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Transformations of n-Hexane over EUROPT-1: Fragments and C_6 Products on Fresh and Partially Deactivated Catalyst

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The reactions of n-hexane have been studied on 6.3% Pt/SiO_2 (EUROPT-1) at different hydrogen and n-hexane pressures, and at 543–633 K, over fresh catalyst and over catalysts deactivated by long runs. Turnover numbers are compared with literature data: the differences are attributed to hydrogen pressure effects. Deactivation influences first of all, selectivity. In addition, the 'depth' and 'pattern' of hydrogenolysis have been determined. At low temperature multiple splitting seems to be favoured. Isomerization gives predominantly 3-methylpentane. At medium temperatures, isomerization, C_5-cyclization and internal splitting prevail; their ratio is controlled by the hydrogen pressure. The ratio of 2-methylpentane to 3-methylpentane is related to the ratio of internal to terminal rupture. Terminal splitting prevails at highest temperature. Aromatization increases with temperature but seems to be independent of the other reactions. The results are interpreted in terms of three different surface states. These correspond to Pt—H, Pt—C—H and Pt—C under increasing severity of conditions.

EUROPT-1 is a 6.3% Pt-on-silica catalyst which has been intensively studied in several laboratories and can be regarded now as a well characterised catalyst.[1–5] Studies on its reactivity in hydrocarbon transformations included among others, structure-sensitive, 'skeletal' reactions of alkanes; a brief summary of these data (some of them otherwise unpublished) has been given by Bond *et al.*[6]

Most of the results obtained with C_5–C_7 alkanes have been carried out in large hydrogen excess, the ratio of hydrogen-to-hydrocarbon pressure being between 9 : 1 and 260 : 1 [*cf.* table 4 in ref. (6)]. We reported recently[7] the dependence of turnover numbers and selectivities of n-hexane reactions as a function of the hydrogen and n-hexane pressure, $p(H_2)$ and p(nH), respectively in the temperature range 543–633 K. The ratio $p(H_2)$ to p(nH) varied between 1.5 : 1 and 96 : 1. The temperature range was somewhat higher, and the hydrogen excess lower than the typical values reported in ref. (6). Hence we found fewer fragments and isomers, and more methylcyclopentane and benzene. At higher temperatures and p(nH) values, considerable amounts of alkenes were also observed.

The plotting of initial selectivities (extrapolated to zero conversion, X) as a function of conversion values, can be an indication of primary and secondary products.[8] Accordingly, alkenes have been found to be likely exclusive primary products at low hydrogen and higher hydrocarbon pressures whereas the catalyst showed an intrinsic initial activity for isomerization and aromatization at high $p(H_2)$ and lower p(nH).[9] The primary character of hydrogenolysis remained undecided. On clean Pt, in turn, they were assumed to be the only reaction products.[10,11]

In addition to results on hydrogenolysis activity and selectivity,[7] the distribution of various fragments may offer a host of information for possible reaction routes and active sites. Bond and Xu Yide[12] reported Arrhenius parameters for the hydrogenolysis of ethane, propane and n-butane on EUROPT-1 as well as the probability of various C—C bond breaking in n-butane, which is 0.25–0.42 for the internal C—C bond. Similar values were observed on $Pt\text{-}Re/Al_2O_3$ and much lower ones on Pt/Al_2O_3.[13] That probability increased with the temperature and showed a rather marked dependence on the pretreatment and/or on the actual state of the catalyst with 'thermal cycling' without regeneration. Tendencies analogous to those reported for Pt/SiO_2 were also found over various Pt/C catalysts.[14] Isomerization of butane was not important as compared to hydrogenolysis.[12–14]

Apart from the more rigorous kinetic treatments applicable for lower alkanes,[13,14] various parameters were suggested for characterizing catalytic hydrogenolysis. For example, a 'fission parameter' M_f has been defined.[15,16] Its value is 1 with terminal splitting while $M_f < 1$ with multiple and $M_f > 1$ with internal or random splitting. The 'fragmentation factor', ζ, gives the average number of fragments per parent molecule broken up.[17] Pt was found to be essentially a single hydrogenolysing metal, *i.e.* $\zeta \approx 2$. Under such conditions it is possible to estimate whether the rupture of the molecule occurs in a random way or some positions are preferred. Leclercq *et al.*[18] defined an ω parameter being the ratio of the actual rate of rupture in each position to the random rate of rupture.

The molecules of hexane or heptane did not break evenly: the splitting of a C_3—C_4 bond was preferential in high hydrogen excess over various single crystal planes,[19] Pt-black,[20] Pt/SiO_2 [15,16] and Pt/Al_2O_3.[18] Hydrogen pressure changes influenced the ω-values rather markedly: at lower $p(H_2)$ terminal splitting dominated but at higher $p(H_2)$, internal splitting dominated.[21,22] The rupture of C_2—C_3 bond was never preferred.

It seemed worth investigating these parameters for Pt/SiO_2 under conditions analogous to those reported earlier.[7] In addition to runs of fixed time (5 min), those of longer duration were added; here the gradual deactivation and the concomitant selectivity changes could be followed. Since isomerization and hydrogenolysis have been reported to be related processes,[14,23,24] the ratio of isomers, 2-methylpentane/3-methylpentane (2MP/3MP) was also investigated, in conjunction with the parameters of hydrogenolysis. This isomer ratio seemed to be rather sensitive to SMSI phenomena. In this way we expected to obtain

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information on the possible state of Pt in Pt/SiO_2 during reactions and the likely active sites for various processes.[22,25,26]

Experimental

The experimental details have been described earlier.[7] Briefly, a static-circulation system was filled with a mixture of n-hexane and hydrogen of different pressures. The value of p(nH) was 5–80 Torr, and $p(H_2)$, was 60–480 Torr. The same charge of catalyst was used and regenerated with air and subsequent hydrogen treatment.[7] Runs of 5–50 min were carried out. Details on activity and selectivity measurements are given together with the corresponding results. The mixture was analysed by GC on a non-polar capillary column;[7] the evaluation was based on the concentrations measured. Turnover numbers (T.O.N.) were, however, calculated from the amount of parent hexane molecules transformed. The ω-values for bond breaking in positions 1, 2, 3 were calculated by summing up the fragments C_3, C_4, C_5 and relating their respective ratio to the average of this value. This way, a subsequent hydrogenolysis of these fragments to smaller ones was left out of consideration.

Results

Activity

Table 1 summarizes our results for overall activities expressed in turnover numbers (T.O.N.). The experiments reported in ref. (7) were used for this table, with two corrections: for the sake of comparison with ref. (6), the values are given in units of h^{-1} instead of s^{-1} and the number of surface Pt atoms has been adjusted according to ref. (6) (dispersion 60%); being thus 1.20×10^{18} Pt_{surf} on our 10 mg catalyst.

Maxima are observed as a function of $p(H_2)$ at lower temperatures and a monotonic increase at higher ones. The initial steeper increase of T.O.N. as a function of p(nH) levelling out somewhat at higher hexane pressures may indicate a Langmuir–Hinshelwood behaviour.[6]

Selectivity

Selected results on selectivity are presented in table 2 with an emphasis on $T = 603$ K often used as a reference temperature in our laboratory.[7,21,25,27] Extreme $p(nH) : p(H_2)$ ratios are shown at other temperatures together with one set at constant pressure ratios (1 : 12).

Table 1. Turnover numbers/h^{-1} of overall n-hexane transformation

		$p(H_2)$/Torr			
T/K	p(nH)/Torr	60	120	240	480
543	5	17.7	17.9	12.2	5.6
	10	32.7	39.8 (25)[a]	25.5	11.1
	20	69.7	67.7	44.6	22.2
	40	77.4	73.0	76.8	47.8
	80	—	—	—	87
573	5	20.8	31.3	32.3	26.4
	10	38.4	59.7 (37)[a]	75.9	59.8
	20	82.3	98.9	102	63.7
	40	103.3	169	176	90
	80	—	—	—	105
603	5	22.3	42.2	63	59
	10	46.5	81.7[b] (52)[a]	121	125
	20	122	133	190	191
	40	153	239	299	308
	80	—	—	—	409
633	5	27.3	43.4	75.7	113
	10	51.9	77.2 (59)[a]	135	176
	20	138	139	259	341
	40	161	270	445	631
	80	—	—	—	862

[a] In brackets: results from the first run on fresh catalyst. [b] Result of one single run in a series (543–633 K).

High temperature and low hydrogen pressure favour the formation of benzene and alkenes.[7] These latter consist of almost exclusively n-hexene isomers; branched hexenes (isomers with double bond adjacent to the tertiary C atom such as 2-methylpent-2- or-4-enes or 3-methylpent-2-enes) are present in minor amounts at high temperature and high p(nH) only. At constant $p(nH) : p(H_2)$ ratio, the methylcyclopentane (MCP) selectivity is almost constant; this compound is the main product in most cases shown. Isomers have nearly constant selectivity at 543 K but the increase of reactant pressure favours their production at 633 K. As a rule, high p(nH) favours MCP formation, and low p(nH) favours isomerization.

The ratio of products of skeletal isomerization, 2-methylpentane to 3-methylpentane (2MP/3MP) may give useful information on the possible isomerization pathway(s) and intermediates.[25,28–30] 2MP/3MP is, as a rule, near to or just above 2, *i.e.* to the statistical value expected with random rupture of the assumed C_5-cyclic surface intermediate. At high T and low hydrogen pressure and also at low T and high n-hexane pressure, this ratio drops even below unity. This apparently similar deviation under opposite experimental conditions is likely to be attributed to different reasons. The peculiar variations of hydrogenolysis selectivity (*e.g.* minima as a function of temperature[7,23]) point to more than one type of hydrogenolysis mechanism.

Characteristics of Hydrogenolysis

Table 3 presents turnover numbers for hydrogenolysis (expressed as n-hexane molecules split up) as well as fragment distribution under conditions analogous to those of table 2. It is seen that (i) the increase of overall pressure increases the turnover number; at lower temperature this increase is higher, at higher temperatures lower than the overall increase of turnover number with pressure (*cf.* table 1); (ii) the fragment distribution does not depend very much on the conditions, except for an enhanced methane formation at both low T and high $p(H_2)$ and high T and low $p(H_2)$ [compare data obtained at $p(nH) : p(H_2) = 40 : 60$ with increasing T and 5 : 480 at 543 K].

Selected results of hydrogenolysis parameters are shown in tables 3 and 4. Since the product distribution is rather insensitive to p(nH), results obtained at $p(nH) = 10$ Torr have been collected in table 4. The increase of $p(H_2)$ does not bring about a dramatic increase in turnover numbers.

The values of $\zeta > 2$ indicate that the assumption of 'single rupture' is, at most, an approximation. The M_f values show a random or internal hydrogenolysis; they are lower than the values reported[16] for another Pt/SiO_2 which are above 10. The values, in turn, indicate that the fragmentation is not perfectly random: the rupture between C_3–C_4 (giving two propane molecules) is preferred, as was also found with Pt-black at sufficiently high hydrogen pressures.[20,22]

Since $\zeta > 2$ even at lowest temperatures and conversion values, it is not likely that the additional fragments were due to secondary hydrogenolysis of larger fragments; instead, we assume that a small fraction of molecules undergoes multiple or sequential terminal hydrogenolysis during one sojourn on the surface. Considering also other data obtained with Pt-black,[31,32] we suggest that under hydrogen-rich conditions (*cf.* results at 5 : 480), a slight *multiple* fragmentation is superimposed on single rupture.

Under hydrogen-deficient conditions (*cf.* results at 40 : 60 at higher temperatures), the M_f values drop drastically; at the same time, the ω_1 value also increases above unity: terminal

Table 2. Product selectivity from n-hexane under various conditions

T/K	ratio, p(nH) : p(H$_2$)	product selectivity (%) $<C_6$	isomer	MCP	alkene	benzene	2MP/3MP
543	40 : 60	3.7	14.8	46.4	28.9	6.2	0.85
	5 : 60	5.2	33.7	52.4	—	8.6	2.21
	10 : 120	6.9	40.1	49.9	—	6.1	2.40
	20 : 240	13.4	32.7	49.5	—	4.6	1.93
	40 : 480	25.7	24.3	48.2	—	2.2	0.83
	20 : 480	30.0	23.2	44.6	—	2.7	1.12
	10 : 480	33.2	24.0	39.0	—	2.6	1.75
	5 : 480	41.1	25.2	31.7	—	2.4	2.10
573	40 : 60	8.1	11.0	37.8	35.6	7.4	0.81
	5 : 60	11.4	22.7	50.7	3.5	11.8	1.66
	10 : 120	9.3	34.3	46.5	1.5	8.3	2.14
	20 : 240	11.2	37.3	43.4	1.5	6.7	2.23
	40 : 480	20.2	26.6	47.5	1.0	4.8	1.52
	5 : 480	22.7	48.6	21.9	—	6.8	2.66
603	40 : 60	10.0	5.8	19.7	52.4	12.1	0.69
	20 : 60	13.5	6.0	21.3	45.2	13.7	1.22
	10 : 60	15.1	9.3	32.0	26.1	16.7	1.44
	5 : 60	18.6	13.0	38.0	10.3	19.0	1.66
	10 : 120[a]	13.4	24.8	41.4	8.0	12.4	1.85
	20 : 240	12.2	31.6	39.5	7.5	9.1	2.10
	40 : 480	14.5	34.8	34.7	9.3	6.9	2.19
	20 : 480	15.0	43.1	29.3	5.4	8.0	2.33
	10 : 480	16.7	52.3	20.9	0.5	9.5	2.37
	5 : 480	19.6	54.5	14.7	0.2	11.0	2.27
633	40 : 60	12.0	2.7	6.4	62.6	16.2	0.47
	5 : 60	27.9	4.7	15.2	20.6	27.9	1.42
	10 : 120	23.0	13.8	30.8	11.3	19.4	1.66
	20 : 240	16.4	23.7	36.2	9.9	16.9	1.85
	40 : 480	15.6	33.9	33.5	6.6	10.0	2.09
	5 : 480	23.9	46.0	13.4	0.7	15.8	1.91

[a] One single run in the series; average of several runs, see table 6.

rupture prevails. This is also supported by the fragment distribution (table 3): the monotonic concentration drop from C_1 to C_5 (40 : 60 at higher T) must have originated from a sequential terminal hydrogenolysis while higher methane values, *e.g.* at 543 with 5 : 480 are concomitant with $C_3 > C_2$ formed. This way one can distinguish real multiple and rapid sequential terminal rupture which, ultimately, gives also methane.

Table 3. Distribution of hydrogenolysis products

T/K	ratio p(nH) : p(H$_2$)	T.O.N. to fragments[a] /h^{-1}	fragment distribution (%) C_1	C_2	C_3	C_4	C_5	ζ
543	40 : 60[b]	1.46	27	20	23	17	13	2.25
	5 : 60[b]	0.46	28	22	22	16	12	2.30
	10 : 120[c]	1.40	38		30	19	13	2.09
	20 : 240	3.09	28	19	27	15	11	2.29
	40 : 480	6.65	29	17	29	14	11	2.14
	5 : 480	1.24	36	16	27	12	9	2.49
573	40 : 60	3.73	34	19	19	14	14	2.35
	5 : 60	1.10	35	21	19	13	12	2.43
	10 : 120	2.54	29	21	23	15	12	2.31
	20 : 240	5.37	27	20	26	16	11	2.27
	40 : 480	8.60	32	18	26	14	10	2.39
	5 : 480	3.03	27	19	26	16	12	2.26
603	40 : 60	6.32	45	15	16	11	13	2.58
	5 : 60	2.24	45	19	15	10	11	2.70
	10 : 120	4.91	35	20	20	13	12	2.43
	20 : 240	10.90	29	20	24	15	12	2.29
	40 : 480	21.60	26	19	27	16	12	2.24
	5 : 480	6.64	28	20	24	16	12	2.27
633	40 : 60	6.71	62	13	10	6	9	3.22
	5 : 60	2.54	62	14	10	6	8	3.26
	10 : 120	7.84	45	17	16	10	12	2.66
	20 : 240	19.60	34	19	21	14	12	2.40
	40 : 480	47.70	27	20	25	16	12	2.26
	5 : 480	13.40	32	19	22	14	13	2.34

[a] Calculated as n-hexane transformed to fragments (*i.e.* considering the mole number increase during fragmentation). [b] Values obtained at 20 min reaction time, due to too low conversion at 5 min. [c] No reliable separation of C_1–C_2 owing to low absolute concentrations: was estimated assuming $C_1 = C_2$.

Table 4. Characteristics of n-hexane hydrogenolysis

T/K	ratio p(nH) : p(H$_2$)	T.O.N.[a] /h^{-1}	ζ^b	$M_f{}^b$	ω_3	ω_2	ω_1
543	10 : 60	0.89	2.13	—[c]	1.33	1.00	0.66
	10 : 120	1.36	2.09	—[c]	1.45	0.93	0.62
	10 : 240	1.71	2.29	6.09	1.50	0.88	0.62
	10 : 480	1.89	2.42	5.31	1.66	0.79	0.55
573	10 : 60	1.75	2.45	4.95	1.35	0.87	0.78
	10 : 120	2.54	2.31	6.67	1.38	0.94	0.69
	10 : 240	3.14	2.21	8.10	1.50	0.93	0.66
	10 : 480	5.84	2.21	8.39	1.49	0.88	0.63
603	10 : 60	2.89	2.67	3.22	1.28	0.77	0.96
	10 : 120	4.41	2.43	5.04	1.35	0.85	0.79
	10 : 240	7.40	2.30	6.78	1.39	0.90	0.71
	10 : 480	10.30	2.23	7.93	1.43	0.90	0.66
633	10 : 60	4.02	3.23	1.64	1.21	0.69	1.10
	10 : 120	7.84	2.66	3.29	1.27	0.81	0.91
	10 : 240	11.8	2.42	5.13	1.35	0.85	0.79
	10 : 480	17.2	2.29	6.57	1.38	0.87	0.70

[a] See footnote [a] in table 3. [b] Definitions

$$M_f = \Sigma C_i(n-i)/C_1 \qquad \zeta = \sum_{i=1}^{n-1} C_i \Big/ \sum_{i=1}^{n-1} \frac{i}{n} C_i .$$

[c] Owing to low conversion, the separation of methane and ethane was not complete, therefore M_f could not be calculated. For calculating ζ, the two fragments were taken to be equal. Even if no ethane had been present, ζ would not have exceeded 2.30.

Deactivation and Regeneration of the Catalyst

We selected a reference set of conditions, namely p(nH) : p(H$_2$) = 10 : 120, 5 min runs after standard regeneration.[7] Table 5 shows a fair reproducibility in activity and an even better one in selectivity and in various derived ratios. The only really large spread of data is observed in the alkene selectivity.

Deactivation was studied in runs of 50 min with sampling at 5, 20, 35 and 50 min time-on-stream, at p(H$_2$) = 60 Torr at varying p(nH) and T; also with p(nH) = 10 Torr at 603 K and varying p(H$_2$). The *activity vs.* time was not linear any more, as shown by the decreasing distances between data on the X-axes in fig. 1 and 2 (corresponding to equal sampling times). The *selectivities* [fig. 1(A) and 1(B)] at low and high p(nH) : p(H$_2$) ratios indicate also that the role of alkenes can be different.[9] While benzene, MCP and isomers (and, of course, alkenes) seem to be possible primary products at at ratio of 5 : 60 [fig. 1(A)], this can be stated for alkenes at a ratio of 40 : 60 [fig. 1(B)] only with, perhaps, some primary isomerization and aromatization at lowest temperatures.

Fig. 2 shows the selectivity variations down to low conversions, including also another set of results.[33] The averages of table 4 fit well to the curves; also, the reproducibility between runs carried out in different times and with catalysts of different past history is fair enough, or, with MCP, benzene (Bz) and isomers, even good. Higher alkene and lower hydrogenolysis selectivities are concomitant and *vice versa.*

Fig. 3 shows fragmentation characteristics for deactivation runs. The lower part of the figure confirms that both high and low p(nH) : p(H$_2$) ratios lead to enhanced hydrogenolysis selectivity. The composition of the fragments is, however, quite different. Whereas at increasing hydrogen pressure (and at low temperature: data at 543 K) a typical internal rupture is indicated by the high M_f values (upper half of fig. 3), under hydrogen-deficient conditions, M_f approaches unity, *i.e.* terminal hydrogenolysis takes place. This becomes more pronounced as the time-on-stream increases.

After deactivation at 603 K with runs of 50 min, test runs under reference conditions were carried out without regeneration (table 6). Depending on the conditions of previous runs, the catalyst retained 23–44% of its original activity. Previous runs with more hydrocarbon and less hydrogen present caused a more severe deactivation. The selectivity pattern changed more markedly than the activity: with almost identical aromatization selectivity, that of isomerization dropped

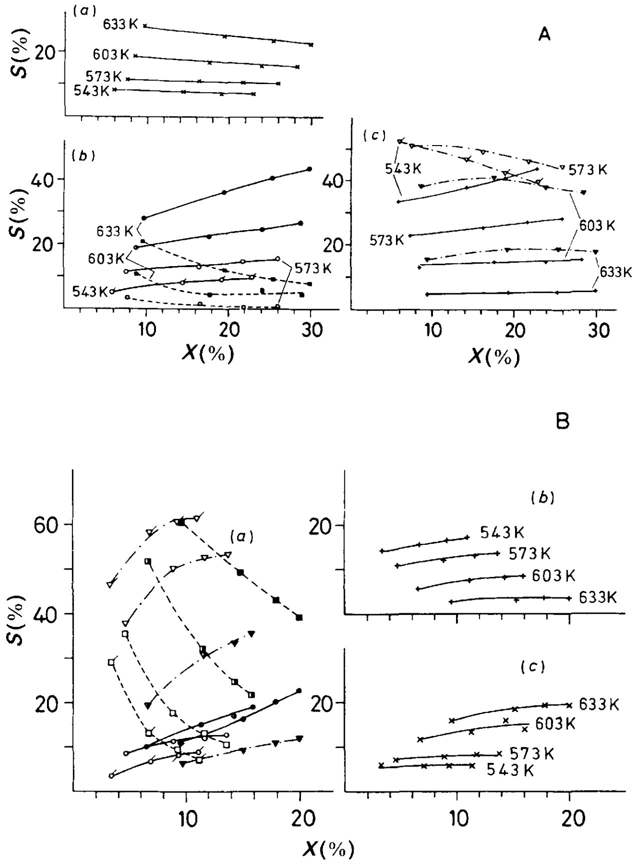

Fig. 1. Selectivity of various product classes formed from n-hexane over 6.3% Pt/SiO$_2$ as a function of the overall conversion. A: p(nH):p(H$_2$) = 5:60. (*a*) Benzene, (*b*) fragments (full line); alkenes (dashed line). (*c*) Isomers (full line); MCP (dashed-dotted line). B: p(nH):p(H$_2$) = 40:60. (*a*) MCP, triangles and dash-dotted line; alkenes, squares and dashed line; fragments, circles and full line. Flagged symbols: 543 K; empty symbols: 573 K; half-filled symbols: 603 K; filled symbols: 633 K. (*b*) Isomers. (*c*) Benzene.

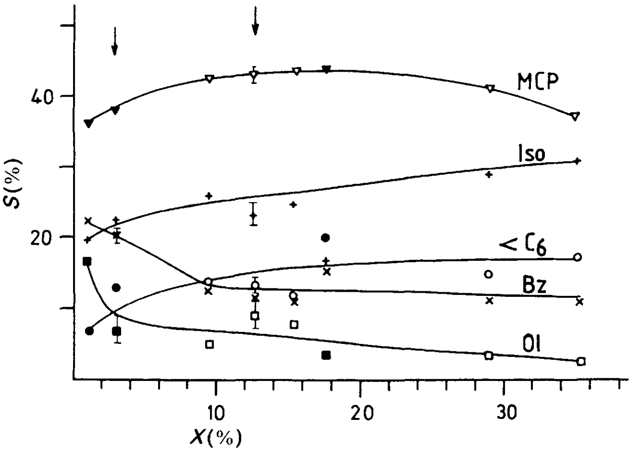

Fig. 2. Selectivity of various product classes as a function of the overall conversion. T = 603 K; p(nH):p(H$_2$) = 10:120. Shaded points have been taken from another series.[34] Data denoted with arrow are averages: that at $X \approx 3\%$, of 12 experiments; that at $X \approx 13\%$, of 22 experiments (*cf.* table 5.) Error bars are shown, otherwise the standard deviation is about the same as the size of the symbol.

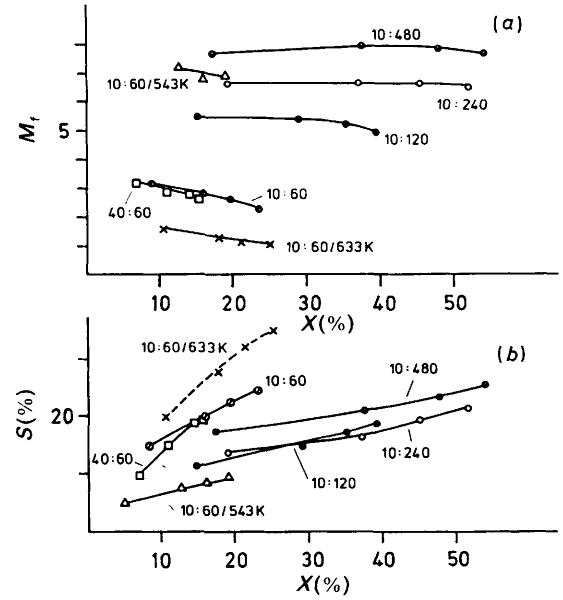

Fig. 3. Hydrogenolysis selectivity (within the overall conversion) and the fission parameter, M_f as a function of the overall conversion for various n-hexane-to-hydrogen ratios. $T = 603$ K, unless otherwise stated.

to less than a half, that of C_5-cyclization, to $\frac{3}{4}$ of its original value. Aromatization is deactivated in proportion to the overall activity, whereas the formation of saturated C_6 products is deactivated selectively. A two or fourfold increase in olefin selectivity means that the absolute values of alkene yields remained almost unchanged. This may be due to two reasons: first, the further reactions of alkenes are hindered over a deactivated catalyst; second, the above-mentioned 'mechanism changeover' means that over a more carbonized catalyst, a higher relative fraction of molecules react to form alkenes as primary products. A slight increase of hydrogenolysis selectivity concomitant with changes in hydrogenolysis parameters points to the direction discussed above: a more pronounced terminal splitting on deactivated catalysts is indicated by ζ, M_f and the increased ω_1 values (ω_1 may be equal to or higher than ω_2).

The seven samples shown here do not differ from each other drastically: they all show a selectivity and hydrogenolysis pattern typical of a deactivated catalyst, even though the residual activity was 25 or 45% of the original value. The reverse is also true. Even if regeneration could not restore the activity completely (*e.g.* pretreatment, 40 : 60, activity after regeneration: 77% of the reference value); all the characteristics were close to those given in table 5.

Correlation between Hydrogenolysis and Isomerization Pattern

Because of the possible correlation between internal hydrogenolysis and isomerization,[13,23,24,30,32] it seemed worthwhile attempting to correlate the ratio of various fragments to that of the isomer ratio, 2MP/3MP. Fig. 4 shows a distinct correlation between the ratio of internal to terminal rupture and the ratio 2MP/3MP. Data obtained under various conditions represent different ranges. As a rule, both ratios decrease with decreasing hydrogen pressure.

The anomalous low 2MP/3MP ratios observed at low temperatures and high n-hexane pressures, deviate from the general correlation (flagged points in fig. 4). This is the more significant the higher the hydrogen pressure and the lower the temperature. These low ratios must be caused by another reason than those observed at low $p(H_2)$ and high T.

Table 5. Reaction of n-hexane under reference conditions[a]

conversion (%)[b]	12.84 ± 1.22 (9.5%)
selectivity (%)	
$<C_6$	13.44 ± 0.76 (5.6%)
isomer	23.00 ± 1.47 (6.4%)
MCP	42.63 ± 1.06 (2.5%)
alkenes	8.73 ± 1.98 (22.7%)
benzene	11.88 ± 0.32 (2.7%)
2MP/3MP	1.87 ± 0.04 (2.1%)
ζ	2.42 ± 0.02 (0.8%)
M_f	5.04 ± 0.22 (4.4%)
ω_3	1.34 ± 0.02 (1.5%)
ω_2	0.87 ± 0.02 (2.3%)
ω_1	0.78 ± 0.02 (2.8%)

[a] $p(nH) = 10$ Torr, $p(H_2) = 120$ Torr: average of 22 runs of 5 min over regenerated catalysts. The relative standard deviations are given in brackets. [b] From effluent analysis (100%–n-hexane %). The value of corresponding T.O.N. is 72 h^{-1}. [c] The sum does not give 100%. The rest (0.31%) is cyclopentane which was not added either to the fragments ($<C_6$) or to C_5-cyclics.

Table 6. Test runs with n-hexane under reference conditions over deactivated catalysts[a]

	previous runs at 603 K for 50 min at $p(nH) : p(H_2)$						
	5 : 60	10 : 60	20 : 60	40 : 60	10 : 120	10 : 240	10 : 480
conversion (%)	4.66	4.59	3.02	3.36	4.96	5.45	5.70
residual activity (%)[b]	36.3	35.8	23.5	26.2	38.6	42.5	44.4
selectivity (%)							
$<C_6$	18.1	17.9	23.2	18.8	17.3	17.7	18.8
isomer	10.3	9.2	9.6	9.3	10.7	13.0	11.8
MCP	31.8	29.2	30.8	27.4	33.9	34.3	33.9
alkene	27.5	31.4	22.2	33.6	26.2	21.9	23.4
benzene	12.2	12.4	14.2	11.9	12.1	13.1	12.1
2MP/3MP	1.18	1.10	0.93	1.00	1.30	1.45	1.39
ζ	2.48	2.51	2.56	2.54	2.47	2.41	2.41
M_f	3.85	3.70	3.53	3.48	4.06	4.47	4.40
ω_3	1.17	1.15	1.18	1.15	1.21	1.23	1.19
ω_2	0.92	0.88	0.86	0.92	0.89	0.89	0.89
ω_1	0.92	0.97	0.96	0.92	0.89	0.89	0.94

[a] Reference conditions: see table 5, no regeneration between previous run and test run. [b] Expressed in % conversion measured over regenerated catalyst (table 5).

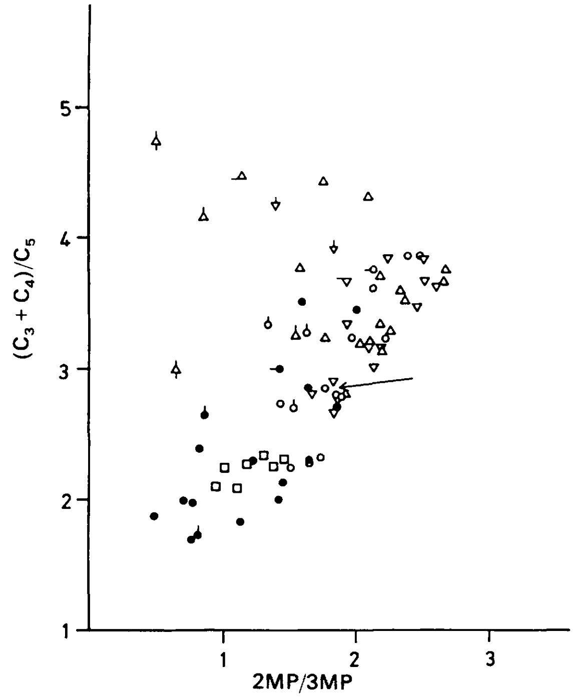

Fig. 4. Ratio of products of internal fission to that of terminal fission (propane plus butanes to pentanes) as a function of the ratio 2-methylpentane-to-3-methylpentane (2MP/3MP). All data obtained at different temperatures, hydrogen and n-hexane pressures, on regenerated and deactivated catalysts are plotted in the same figure. ●, 60; ○, 120; ▽, 240; △, 480 Torr H_2; □, $p(H'_2) = 120$ Torr, deactivated catalyst. The point of the arrow corresponds to the average value for nH : H_2 = 10 : 120 (*cf.* table 5). Points obtained at low temperatures and higher p(nH) are flagged as follows: horizontal flag: p(nH) = 20 Torr at 543 K; upper flag: p(nH) = 40 Torr at 543 and 573 K; upper and lower flag: p(nH) = 80 Torr at 543 and 573 K.

Both C_3/C_5 and C_4/C_5 alone show similar correlation with 2MP/3MP. The plot for C_3/C_5 is steeper than that of C_4/C_5 and the deviating points are farther from the majority of data which show a smaller spread on themselves. Therefore, it is likely that the relationship shown in fig. 4 is mainly due to the variation of the amount of C_3 fragments.

The ratio C_3/C_4 seemed to be independent of the 2MP/3MP ratio (fig. 5). The data belonging to 480 Torr hydrogen pressure are somewhat higher (C_3 formation preferred) but these become mixed with those belonging to 60 Torr hydrogen pressure at lowest 2MP/3MP ratio.

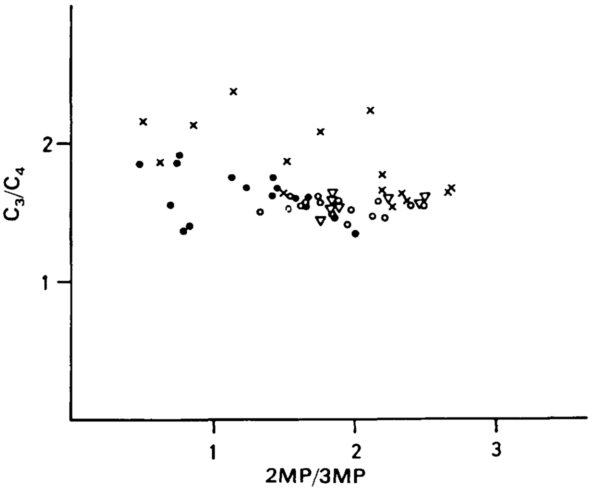

Fig. 5. Ratio of propane to butanes as a function of the ratio 2MP/3MP. Symbols as for fig. 4. No symbols are flagged; the highest values at $p(H_2)$ = 480 Torr (X) were obtained at 543 K, at p(nH) = 5–80 Torr.

Discussion

Activity

The slight maxima in overall conversion as a function of the hydrogen pressure point to the lesser hindering of the reactivity by increasing hydrogen coverages as compared to unsupported Pt.[22,28,34] The data are in fair agreement with those observed with n-heptane over Pt/SiO_2 and Pt/Al_2O_3.[27] That this maximum (table 1) is confined to lower temperatures only corresponds to the observation that maximum yields are shifted to higher $p(H_2)$ values at higher temperatures.[35] This observation seems to be valid on supported Pt, too.

A T.O.N. value of 9.4 h^{-1} has been suggested as a 'reference value' for n-hexane transformation at 573 K, atmospheric pressure, in a flow-through reactor, with p(nH) being 0.04–0.08 atm (*i.e.* 30–60 Torr).[6] Analogous values in table 1 are 60–90 h^{-1}. The difference can be due to several reasons. First, the hydrogen pressure in ref. (6) was much higher than in our experiments: with Pt-black, its increase from 480 to 750 Torr could well invoke a tenfold activity decrease.[7,22,25,36] A similar but less pronounced effect can be expected here, too. Secondly, in the static-circulation system, presumably, *all* the volume comes rapidly in contact with the catalyst, as opposed to a narrow front of reactant moving continuously forward along the bed in a single-pass reactor. In the latter case the different cross-sections may correspond to different states of deactivation, thus, the number of actually active Pt_{surf} in the denominator of the T.O.N. may be lower than that corresponding to the charge of catalyst.

In the first runs, lower turnover numbers were observed (table 1); they may be as low as *ca.* 10 h^{-1}, depending on the way of catalyst activation.[37] A sampling time of 5 min gives good reproducibility over a well run-in catalyst. (At lower sampling times, somewhat different selectivities were obtained over both Pt-black[32] and Pt/SiO_2.[37])

The question arises whether all these phenomena and also those connected with deactivation could be attributed to changes of Pt dispersion during runs. Although a final answer could only be supplied *e.g.* by direct hydrogen titrations before and after run (such results are not available at the moment), we tentatively reject this possibility on the basis of related XRD and XPS studies. XRD[38] demonstrates that treatments in oxygen at 723 K may cause a little sintering of Pt particles in EUROPT-1 which, however, is fully reversible upon a subsequent contact with hydrogen. A redistribution of Pt particles occurs when the catalyst is heated in hydrogen from 300 to 573 K but the *average* particle size remains the same.[39] Reduction in CO does not bring about drastic dispersion changes, either.[38] XPS, in turn, detects clearly the gradual removal of a residual carbon overlayer during activation in hydrogen at 573 and 673 K, respectively;[37] a practically carbon-free catalyst can be obtained by heating in O_2 ambient at 723 K.[39]

Selectivity

The selectivity of *aromatization* decreases with increasing overall pressures, its value being higher and higher as temperature increases. Although thermodynamics favour benzene formation at higher temperatures, and equilibrium mixture should contain more benzene even at 600 K.[40] Benzene selectivity is proportional to the overall activity (table 6 and fig. 1). This is not necessarily the situation over Pt-black.[11,32,34]

The reaction route ('direct' or 'stepwise'[7]) seems to be of little importance. Aromatization *via* enlargement of C_6-rings (the bifunctional route[28,35]) is not likely here: C_5-cyclic hydrocarbons gave rather small amounts of aromatics over EUROPT-1.[41]

It was stated[23] that hydrogenolysis and isomerization selectivities are mirror images of each other. The situation is not so simple: *all* products other than benzene show a closer and rather complex interdependence. The formation of C_6 *saturated* products prevails under most conditions. Above 573 K alkenes also appear; their amount is considerable at extremely high n-hexane : hydrogen ratios only [table 2 and fig. 1(*b*)]. They decompose gradually at increasing conversion values. Although they may be intermediates of aromatization,[9,35] the slight simultaneous increase of the aromatics selectivity alone does not account for the consumption of alkenes. Hence, it is likely that intermediates which give alkenes may also give rise to C_5-cyclization and/or C_5-cyclic isomerization. One has to remember here that a hydrogenative desorption of firmly-held surface species from Pt-black gave mostly methylcyclopentane in the first moments of desorption; firmly-held n-hexane came later.[26] This means the presence of dehydrogenated species on the surface that may be the precursors of MCP. It is an open question whether they have a structure corresponding to the dicarbene[42] or cyclopentadienic[43] (or both) intermediates of 'dehydrogenative C_5-cyclization'.[35] The C_5-cyclic route of isomerization seems to prevail here, too, as with other Pt-catalysts:[29,44] MCP is consumed at longer reaction times and the isomer selectivity increases accordingly (fig. 1 and 2). Higher reactant (and hydrogen) pressures favour isomerization (table 2). Therefore, we regard isomerization as occurring predominantly *via* a *hydrogenative* reaction of the original species, the dehydrogenation of which is a possibility rather than a necessity.

The characteristics of *hydrogenolysis* show that either a terminal or a multiple fission is superimposed on the single hydrogenolysis prevailing. We suggest that both of them occur but under opposite conditions: at high $p(H_2)$ and at lower temperatures a multiple splitting is added to random hydrogenolysis (data at 5 : 480 at 543 K) whereas a terminal splitting will gradually take over at higher temperatures and over catalysts which contain more carbon on their surfaces *i.e.* higher p(nH) or longer reaction times (*cf.* table 6, fig. 3).

Surface States and Possible Active Sites

These results can be rationalized in terms of different surface states prevailing under different conditions. At *lowest temperatures* the given hydrogen excess is sufficient that the reactant meets essentially a Pt—H surface. Here sites for multiple hydrogenolysis are available (although they represent a fraction of surface sites only: multiple splitting is not the only reaction as it was in the case of small Pt particles[10]). Isomerization occurs to give 3MP as the main product: hydrogenolysis and isomerization seem to be independent.

Anderson *et al.*[45] found great deviations in the 2MP/3MP ratio depending on the total or partially removed SMSI state of Pt/TiO_2 catalyst with practically unchanged fragmentation pattern. They suggested single-atom active sites for such reactions. Indeed, one metal atom has been found to be sufficient for C_5-cyclic reactions at rather low temperatures.[46] Isomerization leading to low 2MP/3MP ratios requires higher n-hexane pressures, *i.e.* high hydrocarbon coverages. At lower temperatures these adsorbed hydrocarbon species may not be able to undergo deep dehydrogenation but they create 'crowded' conditions on the surface: in this way, an edgewise adsorption on single-atom reaction centres will be preferred. The intermediate may be a 'tilted' C_5-cyclic species bonded to one Pt atom.[22] The situation may be analogous to Pt/zeolite catalysts where another type of geometric constraint (the presence of zeolitic channels) was found to lead to enhanced 3MP formation.[47] Similarly, single-atom sites may be responsible for multiple hydrogenolysis;[45] they should be, however, surrounded by hydrogen atoms. (Remember that methane formation involves the uptake of more hydrogen atoms than single rupture.)

At *medium T* and *p* values, hexane can displace surface hydrogen and becomes attached by more than one C atom to the metal. This state can be called 'Pt—C—H'.[26] The appearance of alkenes may indicate that this state has been reached. Surface intermediates bonded *via* 1,3-interactions to the catalyst were suggested for C_5-cyclic reactions.[22] These 'C_5-cyclic surface intermediates'[28] may desorb as hexanes or MCP: if they give isomers, their rupture occurs predominantly in a random way, providing a ratio 2MP/3MP near to 2. The same species may transform into 1,1,3-bonded ones, giving rise to internal hydrogenolysis according to, *e.g.*, the Anderson–Avery mechanism.[48]

Under *most severe* conditions, not only the relative amount of isomers but also the ratio 2MP/3MP decreases gradually; terminal splitting also becomes more important (fig. 4). More alkenes, even branched alkenes appear. The changes of the preferred position of MCP ring opening at increasing temperatures have been found to be in correlation with the appearance of methylcyclopentene, *i.e.* with the dehydrogenative processes becoming more and more important.[30] The shift of the ratio 2MP/3MP can also be explained this way. Under these conditions, the firmly-held hydrocarbons start to split up *and* remain on the surface as CH_x species.[49] This state of Pt can be called 'Pt—C'. The active sites correspond to Ponec's sites for terminal splitting[23] and also to Type II sites on Pt/Al_2O_3, splitting butane in the terminal position. It is not surprising that they were found to be more resistant to deactivation,[13] since these are just the sites characteristic of deactivated Pt.

Finally, an attempt will be made to correlate our results with the possible catalyst structure. We feel justified to assume that no redispersion occurs under reaction conditions. EUROPT-1 has reportedly very small crystallites (1–1.5 nm).[3,50] X-Ray diffraction[38] shows that *ca.* 90% of its Pt-particles are present at 573 K in hydrogen atmosphere as cubo-octahedra of 55 Pt-atoms, *i.e.* with three Pt-atoms on each edge[38] (fig. 6). The dispersion of such particles is 76%. *i.e.* larger particles should also be present to contribute to the actual value of 60%.[6] Indeed, smaller maxima are observed on the distribution curve at 309 atoms (5 atoms per edge) and 923 atoms (7 atoms per edge).

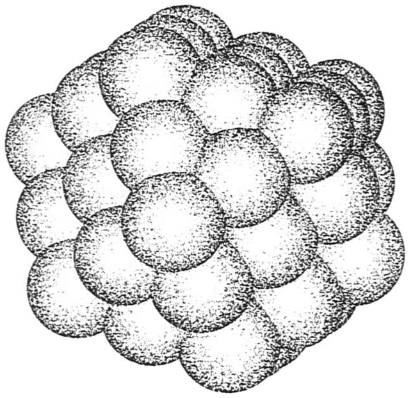

Fig. 6. A cubo-octahedral particle consisting of 55 atoms. Drawn in the Fritz-Haber-Institut, Berlin, program SCHAKAL. Courtesy of Dr W. Vogel.

Any of these exposed atoms may be active as single-atom sites under the mildest conditions. The role of edges may be more important for hydrogenolysis (*cf.* the increasing selectivity of hydrogenolysis on stepped and kinked Pt[51]). That isomerization occurs under 'crowded' conditions may point rather to the role of small flat planes in this reaction. Two-atom ensembles were suggested for the 1,3-adsorbed intermediates[22,35] while aromatizing sites may consist of three Pt atoms.[22,52] It may be surprising that two-atom sites deactivate but three-atom ensembles do not: if this is true, one has to assume that the two types of reaction require different sites. Aromatization was favoured by stepped or kinked single-crystal planes with (111) symmetry[19] whereas ring opening of MCP was much less crystal-plane sensitive.[53]

The (111) planes of the particles of 55 atoms contain six atoms (fig. 6). Benzene formation can then be attributed to these planes. These sites are either active or not: their availability is proportional to the overall catalyst activity. C_5-cyclic reactions can occur, in principle, anywhere. If they are really independent of aromatization, the (100) planes should be responsible for these processes. These active sites may also selectively deactivate: depending on the actual surface state, alkenes or MCP or isomers appear as products. For these dimensions, no macroscopic coke is necessary for deactivation: one or two strongly chemisorbed hexane molecules are sufficient to deactivate one plane. Again the partial deactivation of the 3×3 atom (100) plane can be visualized as opposed to (111) which could be covered by one C_6 entity. Such small particles may be less active than, *e.g.* Pt-black, in Anderson–Avery hydrogenolysis (requiring active sites of several atoms). It is not surprising, therefore, that EUROPT-1 shows a much lower hydrogenolysis selectivity than Pt-black or other supported Pt-catalysts.[7,11,27]

Special sites at the metal–support interface have not been considered here. They influenced the ratio of 2MP/nH from MCP ring opening[39,54] but had hardly any effect on the ratio 2MP/3MP[39] from MCP. Hence, presumably, the same is valid for n-hexane reactant.

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