JOURNAL OF CATALYSIS **147**, 333–341 (1994)

Reactions of *n*-Hexane over Pt-Zeolite Catalysts of Different Acidity

Z. Zhan,*,[1] I. Manninger,* Z. Paál,* and D. Barthomeuf†

Institute of Isotopes of the Hungarian Academy of Sciences, P. O. Box 77, H-1525 Budapest, Hungary; and †Laboratoire de Réactivité des Surfaces et Structure, Université Pierre et Marie Curie, U. A. 1106 du CNRS, 75252 Paris Cedex, France

Received April 28, 1993; revised November 5, 1993

Pt-HY, Pt-NaHY, Pt-NaY, and Pt-NaX catalysts, which possess decreasing acidity and increasing basicity in the above sequence, were tested at 603 K in *n*-hexane conversion as a model reaction. Pt-HY and Pt-NaHY, which are acidic, are more active by about an order of magnitude than the two non-acidic catalysts. Selectivities measured at different hydrocarbon and hydrogen pressures are presented as a function of the overall conversion. Pt-HY and Pt-NaHY produce mainly skeletal isomers, fragments and, at most, minor amounts of benzene. Fragment composition indicated that pronounced cracking occurs over Pt-HY only, together with minor hydrogenolysis on the metallic centers. This latter reaction is responsible for most fragments over the other three catalysts. Metal-catalyzed C_5-cyclic isomerization, ring closure, and pronounced aromatization prevail over Pt-NaY and Pt-NaX. The latter behaves like a typical non-acidic metal catalyst. Pt-NaY exhibits an outstanding aromatization selectivity which can possibly be attributed to the interaction of basic centers of the framework with the Pt particles rather than to geometric reasons.

INTRODUCTION

Pt-zeolite catalysts have obtained a considerable importance in reforming C_6–C_7 hydrocarbons (1). Their zeolite supports are, as a rule, non-acidic (e.g., K- or Ba-L zeolite). Hydrocarbons should, therefore, undergo *metal-catalyzed* transformations over these catalysts, as opposed to the bifunctional reactions occurring over traditional reforming catalysts (2) or metals supported on strongly acidic zeolites. The detailed mechanism of action of these catalysts is still not clear: either geometric or metal-support interactions have been suggested as possible reasons for their outstanding activity. The "confinement model" (3) belongs to the first category: it assumes a direct ring closure in the narrow zeolite channels over single Pt atoms exposed in zeolite windows. Another explanation assumes a hindered deactivation of metallic sites in the narrow zeolite pores which present unfavorable geometry for polymerization of unsaturated residues (4). The possible interplay of metallic sites and acidic sites of various strength would render a bifunctional mechanism possible. The introduction of Pt into the zeolite by ion exchange and its subsequent reduction by H_2 creates acidic sites in the vicinity of metal particles (5) which can and do participate in skeletal hydrocarbon transformations. For example, enhanced isomerization of *n*-hexane has been reported over Pt-KL reduced by H_2 as opposed to a Pt-KL where acidity was suppressed by second ion exchange with KNO_3 after reduction (6). On the other hand, Pt catalysts on basic supports have been found to be favourable for aromatization (7).

The problem of the catalytic properties of metallic and acidic/basic sites present simultaneously can be studied systematically with Pt over zeolitic supports of controlled acidity. Such catalysts have been prepared and characterized recently (8–10). The infrared wavenumbers of linearly adsorbed CO indicate that the acidity decreases in the order Pt-HY, Pt-NaHY, Pt-NaY, Pt-NaX. The basicity of framework oxygen increases in the same sequence (11). No benzene formation from *n*-hexane was reported at 773 K over the first two samples at 773 K; the activity of Pt-KL fell between that of Pt-NaY and Pt-NaX (8). Their benzene hydrogenation activity decreased as electron transfer from the support to Pt increased over more and more basic catalysts (9).

n-Hexane is the simplest alkane that is able to undergo C_5-cyclization and C_5-cyclic isomerization as well as aromatization, fragmentation, and other types of metal- and/or acid-catalyzed isomerization processes. Among several possible model hydrocarbons, it seemed to be a sufficiently versatile probe molecule even for testing Pt-KL catalysts of various acidity (6). The present paper reports on its reactions over a series of Pt-zeolite catalysts of low metal loading, high dispersion and different acidity (8, 9). A well-characterized (12) non-acidic 6% Pt/SiO_2 (EUROPT-1) was selected for comparison. Another approach, describing the interplay of metallic and acidic centres in mechanical mixtures of HY and EUROPT-1 is

---

[1] On leave from Lanzhou Institute of Physical Chemistry, Academia Sinica, Lanzhou, PR China. Present address: Univ. of Twente, Fac. Chem. Techn., P.O. Box 217, 7500 AE Euschede, The Netherlands.

0021-9517/94 $6.00

reported in a companion article (13). The temperature of the reaction (603 K) is closer to that of other laboratory studies of model hydrocarbons (14, 15) than to the conditions of industrial reforming. We hope, nevertheless, that the information obtained will be useful in elucidating the actual mechanisms of skeletal hydrocarbon transformations over such catalysts.

EXPERIMENTAL

Four catalysts (Pt-HY, Pt-NaHY, Pt-NaY, and Pt-NaX) have been prepared according to Refs. (8–10). Pt-HY was received as Pt-NH_4Y and decomposed *in situ* in the catalytic reactor. Some of the important characteristics of these catalysts are given in Table 1. About 10 mg of each catalyst was calcined in O_2 (flow rate, 30 liter h^{-1}), according to a temperature programme (10 K h^{-1}) from 300 to 573 K and kept at 573 K for 3 h. The flow was then switched to N_2 and the temperature increased to 623 K during 1 h. Then H_2 was gradually introduced to the N_2 stream and the catalysts were kept in a flow of 3 liter h^{-1} H_2 overnight.

TABLE 1

Characteristics of Pt-Zeolite Catalysts

Catalyst	Na (w/w %)	Na atom (per unit cell)	Pt (w/w %)	Pt m.d.[a] (nm)	D^b (%)
Pt-HY	0.77	4	0.77	1.2	86
Pt-NaHY	5.4	31	0.73	1.1	96
Pt-NaY	8.25	49	0.80	1.2	84
Pt-NaX	13.1	84	0.82	1.3	78

[a] Mean particle diameter, according to Ref. (7).

[b] Dispersion, as determined by hydrogen titration, Ref. (7).

Catalytic runs with *n*-hexane (*n*H) model reactant were carried out in a closed circulation loop (13, 16) at 603 K, at two *n*-hexane pressures (10 and 40 Torr) and two hydrogen pressures (120 and 480 Torr). The total pressure was the sum of the H_2 and *n*-hexane pressure (no inert gas added). Regeneration between runs was carried out by treating the catalyst with O_2, evacuating and then with H_2 (16). The amount of Pt was between 0.07 and 0.13 mg with each catalyst, including also EUROPT-1. A few compara-

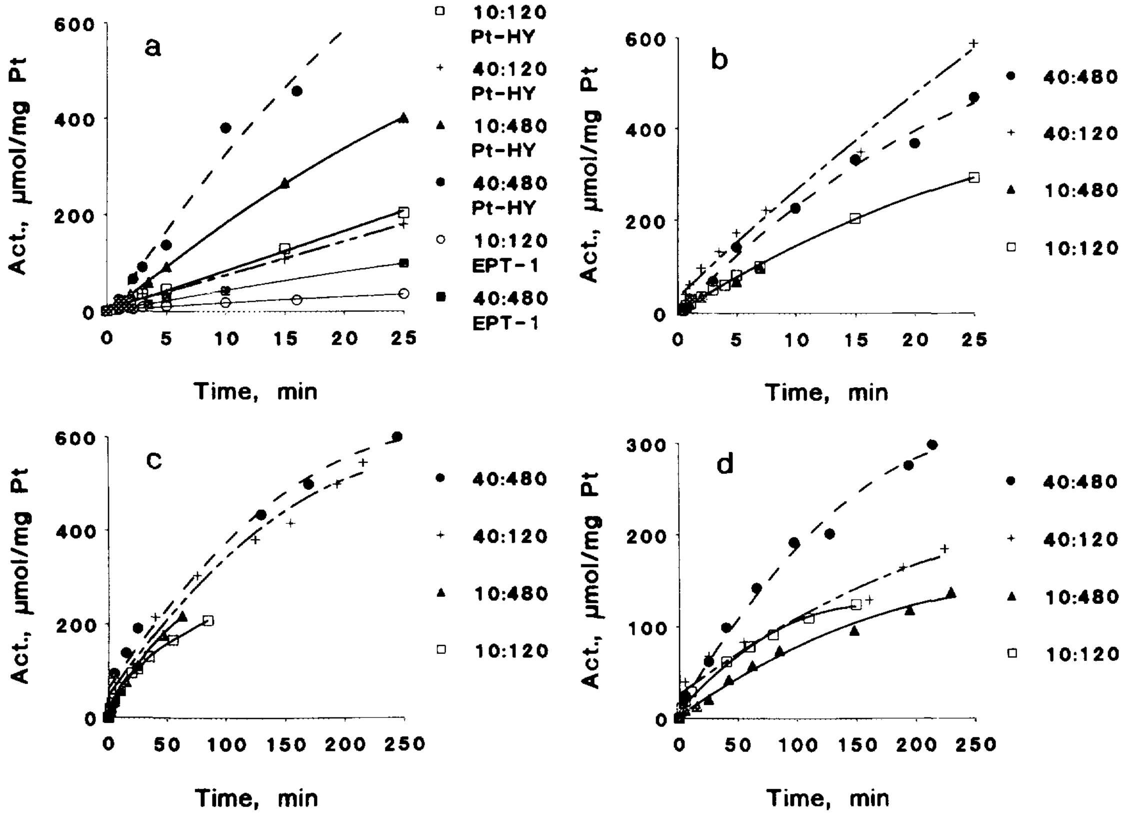

FIG. 1. Specific activity of various catalysts, µmol transformed per unit mass of Pt at various hydrocarbon and hydrogen pressures as a function of the reaction time. T = 603 K. (a) Pt-HY (0.085 mg Pt) and EUROPT-1 (0.13 mg Pt); (b) Pt-NaHY (0.10 mg Pt); (c) Pt-NaY (0.072 mg Pt); (d) Pt-NaX (0.115 mg Pt).

tive runs were also carried out with a pure HY zeolite catalyst (13).

A 50-m by 0.32-mm fused quartz capillary column (coated with CP Sil 5) was used for analysis. It separated well most products from methane to benzene under isothermal conditions except for ethane, ethene, propane, and propene, which could not be separated.

RESULTS

a. Catalyst Activity

Figure 1 shows the amount of transformed *n*-hexane per mass unit of Pt as a function of the sampling time (note the different time and activity scales). The activity of Pt-HY and Pt-NaHY was higher by about an order of magnitude than that of Pt-NaY or Pt-NaX, with EUROPT-1 in an intermediate position. Hardly any deactivation was observed with Pt-HY and Pt-NaHY, as opposed to the other two zeolitic catalysts.

b. Catalyst Selectivity

Selectivity values (S) are shown in Table 2 at similar overall conversions (4–5%) in the sequence of decreasing acidity of the catalysts. Because of the different catalytic activities, different contact times belong to the values shown in the table which, unlike the results shown in Fig. 1, have not been corrected for the different Pt content of the catalysts.

The HY sample without Pt loading produced almost exclusively fragments and isomers. The amount of isomers relative to that of the fragments increased over Pt-containing catalysts. A dramatic drop in the fragmentation

TABLE 2

Selectivity of *n*-Hexane Transformation over Various Pt-Zeolite Catalysts[a]

Catalyst	$p(n\text{H}):p(\text{H}_2)$	Conversion X (%)	Selectivity S (%)				
			$<C_6$	Iso	MCP	Bz	Hexenes
HY (12 mg)	40:120	4.0	63	45	1	0	1
	10:120	3.6	82	16	2	0	0
	40:480	4.4	64	34	1	0	1
	10:480	3.5	82	17	1	0	0
Pt-HY (11 mg)	40:120	4.3	49	34	1	0	16
	10:120	5.1	17	53	1	0	29
	40:480	3.3	14	74	1	1	10
	10:480	3.4	11	79	2	3	5
Pt-NaHY (14 mg)	40:120	5.0	3	51	5	6	35
	10:120	4.2	5	51	9	15	20
	40:480	4.1	5	44	16	15	20
	10:480	4.0	9	38	24	27	2
Pt-NaY (9 mg)	40:120	4.4	3	12	29	30	26
	10:120	5.2	6	11	34	32	17
	40:480	3.9	4	18	40	38	1
	10:480	4.7	6	19	37	38	0
Pt-NaX (14 mg)	40:120	4.2	7	15	41	17	20
	10:120	3.8	7	14	45	15	19
	40:480	4.6	7	44	36	10	3
	10:480	5.5	9	49	32	10	0
EUROPT-1 (2.1 mg)	40:120	3.3	5	8[b]	29	11	47
	10:120	5.3	8	20[b]	44	17	11
	40:480	5.1	8	37[b]	43	10	2
	10:480	4.8	9	45[b]	32	12	2
8% Pt-NaY[c]	40:120	4.1	8	25	25	18	24
	10:120	4.8	12	18	36	24	10
	40:480	5.6	12	28	34	24	2
	10:480	3.8	18	21	35	23	3

[a] $T = 603$ K.

[b] Containing 0.2 to 0.5% 2,3-dimethylbutane.

[c] Sample according to Ref. (17) (pretreated at 633 K).

selectivity (to or below 10%) is seen with Pt-NaHY and with the catalysts having still lower acidity. Isomerization selectivity decreased monotonically in parallel with decreasing catalyst acidity. The isomers consisted mainly of 2- and 3-methylpentanes. While the formation of methylcyclopentane (MCP) was negligible over catalysts HY and Pt-HY, more MCP was formed over Pt-NaHY where also a marked hydrogen effect could be observed. MCP had the highest selectivity over Pt-NaY, Pt-NaX, and EUROPT-1. An opposite hydrogen dependence of isomerization and C_5-cyclization appeared over the latter two catalysts. Pt-NaY produced mostly benzene, aromatic selectivity being less over Pt-NaX with still lower catalyst acidity. Increasing hydrogen pressures favor also aromatization of *n*-hexane over each catalyst, except for Pt-NaX.

The introduction of Pt to a HY zeolite resulted in the appearance of olefins (various *n*-hexene isomers). Their formation was suppressed by increasing hydrogen pressures.

Table 2 also includes results obtained over a 8% Pt-NaY catalyst (17). The general trends were the same in both cases; however, the Pt-NaY catalyst with the higher metal loading had a lower benzene selectivity.

c. Selectivities at Various Contact Times

The change of selectivity varies with increasing conversions (S vs X curves) may supply additional information as far as the possible reaction pathways are concerned. Primary products have finite S values and secondary products have zero S values extrapolated to zero conversion (18, 19). Selectivities as a function of the conversion obtained at $p(n\text{H}):p(\text{H}_2) = 10:120$ over all four zeolite-supported catalysts are shown in Fig. 2.

Isomers and hexenes were the main products over Pt-HY at low conversion values (Fig. 2a). The selectivity of hexenes was not negligible in this range of low conversions, the curves of olefins and isomers having an opposite trend at the beginning of the run. Further on, isomer selectivity remained constant at around 50% and that of fragments increased at the expense of hexenes. Hardly any MCP and no benzene was observed.

Skeletal isomers predominated over Pt-NaHY in the

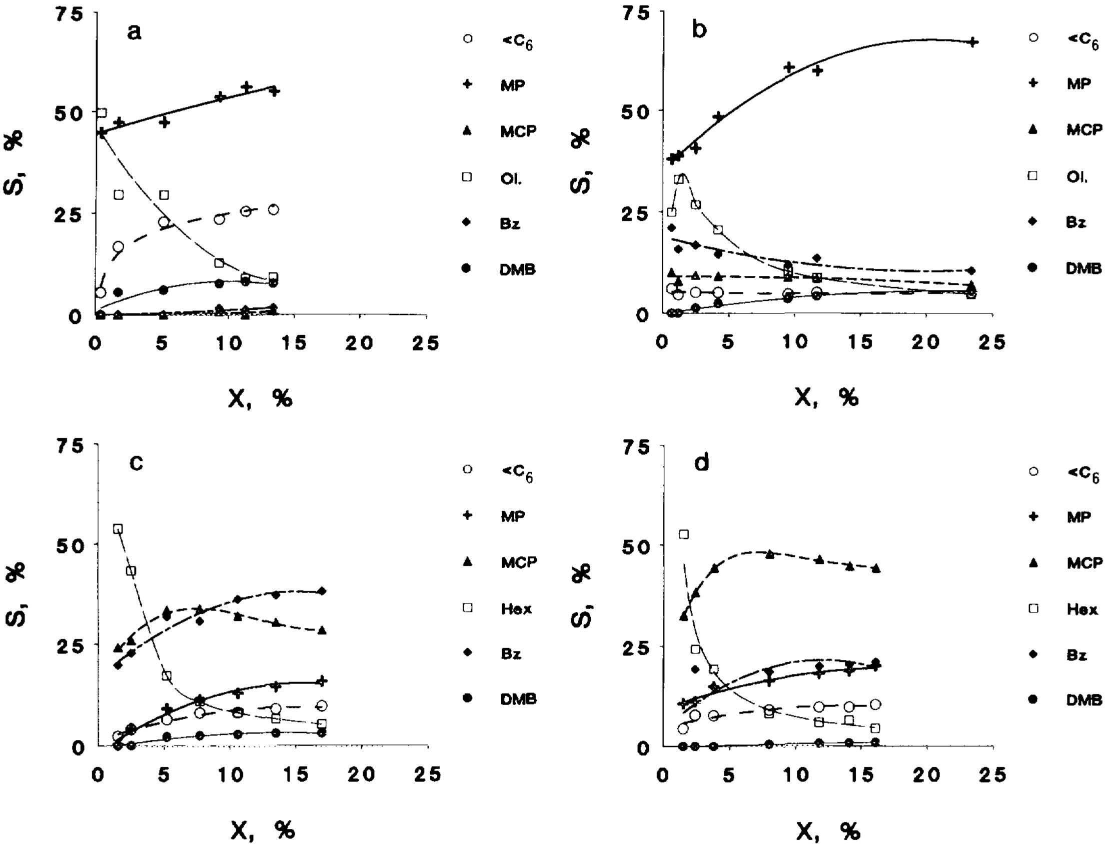

FIG. 2. Selectivities of various product classes ($<C_6$, fragments; MP, methylpentanes; MCP, methylcyclopentane; Bz, benzene; Hex, hexenes; DMB, dimethylbutanes) as a function of the overall conversion, X (%). T = 603 K, $p(n\text{H}):p(\text{H}_2)$ = 10:120. (a) Pt-HY; (b) Pt-NaHY; (c) Pt-NaY; (d) Pt-NaX.

whole conversion range. Their selectivity increased at the expense of hexenes. Benzene selectivity decreased and that of fragments increased, whereas the S value of methylcyclopentane remained practically constant with increasing conversion (Fig. 2b). All these products had non-zero selectivities extrapolated to zero conversion; i.e., all of them were real primary products.

The number of primary products was lower over the other two catalysts. Hexenes belonged to them over both Pt-NaY and Pt-NaX (Figs. 2c and 2d). Their selectivity dropped to rather low values with increasing conversion (the respective contact times were actually higher by almost an order of magnitude with these catalysts than with Pt-NaHY). The aromatizing ability of Pt-NaY was outstanding in the whole conversion range and so was its C_5-cyclization selectivity. Both fragments and isomers seemed to be secondary products (Fig. 2c).

Two primary products, namely hexenes and methylcyclopentane, seemed to be produced over Pt-NaX (Fig. 2d); of these, the selectivity of MCP was highest above ca. 2–3% total conversion.

Methylpentanes represented the main body of skeletal isomers. Dimethylbutanes were present in much lower amounts. These products have been plotted separately in Fig. 2 to demonstrate that their selectivity decreased markedly with decreasing catalyst acidity. 2,2-Dimethylbutane was observed over Pt-HY and Pt-NaHY only, with rather low selectivities (up to 1%).

d. Hydrogen Pressure Sensitivity at Various Conversions

The increase of *absolute* hydrogen pressure did not increase the rate of conversion at 10 Torr *n*-hexane pressure but did so at $p(n\mathrm{H}) = 40$ Torr, except for Pt-NaHY where the relative rate was highest at $p(n\mathrm{H}):p(\mathrm{H}_2) = 40:120$ (Fig. 1). At identical pressure *ratio,* higher rates were observed at the higher total pressure. This was especially marked with Pt-HY and EUROPT-1 (Fig. 1a).

The similar S vs X curves of *n*-hexane reactions had a pronounced hydrogen sensitivity over EUROPT-1 (19). A comparison of these values over three catalysts (Pt-NaHY, Pt-NaY, and Pt-NaX) with a reactant mixture $p(n\mathrm{H}):p(\mathrm{H}_2) = 10:480$ could reveal if there were any hydrogen effects and if so whether they were similar to those observed with the non-acidic EUROPT-1 catalyst.

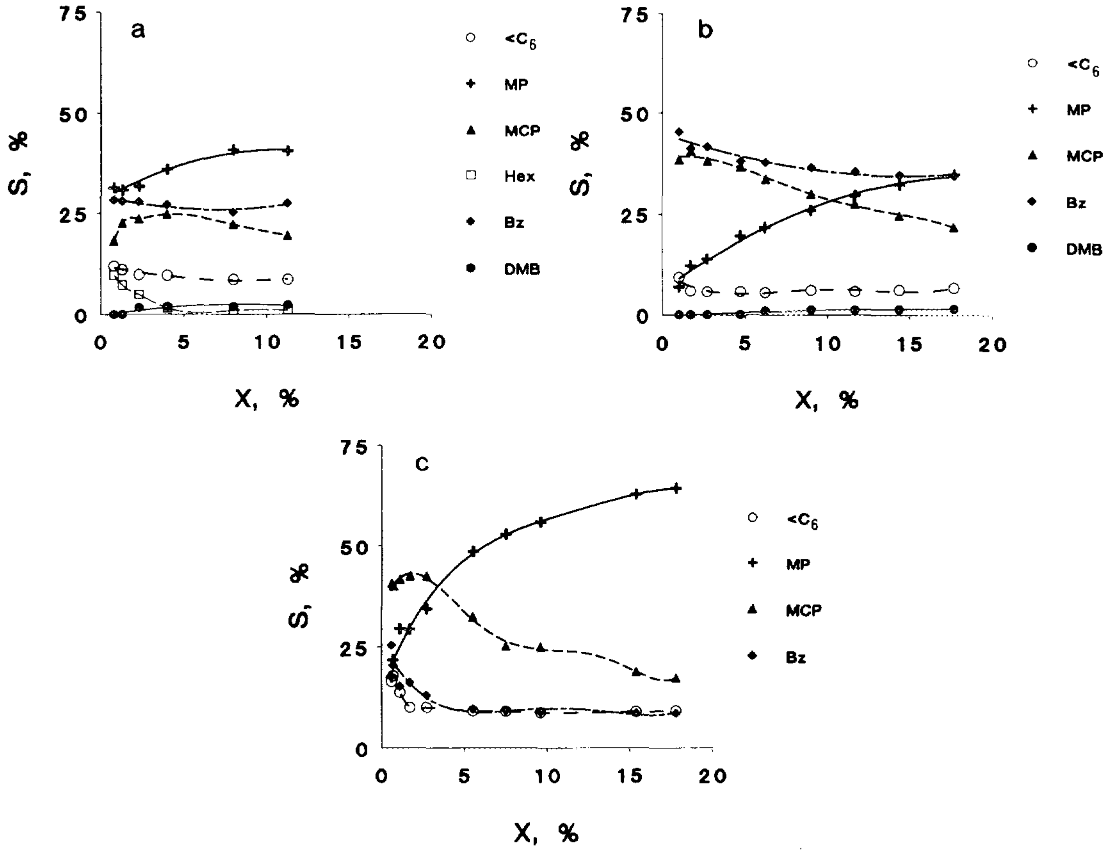

FIG. 3. Selectivities of various product classes as a function of the overall conversion, *X* (%). $T = 603$ K, $p(n\mathrm{H}):p(\mathrm{H}_2) = 10:480$. (a) Pt-NaHY; (b) Pt-NaY; (c) Pt-NaX. Abbreviations are as in Fig. 2.

Essentially the same trends were observed in the S vs X plot over Pt-NaHY in Fig. 3a as in Fig. 2a but the actual S values were different. The selectivity of isomerization was highest but its value remained below 50%; those of C_5-cyclization and aromatization, in turn, increased, together with a much lower initial hexene selectivity.

Hexenes did not appear over Pt-NaY and Pt-NaX at this $p(H_2)$; at the same time, isomers seemed to remain secondary products, in spite of their much higher actual selectivity (Figs. 3b and 3c). C_5-cyclization was more pronounced at a higher hydrogen pressure. This agrees well with previous experience (19, 20); the higher benzene selectivity at higher $p(H_2)$ was, however, unexpected. No marked hydrogen effect appeared in the selectivity of dimethylbutanes.

e. Hydrocarbon Pressure Sensitivity

Higher reaction rates were observed at 40 Torr than at 10 Torr n-hexane pressure at any hydrogen pressure, except for Pt-HY where the rate was higher at the 10 : 120 conditions than at 40 : 120 (Fig. 1).

Higher n-hexane pressure (40 Torr) considerably slowed down the reactions. The results included in Table 2 for a pressure ratio $p(n\mathrm{H}):p(H_2) = 40:120$ can be regarded as typical: an enhanced hexene formation (decreasing much more slowly during the run) and much lower S values of all other products than with a ratio of 10 : 120 were observed. The priorities of product formation over all three catalysts did not exhibit dramatic changes.

The S vs X curves at a pressure ratio $p(n\mathrm{H}):p(H_2) = 40:480$ resembled those observed with $p(n\mathrm{H}):p(H_2) = 10:120$, the hydrocarbon-to-hydrogen ratio being equal to 1 : 12 in both cases. At $p(n\mathrm{H}):p(H_2) = 40:480$, the hexene selectivity dropped more rapidly than at 10 : 120 and, at higher conversions, slight changes of the actual S values were also seen: e.g., S_{iso} went up to 55–60% over Pt-NaHY instead of 65–70%. Both S_{MCP} and S_{iso} were higher over Pt-NaY. Pt-NaX gave lower MCP and higher isomer selectivities.

f. Product Distribution

Various product ratios have been considered as characteristic of the geometry, acidity, or surface state of supported Pt catalysts. For example, the ratio *benzene/(benzene + fragments)* was suggested to be characteristic of the position of Pt in or on zeolites: lower ratios would, accordingly, indicate more particles on the outer zeolite surface (21). This ratio changed roughly parallel to particle size even at this low temperature and pressure (6). In our case, very low values (0.01 to 0.12) were seen with Pt-HY. Much higher ratios (higher than 0.4) appeared with the other three catalysts, the maximum values (0.77 to 0.86) being observed over Pt-NaY. These values *increased* with the conversion under the same conditions (in accordance with Figs. 2 and 3).

The *isomer ratios* (2-methylpentane/3-methylpentane, 2MP/3MP) have been suggested to depend on, among other factors, the acidity of the catalyst, lower values indicating acidic isomerization (6, 22, 23). Hydrogen pressure is another factor (20, 24) together with Pt geometry; this latter factor includes also the presence of "adlineation sites" at the metal-support borderline (25). In the present study, 2MP/3MP was between 1.4 and 1.9 with Pt-HY, Pt-NaHY, and Pt-NaY, whereas values around 2 are observed over Pt-NaX, supporting the importance of acidity in our case.

The *benzene/methylcyclopentane* (Bz/MCP) ratio has been found to increase with temperature and decrease with increasing pressure (26, 27), and may be characteristic of the amount of hydrogen availability on the active centers of Pt catalysts. The values of the *benzene/C_6 saturated* ratio (considering both MCP and isomers as products of the same surface intermediate) have been collected in Table 3. These values depend on the nature of the catalyst rather than on the hydrogen pressure: low values are characteristic of the acidic catalysts (exhibiting high isomerization selectivity) as well as of Pt-NaX where the formation of C_6 saturated products prevails.

The *distribution of fragments* is shown in Fig. 4 for the runs shown also in Table 2 (or similar ones at $X = 4$–5%). Whenever butenes, pentenes, and/or isobutane and isopentane were present (mainly at lower hydrogen excess over Pt-HY and Pt-NaHY), the respective C_4 and C_5 fractions contain also their amounts. Results obtained with a mechanical mixture of EUROPT-1 plus pure HY (13) have also been included in Fig. 4 for comparison.

TABLE 3

Hydrogen Effects on C_5- and C_6 Ring Formation over Various Zeolites

Catalyst	$p(n\mathrm{H}):p(H_2)$	Conversion X (%)	Ratio benzene/ C_6 saturated	Ratio benzene/ MCP
Pt-HY	40 : 120	6.7	0.01	0.8
	10 : 120	11.3	0.02	—
	40 : 480	10.9	0.01	0.6
	10 : 480	8.9	0.02	0.95
Pt-NaHY	40 : 120	10.8	0.08	1.5
	10 : 120	11.7	0.20	1.6
	40 : 480	10.5	0.21	1.1
	10 : 480	11.3	0.46	1.4
Pt-NaY	40 : 120	10.1	0.80	1.3
	10 : 120	10.6	0.81	1.1
	40 : 480	11.3	0.55	1.1
	10 : 480	11.7	0.62	1.3
Pt-NaX	40 : 120	5.3	0.31	0.43
	10 : 120	10.1	0.25	0.35
	40 : 480	8.9	0.11	0.33
	10 : 480	9.6	0.11	0.36

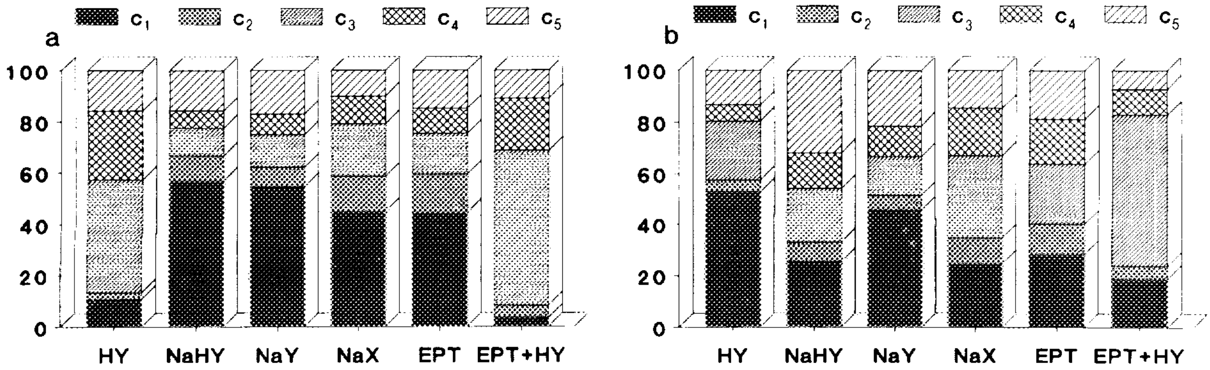

FIG. 4. Distribution of C_1–C_5 fragments over different Pt catalysts, normalized to $<C_6$ 100%. (a) $p(n\mathrm{H}):p(\mathrm{H_2}) = 10:120$; (b) $p(n\mathrm{H}):p(\mathrm{H_2}) = 10:480$. For clarity, only the supports of the Pt catalysts are shown. EPT, EUROPT-1. Product distributions obtained over a mechanical mixture of EUROPT-1 and HY are also included; the results at 10:120 have been taken from the diploma work of M. Räth, those at 10:480 from Ref. (13).

The product composition may be informative whether a hydrogenolysis or cracking mechanism prevails. This is the situation with the mixed catalyst. Pt-HY is the only catalyst where the formation of C_1 and C_2 fragments was minor, especially at $p(\mathrm{H_2}):p(n\mathrm{H}) = 10:120$. A marked methane excess indicates a multiple fragmentation superimposed on single rupture (20) in all other cases. The product distribution resembled that observed over completely non-acidic EUROPT-1 (with a slight preference of middle rupture); hence, it can be stated that *hydrogenolysis* rather than cracking is the main process of fragmentation. Less methane was formed at higher hydrogen pressure (Fig. 4b) and the distributions, even with Pt-HY, were still closer to that appearing over EUROPT-1. However, at higher conversion cracking reactions were more important (e.g., at ca. 25% conversion the amount of propane already exceeded that of the methane over Pt-HY).

DISCUSSION

The activity of the Pt-zeolite catalysts can be classified into two groups: those having more pronounced acidity (Pt-HY and Pt-NaHY) constitute the first group and are more active by an order of magnitude than the others in the second group where acidity is suppressed. EUROPT-1 is between the two classes, similarly to various Pt-KL catalysts (6).

Increasing the hydrocarbon pressure from 10 to 40 Torr (at identical pressure ratio) increased also the reaction rates, although less than proportionally (except with Pt-HY), indicating that a saturation coverage with hexane was approached but not reached. This type of dependence of the overall rate on the n-hexane pressure resembled that observed with EUROPT-1 (12, 16). On the other hand, the effect of hydrogen on overall rate was much less marked.

The deactivation of acidic samples was almost unnoticeable, wheres that of non-acidic samples was pronounced. A specific feature of the applied closed circulation loop is that the hydrogen on the active metal surface of the catalyst ("Pt-H") is gradually replaced by not too deeply dehydrogenated hydrocarbons and becomes a "Pt-C-H" system (28). The degree of the coverage of the metal and the extent of dehydrogenation of sorbed hydrocarbon is a function of the hydrocarbon/hydrogen pressure ratio (28a). Pt deactivation occurs when this surface "hydrocarbon pool" is gradually dehydrogenated further to give a "Pt-C" catalyst (29, 30). (One has to recall earlier assumptions (12) that one C_6 molecule may be sufficient to cover the free metal atoms of a small Pt particle with dimensions of 1–2 nm and that its gradual dehydrogenation can do this work.) Apparently, deactivation is slower in the presence of acidic centers. The present experiments point to a higher rate of migration of coke precursors from metal to the support in the presence of acidic sites. It must be stressed that this statement should be valid for the behavior of *coke precursors during a catalytic run*. The behavior of a "stabilized coke" was reported to be different: coke on acidic support sites was more resistant to oxidation than coke on metallic centers (31).

The main function of Pt on a HY support was dehydrogenation (producing olefins). There was a short initial period (Fig. 2a) with decreasing isomer and increasing olefin selectivity, corresponding to the rapid initial replacement of surface hydrogen by surface hydrocarbons (19). It is just the presence of "Pt-C-H" entities that prevents the complete rehydrogenation of hexenes, as observed also when hexenes were used as reactants over $\mathrm{Pt/SiO_2}$ (30). A further decrease of hexene selectivity was accompanied by a parallel increase of fragmentation. This may mean a rapid deactivation of the metallic sites with a concomitant more and more important fragmentation over acidic sites (cf. Figs. 1a and 2a). The overall activity remained apparently constant during all these selectivity changes. The complete absence of methylcyclopentane over Pt-HY indicates the absence of C_5-cyclic surface intermediates (15), and hence isomers were probably *not* produced over metallic sites in this catalyst.

The predominant reaction over both acidic catalysts was acid-catalyzed isomerization. The acidity of our samples was apparently not sufficient to bring about massive cracking, its extent being comparable with that of isomerization over Pt-HY and rather unimportant over Pt-NaHY. This is confirmed also by the fragment distribution (Fig. 4), which points to detectable cracking over Pt-HY only. A mechanical mixture of EUROPT-1 and HY (13) produced more C_3 fragments and less methane than any of the zeolite-supported Pt catalysts. This indicates that our Pt-zeolite catalysts possessed a lower acidity. The hydrogen effect on Pt-HY is remarkable: at lower hydrogen excess it behaves like the mechanical mixture whereas higher hydrogen pressure enhances the relative importance of hydrogenolysis to a higher extent than with the mixed catalyst.

Isomers were the main products over Pt-NaHY. The rather low selectivity of MCP indicates that some metal-catalyzed isomerization took place. The methylcyclopentane selectivity was higher at higher $p(H_2)$; with a purely metal-catalyzed pathway, it would decrease and that of isomers would increase (19, 20). This inverse hydrogen response points to the minor importance of the metal-catalyzed isomerization pathway over Pt-NaHY, also.

Pt-HY was totally inactive in aromatization. No benzene formation was reported from *n*-hexane over Pt-NaHY at 773 K (1a, 8). Some benzene has been found in the present study but the benzene selectivity was rather low also over Pt-NaHY. Aromatization seems to be a largely metal-catalyzed process under these conditions.

Much higher MCP selectivities were observed over Pt-NaY, together with an enhanced aromatization. The primary character of methylcyclopentane is obvious (Fig. 2c); the maximum in the curve for MCP indicates that it reacted further to give isomers which were not primary products over this catalyst. The response of S_{MCP} and S_{isomer} to hydrogen pressure changes was typical for a metallic catalyst: higher $p(H_2)$ enhances isomerization at the expense of C_5-cyclization (16, 19, 20, 26). It is, however, unexpected that higher hydrogen pressure favors aromatization. The opposite trend of hexene and benzene selectivity (Fig. 2c) indicates that the aromatization route involving unsaturated intermediates (14, 32) prevailed here. Hexenes disappeared more rapidly at $p(nH)$: $p(H_2)$ = 40 : 480, MCP and benzene selectivities being otherwise similar to those shown in Fig. 2c. With high hydrogen excess (Fig. 3b), no hexenes appeared; benzene seemed to be a primary product, formed probably by a "direct route" (33). This may be another example of a "mechanism changeover" caused by hydrogen (19, 20, 34).

The selectivity changes on Pt-NaX (Figs. 2d and 3c) showed a pattern typical of a supported metallic catalyst favoring, first of all, the formation of C_6 saturated products. Their hydrogen response as well as that of benzene (suppressed by higher hydrogen pressure) corresponded to earlier observations (16, 19, 20). The initial selectivity changes (Fig. 3c) were similar to those reported for EUROPT-1 (19), corresponding to the changes from the Pt-H to the Pt-C-H state.

Although the amount of 2,2- and 2,3-dimethylbutanes was marked over acidic Pt-HY and Pt-NaHY only, it has to be stressed that probably a "bond shift"-type of metal-catalyzed isomerization produced some 2,3-dimethylbutane over Pt-NaY, Pt-NaX (Figs. 2c and 2d), and even EUROPT-1 (Table 2).

Two of our catalysts (Pt-HY and Pt-NaHY) behaved like acidic catalysts with some additional metal function, and the two others (Pt-NaY and Pt-NaX) like a metal on a non-acidic support (similar to Pt/SiO_2). The interaction of centers which are acidic and metallic, or alternatively basic and metallic, can be regarded as responsible for the subtle features of each catalyst. The most remarkable of these is the enhanced benzene selectivity over Pt-NaY which shows also a non-typical hydrogen response. Recent results reported high aromatization selectivity on Pt/MgO (7a). One possible explanation of this phenomenon is the enhanced aromatization activity of Pt sites interacting with the basic support (7b, 35). Hence, it is not excluded that the interaction of moderately basic sites with Pt resulting in electron donation to the metal, which has been demonstrated experimentally (8), is the main reason for the outstanding aromatization selectivity. At the same time, the lower aromatization selectivity of the more basic Pt-NaX indicates that other factors such as metal geometry (20, 36, 37) may also be important. The Pt-NaY sample of the present study produced higher benzene selectivities than any of the KL samples previously studied (6) and than any of a series of 8% Pt-NaY catalysts pretreated at different temperatures (17). The series Pt-HY, Pt-NaHY, and Pt-NaY may exemplify that the acid–base properties can be more important than structure effects. Pt-NaX with highest basicity, in turn, was more active in C_5-cyclic reactions than in aromatization (Table 3), indicating that acid–base properties may not represent the exclusive factor responsible for the catalytic properties exhibited in *n*-hexane reactions.

ACKNOWLEDGMENTS

The catalytic experiments were carried out in the Institute of Isotopes. Their completion was supported, in part, by the National Science Foundation, OTKA Grant 1887. The authors thank one of the referees for useful suggestions.

REFERENCES

1. (a) Bernard, J. R., *in* "Proceedings of the 5th International Congress on Zeolites, Naples, 1980" (L. V. C. Rees, Ed.), p. 725. Heyden, London, 1980; (b) Hughes, T. R., Buss, W. C., Tamm, P. W., and Jacobson, R. L., *in* "New Developments in Zeolite Science and Technology" (Y. Murakami, A. Iijima, and J. W. Ward, Eds.), p. 725. Kodansha–Elsevier, Tokyo/Amsterdam, 1986.
2. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., *in* "Chemistry of Catalytic Processes," Chap. 3, p. 184. McGraw–Hill, New York, 1979.
3. Derouane, E. G., and Vanderveken, D. J., *Appl. Catal.* **45,** L15 (1988).
4. Iglesia, E., and Baumgartner, J. E., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guczi, F. Solymosi, and P. Tétényi, Eds.), Part B, p. 993. Elsevier, Amsterdam/Akadémiai Kiadó, Budapest, 1993.
5. Moretti, G., and Sachtler, W. M. H., *J. Catal.* **116,** 350 (1989).
6. Manninger, I., Zhan, Z., Xu, X. L., and Paál, Z., *J. Mol. Catal.* **65,** 223 (1991).
7. (a) Derouane, E. G., Jullien-Lardot, V., Davis, R. J., Blom, N., and Højlund-Nielsen, P. E., *in* "Proceedings, 10th International Congress on Catalysis, Budapest, 1992" (L. Guczi, F. Solymosi, and P. Tétényi, Eds.), Part B, p. 1031. Elsevier, Amsterdam/Akadémiai Kiadó, Budapest, 1993. (b) Clarke, J. K. A., and Rooney, J. J., succeeding discussion to (a), pp. 1040 and 1041.
8. de Mallmann, A., and Barthomeuf, D., *in* "Zeolites as Catalysts, Sorbents and Detergent Builders" (H. G. Karge and J. Weitkamp, Eds.), p. 429. Elsevier, Amsterdam, 1989.
9. de Mallmann, A., and Barthomeuf, D., *J. Chim. Phys. Phys.–Chim. Biol.* **87,** 535 (1990).
10. de Mallmann, A., These d'Etat. Paris, 1987.
11. Barthomeuf, D., *J. Phys. Chem.* **88,** 42 (1984).
12. Bond, G. C., and Paál, Z., *Appl. Catal.* **86,** 1 (1992).
13. Paál, Z., Räth, M., Zhan, Zh., and Gombler, W., *J. Catal.*, in press.
14. Paál, Z., and Tétényi, P., *in* "Catalysis Specialist Periodical Reports" (G. C. Bond and G. Webb, Eds.), Vol. 5, p. 80. The Royal Society of Chemistry, London, 1982.
15. Maire, G., and Garin, F., *in* "Catalysis, Science and Technology" (J. R. Anderson and M. Boudart, Eds.), Vol. 6, p. 161. Springer, Berlin, 1984.
16. Paál, Z., Groeneweg, H., and Zimmer, H., Catal. Today **5,** 199 (1989).
17. Paál, Z., Zhan, Zh., Manninger, I., and Sachtler, W. M. H., in preparation.
18. Margitfalvi, J., Szedlacsek, P., Hegedüs, M., and Nagy, F., *Appl. Catal.* **15,** 69 (1985).
19. Paál, Z., Manninger, I., Zhan, Zh., and Muhler, M., *Appl. Catal.* **66,** 305 (1990).
20. Paál, Z., Groeneweg, H., and Paál-Lukács, J., *J. Chem. Soc., Faraday Trans.* **86,** 3159 (1990).
21. Tauster, S. J., and Steger, J. J., *J. Catal.* **125,** 387 (1990).
22. Christoffel, E. G., and Paál, Z., *J. Catal.* **73,** 30 (1982).
23. Lerner, B. A., Carvill, B. T., and Sachtler, W. M. H., *J. Mol. Catal.* **77,** 99 (1992).
24. Paál, Z., *Catal. Today* **2,** 595 (1988).
25. Kramer, R., and Zuegg, H., *J. Catal.* **80,** 446 (1983); *J. Catal.* **85,** 530 (1984).
26. Paál, Z., *in* "Hydrogen Effects in Catalysis" (Z. Paál and P. G. Menon, Eds.), p. 449. Dekker, New York, 1988.
27. Davis, S. M., Zaera, F., and Somorjai, G. A., *J. Catal.* **85,** 206 (1984).
28. (a) Sárkány, A., *J. Chem. Soc., Faraday Trans. I* **85,** 1523 (1989); (b) Foger, K., and Gruber, H. L., *J. Catal.* **122,** 307 (1990).
29. Webb, G., *Catal. Today* **7,** 139 (1990).
30. Paál, Z., Räth, M., Brose, and Gombler, W., *React. Kinet. Catal. Lett.* **47,** 43 (1992).
31. Barbier, J., *in* "Catalyst Deactivation 1987" (B. Delmon and G. F. Froment, Eds.), p. 1. Elsevier, Amsterdam, 1987.
32. Paál, Z., and Tétényi, P., *J. Catal.* **30,** 350 (1973).
33. Dautzenberg, F. M., and Platteeuw, J. C., *J. Catal.* **19,** 41 (1970).
34. Paál, Z., and Xu, X. L., *Appl. Catal.* **43,** L1 (1988).
35. Baird, T., Kelly, E. J., Patterson, W. R., and Rooney, J. J., *J. Chem. Soc., Chem. Commun.*, 1431 (1992).
36. Derouane, E. G., Jullien-Lardot, V., Pasau-Claerbout, A., Blom, N. J., and Højlund-Nielsen, P. E., *in* "Europacat-1 (Montpellier 1993)," Vol. 2, p. 645. [Abstracts]
37. Sepulveda-Escribano, A., Guerrero-Ruiz, A., and Rodriguez-Ramos, I., *in* "Europacat-1 (Montpellier 1993)," Vol. 2, p. 696. [Abstracts]