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Skeletal Reactions of Heptane Isomers over EUROPT-1: A Comparison with Pt Black

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The reactions of five heptane isomers (*n*-heptane, 3-methylhexane, 3-ethylpentane, 2,4-dimethylpentane, and 3,3-dimethylpentane) are compared over a 6.3% Pt/SiO_2 catalyst (EUROPT-1) as a function of the hydrogen pressure between 6 and 60 kPa. Preferred reactions are isomerization and C_5-cyclization; substituted pentanes exhibit higher reactivity and higher C_5-cyclization ability. Increasing H_2 pressures enhance the reactivities in most cases, except for aromatization and C_5-cyclization, where maxima are observed. The observed product compositions (including fragments involving more than one C–C bond rupture) do not change within a rather wide conversion range. This is explained in terms of the metal catalyst being covered mainly by hydrocarbons; their reactivity, in turn, is determined first of all, by the amount of hydrogen available. Differences between EUROPT-1 and Pt black may be due to their different surface structure and purity. © 1993 Academic Press, Inc.

INTRODUCTION

EUROPT-1 is a well-characterized 6.3% Pt/SiO_2 catalyst which has been intended for use as a standard supported Pt catalyst. Results obtained by various laboratories for its physical characterization (*1–5, 7*) as well as its catalytic properties have been reviewed (*6, 7*). The overall catalyst activity depends on the nature of first activation and is correlated with the residual carbon detected by XPS (*8*). Standard oxygen–hydrogen regeneration cycles repeated several times have resulted in increasing and eventually well-reproducible values for the overall turnover frequency of *n*-hexane transformation (*9*).

The structure of the hydrocarbon reactant has been reported to have a major influence in determining the reaction pathways (*10*). Indeed, the comparison of alkanes of various structure over Pt black catalysts confirmed that their reactivity in various skeletal reactions and the ratio of products of different reactions (hydrogenolysis, isomerization, C_5-cyclization, and aromatization) depends strongly on the reactant structure (*11–13*). Increasing hydrogen pressures increased the selectivities of saturated C_6 formation; more C_5-cyclics than skeletal isomers were formed. A five-membered main chain was favourable for C_5-cyclization and C_5-cyclic isomerization, hydrogenolysis was preferred with a quaternary C atom, while *n*-heptane gave more aromatics than other heptane isomers. The form of the hydrogen dependence was different for Pt black samples of different pretreatment (exhibiting, among others, different crystallite sizes) and was interpreted in terms of "hydrogen availability" for reaction. Also, the "fragmentation patterns" of alkane molecules varies as a function of H_2 pressure (*13, 14*).

EUROPT-1 exhibits quite different selectivities from other supported and unsupported Pt catalysts in reactions of *n*-hexane (*8, 9, 15*) and 2,2-dimethylbutane (*16*) in that it produces *less* fragments and *more* nondegradative products.

The present study reports on the reactivity and selectivities of selected heptane isomers over EUROPT-1. The results are compared with each other and with those

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observed over Pt black catalysts (*11, 13, 14, 17*).

EXPERIMENTAL

The same static-circulation system and analysis was used as in earlier studies (*11, 13, 14*). Approximately 100 mg EUROPT-1 was activated with circulating hydrogen treatment at 603 K, using a liquid-nitrogen trap (*8*). All runs were carried out at 603 K and lasted 5 min, with a hydrocarbon pressure of 1.23 kPa and hydrogen pressure varying between 5 and 70 kPa.

Five selected heptane isomers, namely, *n*-heptane (*n*Hp), 3-methylhexane (3MHx), 3-ethylpentane, (3EP), and 2,4- and 3,3-dimethylpentane (2,4DMP and 3,3DMP, respectively) have been studied. These represent all "archetypes" of hydrocarbons (five, six, and seven C atoms in the main chain, *n*-alkane and isoalkanes with one and two side groups, attached to tertiary and quaternary C atoms) and are identical to those investigated over two Pt black samples (*13*). Further abbreviations used in product denotions are: DMB = dimethylbutane; MP = methylpentane.

Another set of experiments has been carried out with 3MHx and 3,3DMP over another, highly active 3 mg EUROPT-1 sample (used previously in several hexane reactions) where the length of the run was selected as the variable, in order to follow

TABLE I

Turnover Frequencies and Selectivities of Various Products

Hydrocarbon reactant	p (H_2) (kPa)	TOF EUROPT-1 (10^{-4} s^{-1})		TOF Pt black[a] (10^{-4} s^{-1})		Selectivity (%) (EUROPT-1, for Series I)			
		I[b]	II[c]		$<C_n$	Iso.	C_5-cycl.	C_6-cycl.	Arom.
n-Pentane	17	36	—	(10 kPa): 9	30	51	19	—	
	34	45	—	(23 kPa): 9.6	32	61	7	—	
n-Hexane	16	82[d]	—	26[e]	13	25	41.5	8[g]	12.5
	64	125[d]	—	56[e]	17	52	21	0.5[g]	9.5
n-Heptane	16	8	—	12	1	6	79.5	—	13.5
	61	45	—	36	1	71.5	5	11	12.5
3-Methylhexane	15	19	91	13	9	29	45	2[f]	15
	64	45	193	22	10	55.5	19	—	15.5
3-Ethylpentane	16	30	—	26	3	37	58	1	1
	70	78	—	75	6	79	6	2	7
2,4-Dimethylpentane	16	21	—	26	1	16	83	—	0.2
	68	82	—	52	3	76.5	17	2	1.5
3,3-Dimethylpentane	9.5	29	—	—	8	37	39	—	16
	17	—	78	21	26[h]	6[h]	60[h]	—[h]	8[h]
	53	57	—	66	7	67	22	1	3
	64	—	163	—	16[h]	33[h]	39[h]	2[h]	10[h]

[a] Pretreated at 473 K (*13*).
[b] 5-min runs, 100 mg EUROPT-1.
[c] 10-min runs, 3 mg EUROPT-1.
[d] Ref. (9).
[e] Ref. (*17*).
[f] Methylcyclohexane.
[g] Hexenes.
[h] Series II, 10-min runs.

product compositions at various conversion levels.

RESULTS

The overall conversion of all alkanes increases as H_2 pressure increases. Table 1 contains results also for *n*-pentane and *n*-hexane, the latter being most reactive. Of the heptane isomers, reactants with five C atoms in their main chain exhibit higher turnover frequencies. The differences between various alkanes are smaller at higher hydrogen pressure. The overall reactivities are comparable with those observed over Pt black (Table 1). At the same time, differences by a factor of 5 are seen between the runs using 100 mg and 3 mg EUROPT-1. The run length was longer in the latter case; moreover, the regeneration process was tuned to reach the maximum possible activity. Even higher differences were reported upon various pretreatments (*8*).

Turnover frequencies (TOF) increase as hydrogen pressure increases. TOF values to individual product classes are shown in Fig. 1–4. Of the two main reactions, C_5-cyclization (Fig. 1) has maxima as a function of H_2 pressure, while isomerization (Fig. 2) is accelerated monotonically. Substituted pentanes can produce 5–10 times more cyclopentanes than *n*Hp. The low C_5-cyclization reactivity of 3MHx (although this molecule could react also as "2-ethylpentane") has also been observed on Pt black and was interpreted in terms of its geometry unfavorable for cyclization (*18*). This can be valid for EUROPT-1, too.

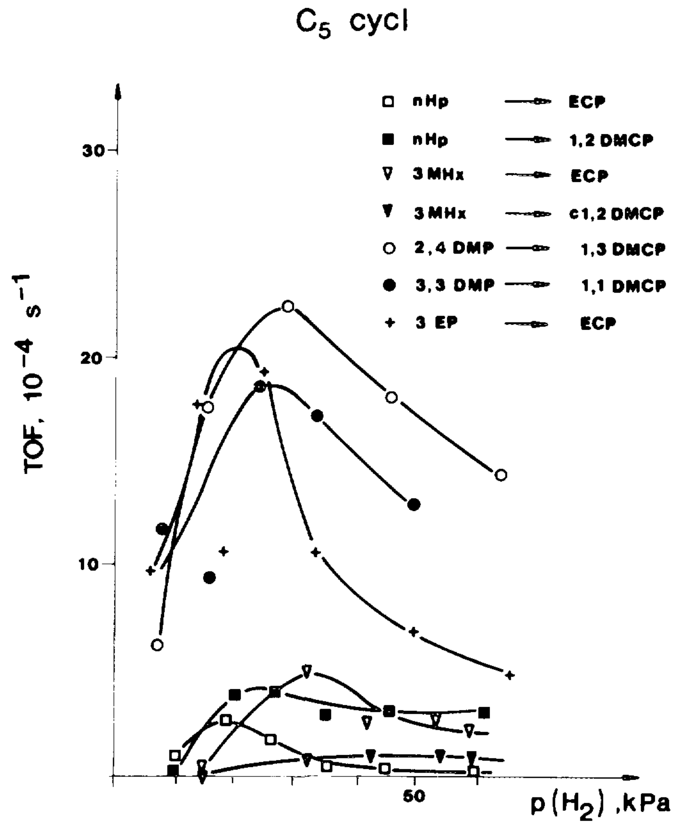

FIG. 1. Turnover frequency of C_5-cyclic products from five heptane isomers over EUROPT-1 as a function of hydrogen pressure [p (H_2)].

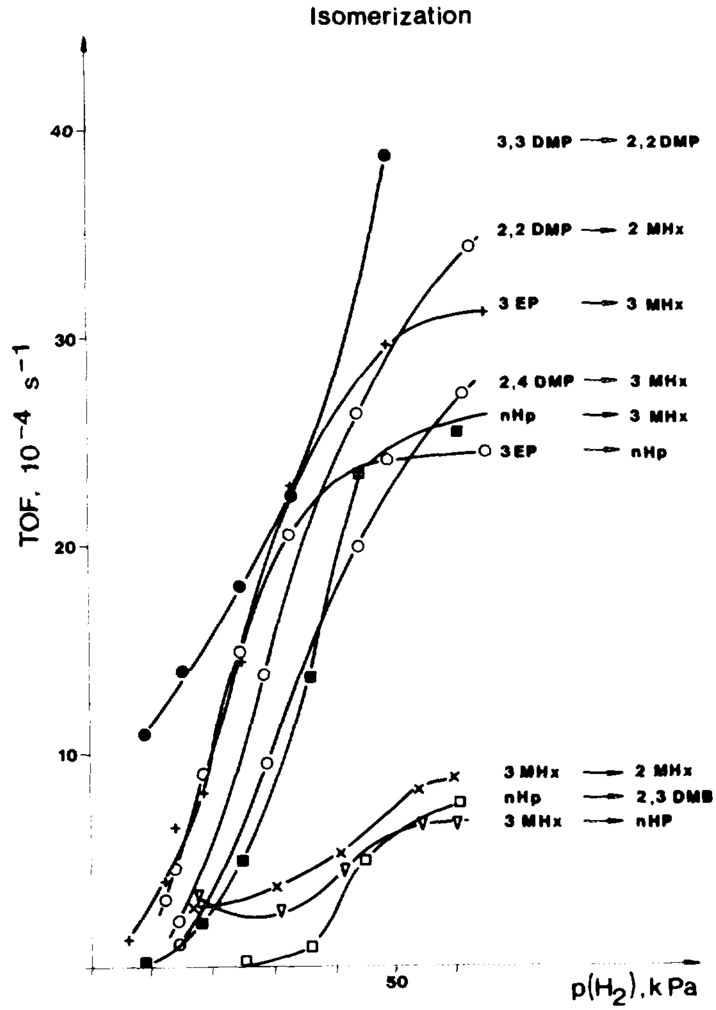

FIG. 2. Turnover frequency of individual isomers produced from five heptane isomers over EUROPT-1 as a function of [p (H_2)]. An additional curve shows the formation of 3,3DMP from 2,2DMP whose hydrogen dependence is similar to that of its reverse reaction, i.e., 3,3DMP isomerization.

Aromatic yields (Fig. 3) are low with 2,4DMP only; high yields are seen with 3,3DMP and 3EP where aromatization also requires skeletal rearrangement. The hydrogen response of these two hydrocarbons is, however, very different.

3,3DMP with a quaternary C atom exhibits a rather sharp maximum at a low H_2 pressure of about 20 kPa. Its aromatization yield is higher there than observed with any other hydrocarbon at any H_2 pressure. This is in agreement with reports that a quaternary C atom facilitates skeletal rearrangement as opposed to tertiary C atoms (*19*).

The turnover frequencies to fragments (Fig. 4) are lower than those observed for nondegradative reactions and increase monotonically with H_2 pressure, except for a maximum observed with 3,3-dimethylpentane. The 10-fold difference in the reactivity of various reactants in hydrogenolysis is worth mentioning.

There were marked differences in the H_2 pressure dependences of the yields of individual product-classes over two Pt black samples presintered at 473 and 633 K (denoted as Pt-473 and P-633, respectively). Maxima as a function of H_2 pressure were characteristic of Pt-473 (*13*). EUROPT-1 resembled this latter Pt black sample. A marked exception is 3,3DMP, where the hydrogen dependence of aromatization and hydrogenolysis dropped at higher p(H_2). Here, however, the aromatic and fragment yields were 2 and 3 times less, respectively, over EUROPT-1 than over Pt-473 at maximum rate. The TOFs for aromatization from *n*Hp and 2,4DMP were about the same over supported and unsupported Pt, while 3EP and 3MHx were much more reactive over EUROPT-1 and also a higher rate could be seen at higher H_2 pressure. As opposed to any of the Pt blacks (*13*), hydrogenolysis over EUROPT-1 was always

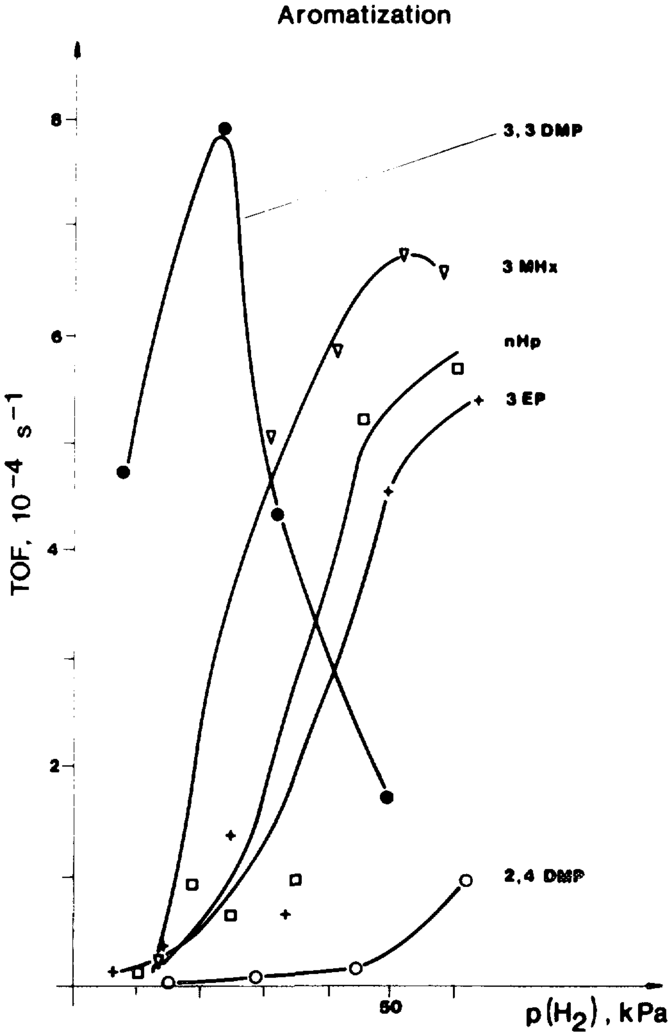

FIG. 3. Turnover frequency of aromatization of five heptane isomers over EUROPT-1 as a function of [p (H_2)].

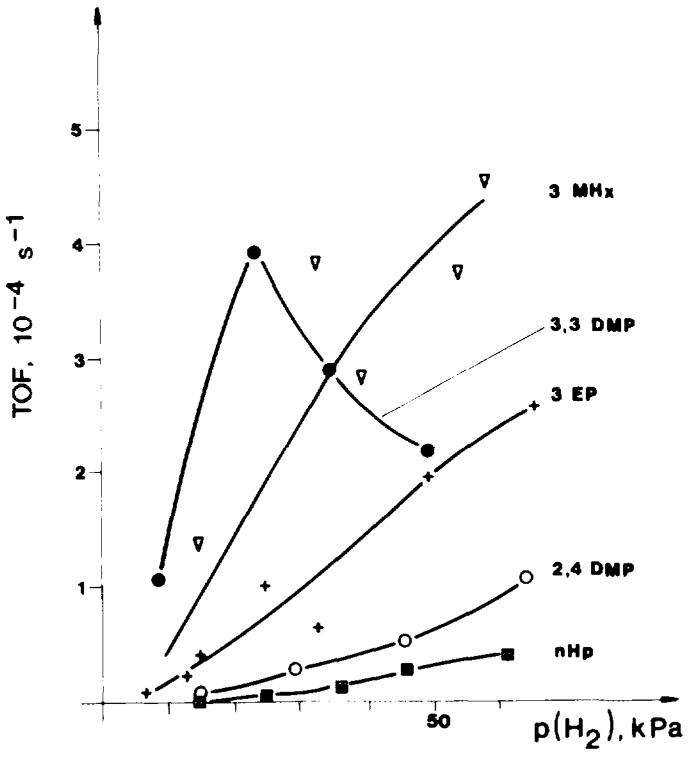

FIG. 4. Turnover frequency of hydrogenolysis of five heptane isomers over EUROPT-1 as a function of [p (H_2)].

lower and so were the amounts of C_5- cyclics; at the same time, EUROPT-1 favored isomerization.

This is also reflected by the selectivities (Table 1). Isomerization and C_5-cyclization have highest values, higher hydrogen pressures favouring isomerization. These two product classes are responsible for 75–99% of all products formed from various heptane isomers. Their share is around 70% from *n*-pentane and *n*-hexane. This distribution is markedly different from that observed over Pt black (*13*) where, as a rule, higher fragmentation (up to 50%) and aromatization (up to 30%) selectivities were reported. Not only the H_2 pressure dependence but also selectivities observed over EUROPT-1 were closer to the sample sintered at 473 K (having smaller crystallites), of the two Pt black samples reported in Ref. (*13*). The two additional runs (discussed in detail below) with lower overall conversions show somewhat different selectivities, in agreement with previously reported results (*9*) indicating that selectivity is rather sensitive to the actual surface state obtained after catalyst regeneration.

Isomerization at higher hydrogen pressures is much more preferred over EUROPT-1 than over any of the Pt blacks (*13*), where the ratio isomers/C_5-cyclics hardly exceeded unity, as opposed to the ratios of well over 10 over EUROPT-1 (Table 2). These ratios are also structure dependent, *n*-heptane and ethylpentane being more liable to isomerization than others. The amount of isomers that can *only* be formed via bond shift (e.g., 2MHx from *n*Hp or 2,3DMP from 2,4DMP) was always below detection limit, in agreement with

TABLE 2

Ratio of Isomers to C_5-Cyclics under Different Conditions

A. Isomer/C_5-cyclics ratio as a function of hydrogen pressure

p (H_2) (kPa)[a]	Isomer/C_5 cyclics ratio from				
	nHp	3MHx	3EP	2,4DMP	3,3DMP
8	0.04	—	0.13	0.03	0.95
16	0.08	0.64	0.64	0.19	1.68
30	0.94	1.12	1.53	1.03	0.97
64	14.3	2.92	13.2	4.5	3.05[b]

B. Ratio of 2,2DMP/1,1DMCP as a function of overall conversion (X)[c]

p (H_2) = 16 kPa		p (H_2) = 64 kPa	
X (%)	2,2DMP/1,1DMCP	X (%)	2,2DMP/1,1DMCP
2.8	0.055	2.2	0.82
6.9	0.063	7.9	0.84
9.5	0.069	12.2	0.87
		23.1	1.01
		34.5	1.19

[a] Pressure scattering is a ca. ±10%; hydrocarbon pressure, 1.33 kPa.

[b] 53 kPa.

[c] Reactant, 3,3DMP, ratio of main isomer to main C_5-cyclic product (cf. Fig. 6).

studies using single-crystal Pt faces and various Pt/Al_2O_3 catalysts (*20*). *n*-Pentane, in turn, gave significant amounts of isopentane; this must have involved bond shift reaction, similarly to the *n*-butane–isobutane reaction (*21*). The probability of the C_5-cyclic surface intermediate producing isomers is obviously larger over Pt/SiO_2 than over unsupported Pt, due to better "hydrogen availability" (*22*) on EUROPT-1.

The hydrogenolysis pattern can be characterized by the ω factor suggested by Leclercq *et al.* (*23*). When the breaking produced one larger and one smaller fragment, only the larger fragment has been considered. This calculation is valid, however, only when multiple fragmentation is absent, i.e., when the complementary fragments (e.g., C_2 and C_5, etc.) are present in nearly equal amounts (i.e., with "single rupture"). The value of the ζ factor (*24*) defined as the number of fragments per molecule broken up can be used to ensure if fragmentation is single. Values of ζ close to 2 indicate that the molecule is broken into two parts. The actual ζ values are slightly over 2 and the excess can be explained by some methane excess.

Actual ω values are shown in Table 3 for three selected heptane isomers (see Fig. 5). The hydrogen pressure dependences of the patterns are roughly similar to those observed over Pt black, but the actual ω values are different. In particular, the "C_5 unit splitting" of *n*-heptane (the formation of *n*-pentane plus ethane) is much more marked over EUROPT-1, indicating the strong preference of a C_5-cyclic reactive chemisorption over this catalyst. This is not true for 3-methylhexane, where the splitting next to the tertiary C atom is much preferred. As mentioned before, the geometry of this alkane is unfavourable for a reactive chemisorption of a C_5 unit, cf. the scheme shown in Ref. (*18*); hence, this long and branched molecule reacts as a "2-pro-

TABLE 3

Reactivity Factor, ω, at H_2 Pressure (kPa) for Various Hydrocarbons on EUROPT-1 and Pt Black[a] Catalysts

A. *n*-Heptane

	EUROPT-1			Pt black	
	16	40	60	31	69
ω_1 (*n*-Hexane)	0.62	0.95	0.90	0.89	1.12
ω_2 (*n*-Pentane)	1.76	1.20	1.08	0.90	0.95
ω_3 (*n*-Butane)	0.62	0.84	1.01	1.21	0.94

B. 3-Methylhexane

	EUROPT-1			Pt black	
	16	35	64	30	70
ω_1 (3-Methylpentane)	0.50	0.62	0.69	1.02	0.79
ω_2 (2-Methylbutane)	0.22	0.54	0.59	0.62	0.97
ω_3 (*n*-Butane)	3.45	2.52	2.05	1.49	1.59
ω_4 (*n*-Hexane)	0.46	0.70	0.85	0	0.31
ω_5 (*n*-Pentane)	0.09	0.54	0.65	1.18	0.66
ω_6 (2-Methylpentane)	1.27	1.08	1.17	1.69	1.68

C. 3,3-Dimethylpentane

	EUROPT-1			Pt black	
	16	36	53	31	64
ω_1 (2,2-Dimethylbutane)[b]	0.31	0.73	0.62	0	0.04
ω_2 (2-Methylbutane)[b]	1.18	2.07	2.23	2.78	2.53
ω_3 (3-Methylpentane)	0.69	0.23	0.15	0.22	0.43

[a] Splitting directions as defined in Fig. 5.

[b] Plus considerable amounts of 2-methylpropane and propane (cf. Fig. 7).

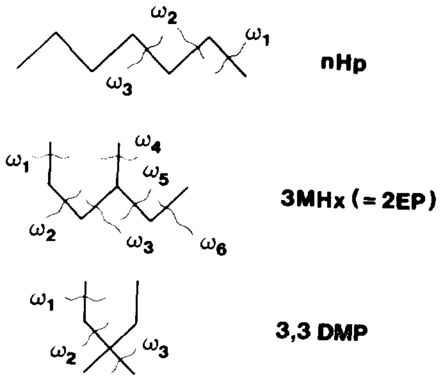

FIG. 5. Possibilities of hydrogenolysis (cf. Table 3) of *n*-heptane (*n*Hp), 3-methylhexane [or "2-ethylpentane"] (3MHx = 2EP), and 3,3-dimethylpentane (3,3DMP).

pylbutane" and breaks preferentially into two almost equal fragments. The fragmentation pattern of 3,3DMP is in agreement with the results reported for 2,2DMB in as much as the splitting between the secondary and quaternary C atom is preferred (*25*); the explanation of its entire fragmentation pattern requires additional considerations (see below).

Since the results presented so far have been obtained with constant sampling times (with overall conversions typically between 10 and 25%) the question arises whether the yield, selectivity, and fragmentation pattern values reflect initial product compositions or are affected (and if so, to what extent) by secondary reactions. In particular, C_5-cyclics may react further to skeletal isomers and primary fragments may undergo secondary rupture. The experiments carried out with 3,3DMP at two hydrogen pressures with various sampling times are expected to give an answer to the problem. Selected yields have been plotted in Fig. 6 as a function of the conversion, giving an "Optimum Performance Envelope" chart (*26*). No zero slope is seen at conversions approaching zero, i.e., none of the products is a "true secondary product." The slope for 1,1DMCP decreases at higher conversions indicating its further transformation, but its secondary reaction may give fragments rather than 2,2DMP, as indicated by the almost linear increase of the yield of the latter compound ("nonreactive primary product"). Toluene formation should also involve more than one pathway. The yield of another isomer, 2,3DMP, which can only be formed via a bond shift pathway, is much lower, in agreement with Fig. 2 and also with the results obtained over Pt black (*12*).

That 2,2DMP is not a secondary product from 1,1DMCP is also confirmed by their ratio as a function of overall conversion in Table 2B being almost independent of the time-on-stream. On the other hand, a very marked hydrogen pressure dependence is seen, justifying, in our view, that data obtained at fixed sampling times are meaningful. Optimum Performance Envelopes and isomer/C_5-cyclic ratios for 3MHx confirm these statements (*27*).

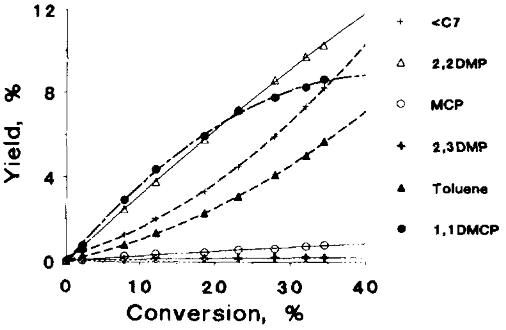

FIG. 6. Yields of some main products and the sum of fragments from 3,3-dimethylpentane, as a function of the overall conversion. Identical line styles have been applied for curves of identical Optimum Performance Envelope behavior (*26*).

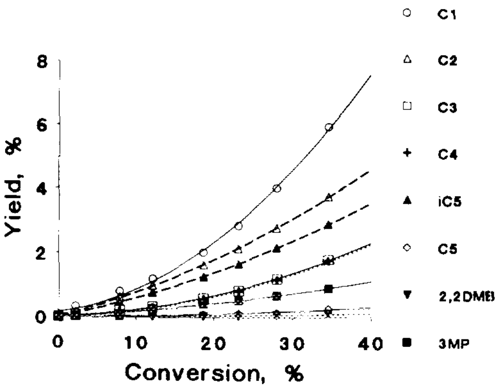

FIG. 7. Yields of main fragments from 3,3-dimethylpentane, as a function of the overall conversion. Identical line styles are applied for curves of the complementary products i-C_5 and C_2. Full symbols denote fragments used for calculating ω values in Table 3.

The accumulation of individual fragments as a function of overall conversion (Fig. 7) indicates a slight secondary fragmentation as conversion increases. The preferential splitting gives nearly equal amounts of isopentane and ethane. On the other hand, the methane excess—as opposed to the amounts of 3MP, 2,2DMB (cf. Table 3), and methylcyclopentane shown in Fig. 6—is rather large, even if we consider that two CH_4 molecules were formed for each *n*-pentane molecule. The large methane and the slight ethane excess indicates some (but by no means predominant) multiple splitting. Propane and butanes must have involved also skeletal rearrangement processes of 3,3DMP (e.g., to 2,2- or 2,3-dimethylpentane) followed by a *strict single C–C bond rupture* as shown by the identical values of the C_3 and C_4 fragments. Their slope is also higher than zero at very low conversions; hence they are also primary products and are formed, probably, by splitting and rearrangement of the reactant molecule during its one sojourn at the surface. Hence, the ω factors themselves give true information on the preferred direction of splitting between the quaternary and one secondary C atom, but any conclusion drawn from the low ω value of the other two fragments (without considering the entire fragmentation pattern) would be misleading.

DISCUSSION

The relative uniform product composition at various conversion levels indicates that the catalyst obtains a relatively high hydrocarbon coverage during the first moment of the run. This picture corresponds to the concept of Sárkány (*15*, *28*) who proposed that a surface covered by not deeply dehydrogenated hydrocarbonaceous species ("Pt–C–H") are present in the stable activity period of the catalyst. These are reactive and the distribution of their products appearing in the gas phase is determined largely by the hydrocarbon/hydrogen ratio (*29*); however, both isomers and C_5-cyclics appear already at very low conversions. Since the initial hydrocarbon coverage must be obtained when *the reactant* is most abundant in the feed, this fact diminishes the chances of product readsorption and further reaction up to rather high conversions which were not practicable to reach due to slow catalyst deactivation. Isomerization by readsorption, in turn, is more likely over a higher amount of catalyst in the closed loop, and this may be the reason why isomer selectivity is higher over the less active 100 mg than over the more active 3 mg EUROPT-1 (Table 1). This idea has obtained a confirmation by reacting hexenes over EUROPT-1 (*30*) where the ratio of competing hydrogenation and double bond isomerization of the reactant molecule remained constant in a wide conversion range up to ca. 95% (when the amount of hexenes started to be negligible), even though alkane isomers could compete more efficiently for surface sites than *n*-hexane with hexenes.

One way visualize the formation of C_7 saturated products in terms of a primary adsorbed "C_5-cyclic surface entity" (*31*) which gives skeletal isomers and alkylcyclopentanes with similar rates even at very low conversions. Isomer formation via a possible readsorption of the C_5-cyclic intermediate increases the amount of isomers only slightly. The above general statement may be valid for several Pt catalysts (*15*, *28*, *29*). All reactions proceed over EUROPT-1 and both Pt black samples described in Ref. (*13*); however, their relative importance is different over various catalysts. Tentative suggestions may be given as far as the correlations between activity and surface structure/purity are concerned.

X-ray diffraction results (*32*, *33*) could be explained by assuming 55-atom cubooctahedra as the *most abundant* (but not exclusive) geometric form of Pt crystallites in EUROPT-1. The skeletal transformations of *n*-hexane have been interpreted in terms of this "55-atom cubooctahedron model," attributing C_5-cyclization, isomerization, and related single hydrogenolysis mainly to the (100) faces, and aromatization, in turn, to the (111) facets (*7*). Dehydrogenation to alkenes could take place, accordingly, on partly deactivated sites, mainly Pt–C ensembles. This idea may be valid here, too. The higher overall reactivity of hydrocarbons with five C atoms in their main chain is probably due to their better geometric accommodation over the small Pt crystallites of the catalyst. Figures 1 and 2 indicate that these compounds are, in fact, more reactive and not only selectivity changes are observed within the total C_6 saturated fraction. Their preferential reactions are C_5-cyclic processes; in addition, toluene formation from 3,3DMP is also favorable. The particle size distribution shows a certain scattering, and hence incomplete cubooctahedra must also be present. The rather low hydrogenolysis selectivity could be explained by these ledge structures (which are present in minor amounts on incomplete cubooctahedra only) being required reportedly for this reaction (*20*). The formation of propane and butanes from 3,3DMP is certainly remarkable and may represent an example of a predominant "skeletal isomerization reaction with hydrogenolysis" (*10*), the isomers themselves being not necessarily present in major amounts (Fig. 6). Their equal amount points to a strictly single rupture which may be favored when this reactant meets a well-regenerated surface (Series II, Table 1).

Pt black exposes (i) larger contiguous ensembles which are predominantly present as islands of clean metal, the rounded shape of the crystallites (*13*) indicating much edge/kink structure; and (ii) it contains also island-like carbonaceous deposits after O_2–H_2 regeneration (*34*). EUROPT-1, in turn, could be cleaned so as to be practically carbon-free (*8*). Both these factors can contribute to the differences observed. Larger exposed metal surfaces and abundant ledge structures may be responsible for higher fragmentation selectivity of Pt black where the probability of finding three-atom ensembles suggested for aromatization (*35*) is also higher. The "hydrogen economy" of Pt black, where no spillover is possible, is obviously poorer: less hydrogen is available for the common "C_5-cyclic surface intermediate" of skeletal isomerization and C_5-cyclization to promote isomerization (*22*). Pt-473 with smaller crystallites and slightly less carbon (*13, 34*) is better in this respect. This explanation is valid for each hydrocarbon; hence, the variation of metal purity and/or structure influences the reactivity of all reactants studied more or less uniformly.

ACKNOWLEDGMENT

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REFERENCES

1. Bond, G. C., and Wells, P. B., *Appl. Catal.* **18,** 221 (1985).

2. Bond, G. C., and Wells, P. B., *Appl. Catal.* **18,** 225 (1985).

3. Geus, J. W., and Wells, P. B., *Appl. Catal.* **18,** 231 (1985).

4. Frennet, A., and Wells, P. B., *Appl. Catal.*, **18,** 243 (1985).

5. Wells, P. B., *Appl. Catal.* **18,** 259 (1985).

6. Bond, G. C., Maire G., and Garin, F., *Appl. Catal.* **41,** 313 (1988).

7. Bond, G. C., and Paál, Z., *Appl. Catal.* **86,** 1 (1992).

8. Paál, Z., Zhan, Zh., Manninger, I., and Muhler, M., *Appl. Catal.* **66,** 301 (1990).

9. Paál, Z., Groeneweg, H., and Paál-Lukács, J., *J. Chem. Soc. Faraday Trans.* **86,** 3159 (1990).

10. Maire, G., and Garin, F., *J. Mol. Catal.* **48,** 99 (1988); Garin, F., and Maire G., *Acc. Chem. Res.* **20,** 100 (1989).

11. Zimmer, H., Paál Z., and Tétényi, P., *Acta Chim. Acad. Sci. Hung.* **111,** 513 (1982).

12. Zimmer, H., Dobrovolszky, M., Tétényi, P., and Paál, Z., *J. Phys. Chem.* **90,** 4758 (1986).

13. Paál, Z., Zimmer, H., Günter, J. R., Schlögl, R., and Muhler, M., *J. Catal.* **119,** 146 (1989).

14. Zimmer, H., Paál, Z., and Tétényi, P., *Acta Chim. Hung.* **124,** 13 (1987)

15. Sárkány, A., *Catal. Today* **5,** 173 (1989).

16. Botman, M. J. P., de Vreugd, K., Zandbergen, H. W., de Block, R., and Ponec, V., *J. Catal.* **116,** 467 (1989).

17. Paál, Z., Zimmer, H., and Günter, J. R., *Z. Phys. Chem. Neue Folge* **164,** 1135 (1989).

18. Zimmer, H., Paál, Z., *in "Proceedings, 8th International Congress on Catalysis, Berlin 1984,"* Vol. III, p. 417. Verlag Chemie, Weinheim, 1984.

19. Paál, Z., *in* "Advances in Catalysis" (D. D. Eley, H. Pines, and P. B. Weisz, Eds.), Vol. 29, p. 273. Academic Press, New York, 1980.

20. Garin, F., Aeiyach, S., Légaré, P., and Maire, G., *J. Catal.* **77,** 323 (1982).

21. Bond, G. C., and Gelsthorpe, M. R., *J. Chem. Soc. Faraday Trans. 1* **85,** 3767 (1989).

22. Paál, Z., *in* "Hydrogen Effects in Catalysis" (Z. Paál and P. G. Menon, Eds.), p. 449. Dekker, New York–Basel, 1988.

23. Leclercq, G., Leclercq, L., and Maurel, R., *J. Catal.* **50,** 87 (1977).

24. Paál, Z., and Tétényi, P., *Nature* **267,** 234 (1977).

25. Paál, Z., and Tétényi, P., *React. Kinet. Catal. Lett.* **12,** 131 (1979).

26. Abbot, J., Corma, A., and Wojciechowski, B. W., *J. Catal* **92,** 398 (1985).

27. Matusek, K., Zimmer, H., and Paál, Z., in preparation.

28. Sárkány, A., *J. Chem. Soc. Faraday Trans. 1* **84,** 2267 (1988).

29. Paál, Z., *Catal. Today* **12,** 297 (1992).

30. Paál, Z., Räth, M., Brose, B., Gombler, W., *React. Kinet. Catal. Lett.* **47,** 43 (1992).

31. Barron, Y., Maire, G., Muller, J. M., and Gault, F. G., *J. Catal.* **5,** 428 (1966).

32. Gnutzmann, V., and Vogel, W., *J. Phys. Chem.* **94,** 4991 (1990).

33. Fülöp, E., Gnutzmann, V., Paál, Z., and Vogel, W., *Appl. Catal.* **66,** 319 (1990).

34. Paál, Z., Schlögl, R., and Ertl, G., *J. Chem. Soc. Faraday Trans.* **88,** 1179 (1992); *Catal. Lett.* **12,** 331 (1992).

35. Biloen, P., Helle, J. N., Verbeek, H., Dautzenberg, F. M., and Sachtler, W. M. H., *J. Catal.* **63,** 112 (1980).