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NOTE

Reactions of *n*-Hexane over EUROPT-1 and Its Mechanical Mixtures with HY in Different Configurations

The classical bifunctional mechanism of hydrocarbon reforming includes both metal-catalyzed and acid-catalyzed reactions (1). The intermediates produced by one of these functions react further on the other type of active site and vice versa. These centers need not be in the immediate vicinity of one another; i.e., the intermediates can be transported from one type of catalytic site to the other in the gas phase; they can even be separated by distances exceeding the free molecular pathway by several orders of magnitude, as shown by experiments using two separate catalyst beds (2, 3).

An interplay of metallic and acidic sites over zeolite-supported Pt catalysts (Pt-KL, Pt-NaY) has been reported to enhance, first of all, the isomerization selectivity (4, 5). The acidic sites arose during the reduction of Pt by H_2 (6)

$$Pt^{n+} + (n/2)H_2 \rightarrow (n/2)Pt^0 + (n/2)H^+$$

and were probably weak since no sign of acid-catalyzed cracking was observed.

It was of interest to test catalysts where the acidic and metallic functions were physically separated. EUROPT-1 (a well-characterized 6.3% Pt/SiO_2 catalyst (7), abbreviated below as EUROPT and also as EP) has been selected as the carrier of the metallic function and HY as the acidic catalyst. The present study is complementary to another one where the *acidity* of the support has been changed systematically (8).

The experiments were carried out in a closed circulation loop (9, 10). This consisted of a closed volume of ca. 180 ml containing an all-glass circulating pump (a glass plunger with a welded-in iron core driven by an electromagnet giving a periodic movement). Four valves ensured that the flow direction was the same during the alternating movement of the plunger. The time required for any gas volume to complete one full circle in the loop was 10–15 s.

The catalyst layer (about 0.2 ml) was placed in a U-tube of inner diameter 5 mm, this tube being separated by two stopcocks during preparation of the initial reactant mixture. Two types of catalyst were used: one a physical mixture of the two entities (denoted as EUROPT + HY) and the other an arrangement of the EUROPT and HY separated by a quartz wool layer of about 3 mm. The U-tube containing the catalyst layers was attached to the loop in two ways in order to ensure two directions of circulation of the reactant mixture, i.e. either from EUROPT to HY or from HY to EUROPT. The two beds were separated by a volume of about 0.1 ml one way and by about the total loop volume (about 180 ml) the other way round. A volume of ca. 50 ml separated the sampling valve from the catalyst layer and the sampling took place after 2–50 min. Since 1 min. contact time comprising four to six full circulations was more than sufficient to reach a rather good mixing in the whole loop (having a very large volume compared to that of the catalyst bed), we feel it justified that the samples reflect the true composition in a well-mixed loop even with relatively short runs. Any differences, therefore, must be due to the different configuration of the catalyst(s).

Results obtained at 603 K with 480 Torr $p(H_2)$ and two *n*-hexane pressures (10 and 40 Torr) will be reported.

The conversion X as a function of time is seen in Fig. 1. The initial activity of all catalysts was nearly the same at $p(n\text{H}):p(H_2) = 40:480$, EUROPT showing signs of deactivation after 20–30 min. The measured activity of the physical mixture was higher than that of the two separate layers, however, after correcting the results for the higher amount of EUROPT in the mixture, this difference became negligible. Pure HY was much less active.

The X vs time plots for $p(n\text{H}):p(H_2) = 10:480$ indicate more rapid transformation. Any attempt to show separate curves representing results for the different configurations in the 10:480 case would result in curves being almost indistinguishably close to each other. That is the reason why Fig. 1 contains only one curve for this case. Bearing in mind, however, that the same percentage conversion represents four times more molecules transformed at $p(n\text{H}) = 40$ Torr, the *activity* is higher in that case.

Table 1 contains selectivities of various product classes at $p(n\text{H}):p(H_2) = 40:480$. A pronounced cracking and some isomerization was characteristic of HY, while a marked dehydrogenation over EUROPT was accompanied by all types of possible skeletal reactions (isomerization, C_5-cyclization aromatization and fragmentation). The olefins almost disappeared in the presence of HY of

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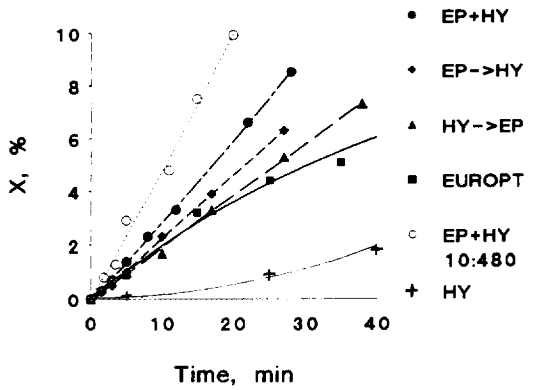

FIG. 1. Overall conversion X (%) of n-hexane as a function of time over various catalysts; $p(n\text{H}):p(\text{H}_2)$ = 40:480, except where noted otherwise.

TABLE 1

Selectivities for Main Product Classes over Different Catalysts ($p(n\text{H}):p(\text{H}_2)$ = 40:480)[a]

Catalyst	Conversion (%)	Selectivity (%)				
		$<C_6$	Iso	MCP	Hex	Bz
HY	3.1	64	34	1	1	—
EUROPT-1	3.4	5	20	31	37	7
EUROPT-1 + HY	3.3	46	43	8	1	2
EP → HY	3.9	46	37	13	1	3
HY → EP[a]	3.3	46	39	12	1	2

[a] Abbreviations: Iso, skeletal isomers (almost exclusively methylpentanes); MCP, methylcyclopentane; Hex, hexenes; Bz: benzene; EP, EUROPT-1.

any configuration, the isomer selectivity being higher, that of fragments being lower than over the pure acidic catalyst. The presence of some methylcyclopentane (MCP) indicates that the metallic function was still operative in the mixture. The low benzene selectivity indicates, however, that hardly any bifunctional aromatization took place, due perhaps to the low temperature. One must not forget that much longer reaction times are required to reach the same conversion over HY than over any of the Pt-containing combinations.

The selectivity values were almost constant in the conversion range between 0 and 10% under these pressure conditions. At $p(n\text{H}):p(\text{H}_2)$ = 10:480, however, the configuration of the bed strongly affects the *initial* selectivi-

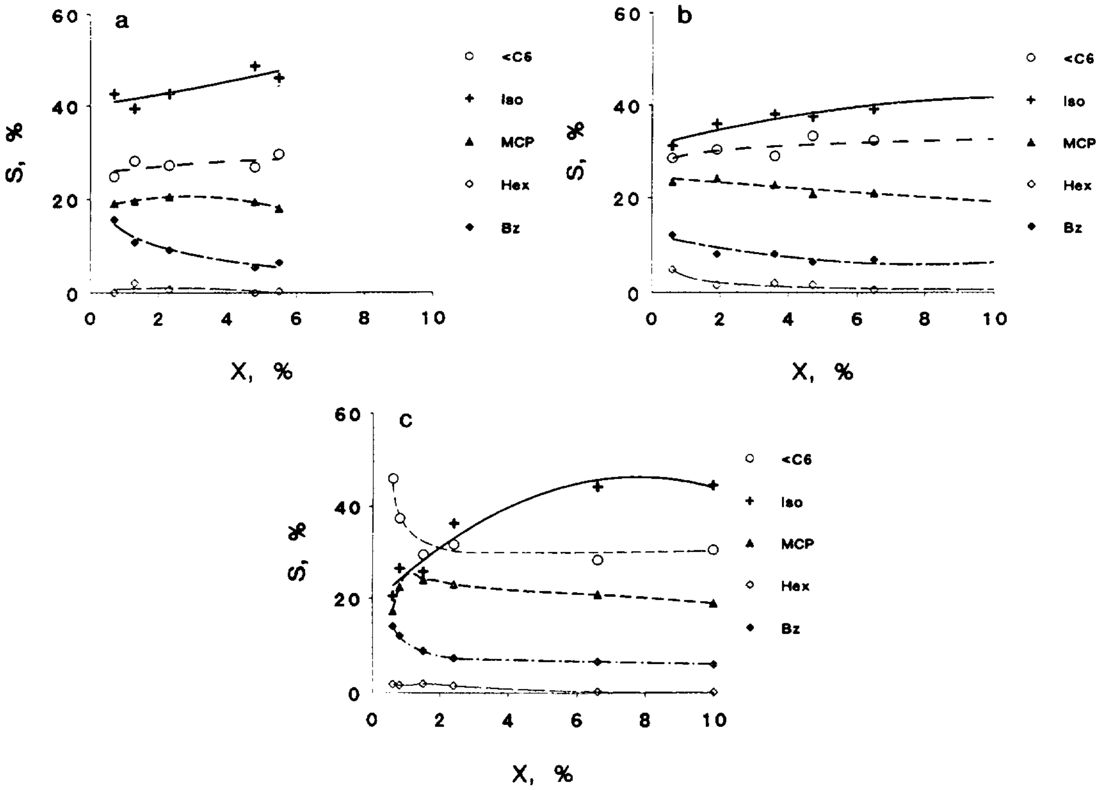

FIG. 2. Selectivity S (%) of various product classes as a function of the overall conversion X (%) at a pressure ratio $p(n\text{H}):p(\text{H}_2)$ = 10:480 for different catalyst configurations. (a) EUROPT-1 + HY (mechanical mixture); (b) separate layers of the catalysts, flow direction from EUROPT-1 to HY; (c) separate layers, flow direction from HY to EUROPT-1.

ties (Fig. 2). The differences were small between EUROPT + HY (Fig. 2a) and the setup EUROPT → HY (Fig. 2b): the somewhat higher initial benzene selectivity over the mixture was due to the metallic sites in this case and so was the more pronounced MCP-to-isomer transformation. The higher cracking selectivity in Fig. 2b should be due to the independent action of the acidic function. Pronounced initial changes were seen, in turn, with the other arrangement, i.e., HY → EUROPT where a maximum in MCP, a slowly increasing isomerization, and a high initial fragment selectivity manifested themselves (Fig. 2c), the benzene selectivity being close to that of the mixed catalyst.

Analysis of the fragment composition throws some light on the reason for these differences. No differentiation could be made between ethane and ethene, and the propane–propene separation was also poor, and hence the data are summarized according to carbon number (see Table 2). The fragments at $p(n\mathrm{H}):p(\mathrm{H_2}) = 40:480$ contained nearly 60% C_3 over the purely acidic HY, the abundance of methane being at or below 10%, corresponding to the expected product distribution from cracking of *n*-hexane over an acidic zeolite (11). A high initial methane formation is seen during the "running-in" period of EUROPT. This was attributed earlier (10) to an initial multiple splitting of *n*-hexane ($C_6 \rightarrow 6CH_4$). The *relative* methane concentration decreased rapidly at higher conversions. The predominant fragmentation reaction in this stage was single *hydrogenolysis* at the middle of the hexane molecule (10). Any possible *cracking* reaction in the presence of HY would add to the abundance of C_3 fragments which was, indeed, higher over the combined catalysts even at low conversions. The single result with high methane amount at $X = 0.3\%$ over EUROPT + HY indicates that the levelling off of the composition may need a short time but this was already complete at the conversions of 2–3% shown. At $p(n\mathrm{H}):p(\mathrm{H_2}) = 10:480$ (Table 2, bottom) the changes were slower. One of the reasons for this may be the much higher methane amount produced initially over EUROPT (in agreement with earlier experience (10)) which must have had a more marked role in determining the fragment composition.

TABLE 2

Fragment Composition at Various Conversions[a]

Catalyst (amount)	Conversion (%)	Fragment composition (%)				
		C_1	C_2	C_3	C_4	C_5
	$p(n\mathrm{H}):p(\mathrm{H_2}) = 40:480$					
HY	0.9	12	3	63	13	9
(12.2 mg)	3.1	4	3	59	20	14
EUROPT-1	0.9	64	10	14	6	6
(2.1 mg)	3.2	47	14	20	10	10
	8.6	31	17	24	15	13
EUROPT-1 + HY	0.3	46	3	42	6	3
(2.1 + 21 mg)	0.7	23	4	53	11	9
	2.3	10	4	57	17	12
EP → HY	0.5	27	5	52	9	7
(1.6 + 17 mg)	2.3	10	5	58	16	11
HY → EP	1	12	5	54	17	12
(17 + 1.6 mg)	3.3	6	4	54	21	15
	$p(n\mathrm{H}):p(\mathrm{H_2}) = 10:480$					
HY	1.4	16	7	69	7	1
	3.4	9	7	74	8	2
EUROPT-1	0.5	88	4	5	3	—
	2.9	67	9	12	7	5
	10	46	13	19	12	10
EUROPT-1 + HY	0.7	64	5	29	2	—
	2.3	33	6	48	8	5
	5.5	19	5	59	10	7
EP → HY	0.5	23	9	59	9	—
	1.9	14	9	58	12	7
	11	11	8	59	13	9
HY → EP	0.5	41	9	46	4	—
	1.5	17	11	54	11	7
	10	15	8	55	13	9

[a] Abbreviations are as in Table 1.

The same reasoning may be valid for the higher *initial* fragment concentration with HY → EUROPT (Fig. 2c) which was also accompanied by a high methane concentration and must have been due, accordingly, to an enhanced initial metal-catalyzed hydrogenolysis (10), including also the fragmentation of the precursors of C_5-cyclic reactions, rather than cracking over HY. Obviously, *n*-hexane can be activated more rapidly over EUROPT than over HY: the intermediates leaving the Pt/SiO_2 layer complete their transformation over the acidic layer. When, in turn, *n*-hexane meets HY first, the intermediates react more pronouncedly over the subsequent metal catalyst layer and the effect of the mixed catalyst manifests itself at a later stage of the run. The contact time required for levelling off in Fig. 2c was about 5 min, which means that any incomplete mixing can be excluded. The initial predominance of the metallic function is reflected in the fragment composition over the mixed catalyst, which must be a more sensitive indicator than the overall selectivity (Fig. 2a).

To sum up, *both* the acidic *and* the metallic function determined the product composition seen over combinations of HY and EUROPT. The influence of the separation of the two catalyst layers manifested itself in the very first moments of the runs only. When the reactant meets a metal catalyst first and thereafter an acidic one, the product composition resembles that obtained with well-mixed catalysts. When the acidic layer is first, the initial composition resembles that observed over the metallic layer. Hence, the *primary* activation of *n*-hexane molecules should be more rapid on metallic sites and the effect of acidic sites manifests itself on the primary intermediates. The primary activation of *n*-hexane over the acidic sites is much slower.

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