coordination-number Pt atoms, the former being active in isomerization, but readily suffering carbon deposition, and the latter being active for hydrogenolysis and remaining fairly clean. This consensus has emerged from studies of single Pt crystals (*14*), of particle size effects (*15–17*) and of the consequences of "carbon" deposition (*18–20*). However, some refinement of this simple view is needed to explain why the rates of *both* reactions are decreased by "carbon" deposition and that both reactions still proceed on the partially deactivated catalyst.

It has been suggested on the basis of Debye function analysis of X-ray diffraction patterns obtained with EUROPT-1 that the particles are well described as being cubooctahedra having predominantly 55 atoms (*21*), and this suggests a possible basis for an explanation. Atoms at the surface of a perfect cubo-octahedron have coordination numbers of 9 in (111) planes, 8 in (100) planes, 7 in edges, and 6 in apices. We propose that atoms within either plane can participate in sites for isomerization, but that those in (111) planes, where the atoms are most densely packed, are inactivated by "carbon" deposition: the alkane-derived species also overhang or otherwise block some of the adjacent edge atoms which are hydrogenolysis sites, and so rates for both reactions are decreased. These Type-I sites constitute about half the total, which is roughly as expected for a cubo-octahedron. Type-II sites comprise atoms in and adjacent to (100) planes, and these remain active for both reactions. This assignment is consistent with the observation (*14*) that internal C–C bond-breaking is more favoured over Pt(100) than over Pt(111). Statistically one would expect most particles not to possess the precise number of atoms needed for a perfect crystal form, having instead an incomplete outer shell. This possibility complicates any interpretation, but it may be that atom mobility during reduction, coupled with the greater stability of the perfect forms, leads to their predominating in the finished catalyst.

There are clear indications that some at least of the TiO_2 is in contact with the metal particles, because the total rate is decreased (Tables 4 and 7) and in particular the isomerization rate is lowered (Figs. 7 and 8). However, activation energies for hydrogenolysis are unchanged, although the catalysts still suffer deactivation (except at the highest Ti/Pt_s ratio after HTR): the TiO_2 therefore brings no electronic effect over and above that caused by the carbonaceous species which force the reaction to Type-II sites. However, it effectively blocks isomerization sites both for butane and hexane; we therefore suppose that TiO_2 (or more probably the TiO^+ ion) occupies positions on both (111) and (100) planes, giving marked decreases in isomerization rates and selectivity, but also of necessity blocking some of the edge atoms active in hydrogenolysis. "Carbon" deposits then fill the remaining Type-I sites not occupied by TiO^+ ions, thus giving rise to the inverse correlations shown in Figs. 9 and 10. In stages 2 to 4 at the highest Ti/Pt_s ratio (Table 7), some 90–95% of all sites are covered either by TiO^+ or by "carbon," the few remaining sites, perhaps at the apices, being active only for hydrogenolysis. We note that a model based on reduction of the mean size of Pt ensembles in low-Miller-index planes would lead to a selective *lowering* of hydrogenolysis selectivity, which is not what is found, and similarly the elimination of small Pt particles by total encapsulation would have the same effect (*16, 18*).

Thus although the results in some ways resemble those shown by Pt/TiO_2 catalysts (*3, 4*), there is no evidence for marked lowering of H_2 chemisorption capacity, which may therefore be caused by Ti^{3+} ions lying below or around the metal particles, and similarly no effect on transition state energetics, which might also reflect electronic changes. Simple site-blocking seems to be an adequate model to describe what we see.

When Al_2O_3 is used as modifier, much clearly exists on the support, and the metal is little affected (except in respect of H_2 chemisorption) until the Al/Pt_s ratio reaches the very high value of 18 (Figs. 7 and 8). Activation energies do not change, and no electronic modification of the metal particles is evident; deactivation still occurs after stage 1 (Tables 3 and 6). That there is no fundamental difference between the effects of TiO^+ ion and of AlO^+ ion (arising from Al_2O_3) is shown by the concordance between the points for the two modifiers in Figs. 9 and 10. The distinction between them lies in (i) a lower tendency for AlO^+ to interact with the metal surface than is shown by TiO^+, so that a higher ratio of Al/Pt_s is needed before significant effects are seen, and (ii) the AlO^+ prefers to decorate the edge atoms in preference to those of higher coordination number, thus causing S_i to increase. The lack of correspondence between the decrease in rate and the lowering of the H/Pt ratio may reflect both the size of the active centre required for reaction, and the inability of H_2 to titrate correctly the number of free Pt atoms, due perhaps to spillover onto the Al_2O_3.

CONCLUSIONS

The prospect of promoting, selectively poisoning or, more generally, modifying supported metals to improve their selectivity is attractive by reason of the ease with which the nature and concentration of the modifier can be changed. To make such alterations to one standard catalyst is even more useful, since comparisons can then be meaningfully drawn between the materials thus made. However, we cannot be certain in advance that adding a modifier to a Pt/SiO_2 or similar catalyst will produce the same effects as using that modifier as the support. Although there are now numerous reports in the literature of the modification of supported metals as we have practised here (*22–26*), there has been no previous study of our particular systems. The Pt–TiO_2/Al_2O_3 system has, however, been described and used for alkane transformations (*27*).

We have argued previously (*1, 22, 24*) that the controlled addition of the modifier also permits subtler distinctions to be drawn between the various possible roles which it might adopt in the context of SMSI, if used as support. Specifically, in our example, we can only have TiO^+ species on the surface or at the periphery of the Pt particles: no possibility exists of Ti^{3+} ions beneath the particle affecting its shape or electronic structure. This may explain the absence of effects on activation energies, and on H_2 chemisorption behaviour.

Most previous studies of the effects of carbon deposition (*18, 19*), of particle size (*16, 17*), and of temperature and H_2 pressure (*20*) have been conducted with *n*-hexane or other molecules capable of reacting in a multiplicity of ways, and in such ways that it is difficult to disentangle the separate contribution of each variable. Although propane and butane lack this rich variety of reaction possibilities, we feel that, at this stage of our understanding of structure–activity relations in supported metals, it is preferable to clear the ground by examination of simpler reactions using catalysts and procedures capable of giving well-controlled and reproducible behaviour.

We stress the well-behaved character of the Pt–TiO_2/SiO_2 system, in terms of the reproducibility of the phenomena we have described. Further work with molecules better able to reveal the precise nature and structures of the active centres, and more exact investigation of reaction kinetics, is required before the full benefits of modification procedures can be appreciated. It appears that Al_2O_3 is more tempted to interact with the SiO_2 than with the Pt particles, and is therefore somewhat less useful as a modifying agent. The literature (*28, 29*) suggests too that the interaction of modifying species such as TiO_x with different metals varies considerably; even Al_2O_3 alters the behaviour of a Rh/SiO_2 catalyst (*26*). The further development of techniques (*4, 5*) designed to place the modifier directly on the metal should extend the scope of the modification of supported metals in directions having practical as well as theoretical interest.

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