RESULTS AND DISCUSSION

CHAPTER 3

RESULTS AND DISCUSSION

3.1 n-Hexane Hydroconversion Using H-ZSM-5-containing Catalysts

3.1.1 Unloaded H-ZSM-5 Zeolite Catalyst (H-Z Catalyst)

The catalytic activity of H-ZSM-5 zeolite (H-Z catalyst) for n-hexane hydroconversion is of a moderate level (Table 1 and Fig. 1), i.e., 1.8-37.5 % at temperatures between 350 and 500 °C, respectively, where the hydrocracked components are the major products; they comprise 1.8-36.2 % during this temperature range. Hence the principal reaction using H-ZSM-5 zeolite as a catalyst is hydrocracking. Although this catalyst does not contain metal sites, hydrocracked products (saturated) are almost only obtained indicating that H-ZSM-5 zeolite can work via hydrogen transfer and it can be said to possess self-hydrogenating capability.

Platteeuw et al. **[192]** have found that amorphous silica-alumina possesses a self-hydrogenating activity which is accomplished via hydrogen transfer for a period of time, even in the absence of hydrogen. ***Aboul-Gheit et al.*** have also assumed that γ-alumina **[193]** and H-mordenite zeolite **[194]** possess self-hydrogenating activities. On the

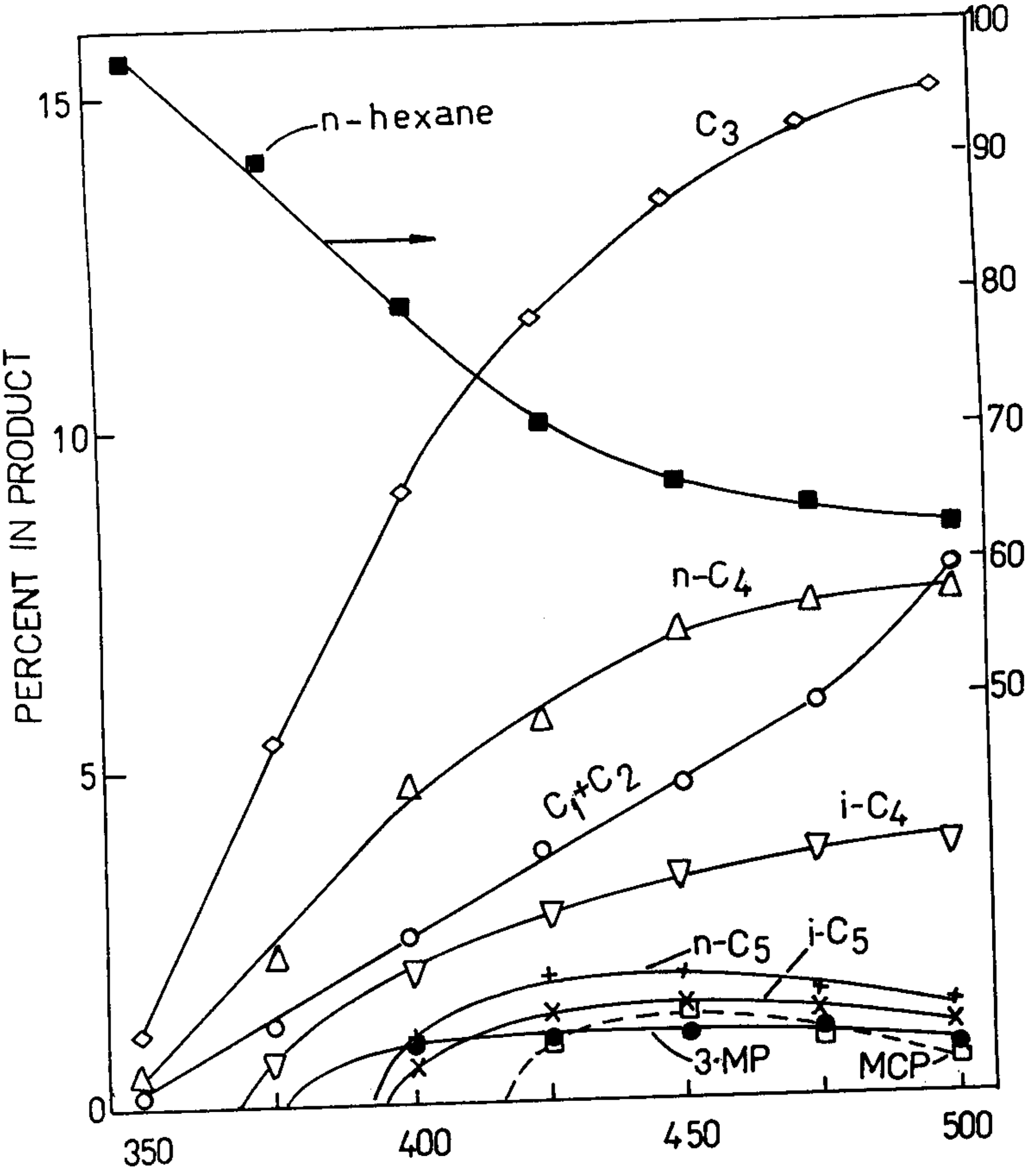

Fig. 1. Hydroconversion products of n-hexane using the H-Z Catalyst

Table 1: Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using Unloaded H-Z catalyst

Component in Product, %	Reaction, Temperature, C°						
	350	375	400	425	450	475	500
Methane + Ethane	0.2	1.2	2.5	3.7	4.7	5.9	7.7
Propane	1.1	5.4	9.1	11.5	13.3	14.4	14.9
Isobutane	0.0	0.6	1.9	3.4	3.3	3.5	3.7
n-butane	0.5	2.2	4.7	6.0	7.0	7.4	7.5
Isopentane	0.0	0.0	0.6	1.3	1.4	1.3	1.1
n-Pentane	0.0	0.0	0.9	1.9	1.8	1.5	1.3
2,2-Dimethylbutane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-Methylpentane + 2,3-Dimethylbutane	0.0	0.0	0.3	0.5	0.5	0.5	0.5
3-Methylpentane	0.0	0.0	0.6	0.5	0.4	0.5	0.3
n-Hexane	98.2	90.6	79.4	70.3	66.3	64.2	62.5
Methylcyclopentane	0.0	0.0	0.0	0.9	1.3	0.8	0.5
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrocracking %	1.8	9.4	19.7	27.8	31.5	34.0	36.2
Hydroisomerization %	0.0	0.0	0.9	1.0	0.9	1.0	0.8
Hydrocyclization %	0.0	0.0	0.0	0.9	1.3	0.8	0.5
Total Conversion	1.8	9.4	20.6	29.7	33.7	35.8	37.5
Hydrocracking Selectivity	100	100	95.6	93.6	93.5	95.0	96.5
Hydroisomerization Selectivity	0.0	0.0	4.4	3.0	2.7	2.8	2.1
Hydrocyclization Selectivity	0.0	0.0	0.0	3.0	3.9	2.2	1.3
Isobutane/n-Butane	0.0	0.27	0.4	0.57	0.47	0.47	0.49
Isopentane/n-Pentane	0.0	0.0	0.67	0.68	0.78	0.87	0.85

other hand, hydroisomerization using the H-Z catalyst is of negligible extent (≤1.0 %).

The ratio of iso-butane/n-butane in the product of n-hexane hydroconversion using the unloaded H-Z catalyst ranges between o.27 and 0.49 % at temperatures of 375-500 ° C, whereas that of iso-pentane/n-pentane ranges between 0.67 and 0.87 (Table 1). The percentage of pentanes in product is always lower than that of butanes; indicating that splitting off of a methyl group from a n-hexane molecule on the H-Z catalyst is more difficult than the splitting off of an ethyl group. The largest hydrocracked product is propane; e.g., at a temperature of 400 ° C, propane comprises 9.1 % compared to 6.6 and 1.5% for butanes and pentanes, respectively, indicating that C-C bond rupture at or near the middle of n-hexane molecule is more favourable than at the terminal of the molecule. As reaction temperature increases beyond 450 ° C, pentanes decrease in product as a result of some secondary hydrocracking; i.e., the pentane molecules produced undergo further hydrocracking. This can be supported by a relative increase of the percentage of C_1+C_2 in the product (Fig. 2).

The C_1+C_2 percentage in the product using the H-Z zeolite catalyst increases from as low as 0.2 % at 350 °C to 7.7 % at 500 ° C. However, in other words, i.e., the percentage of methane plus ethane in the total hydrocracked product $(C_1+C_2)100/\ \Sigma(C1\rightarrow C5)$, increases from 11.1% at 350 °C to 21.3% at 500 °C (Fig. 2). It is evident that the value of

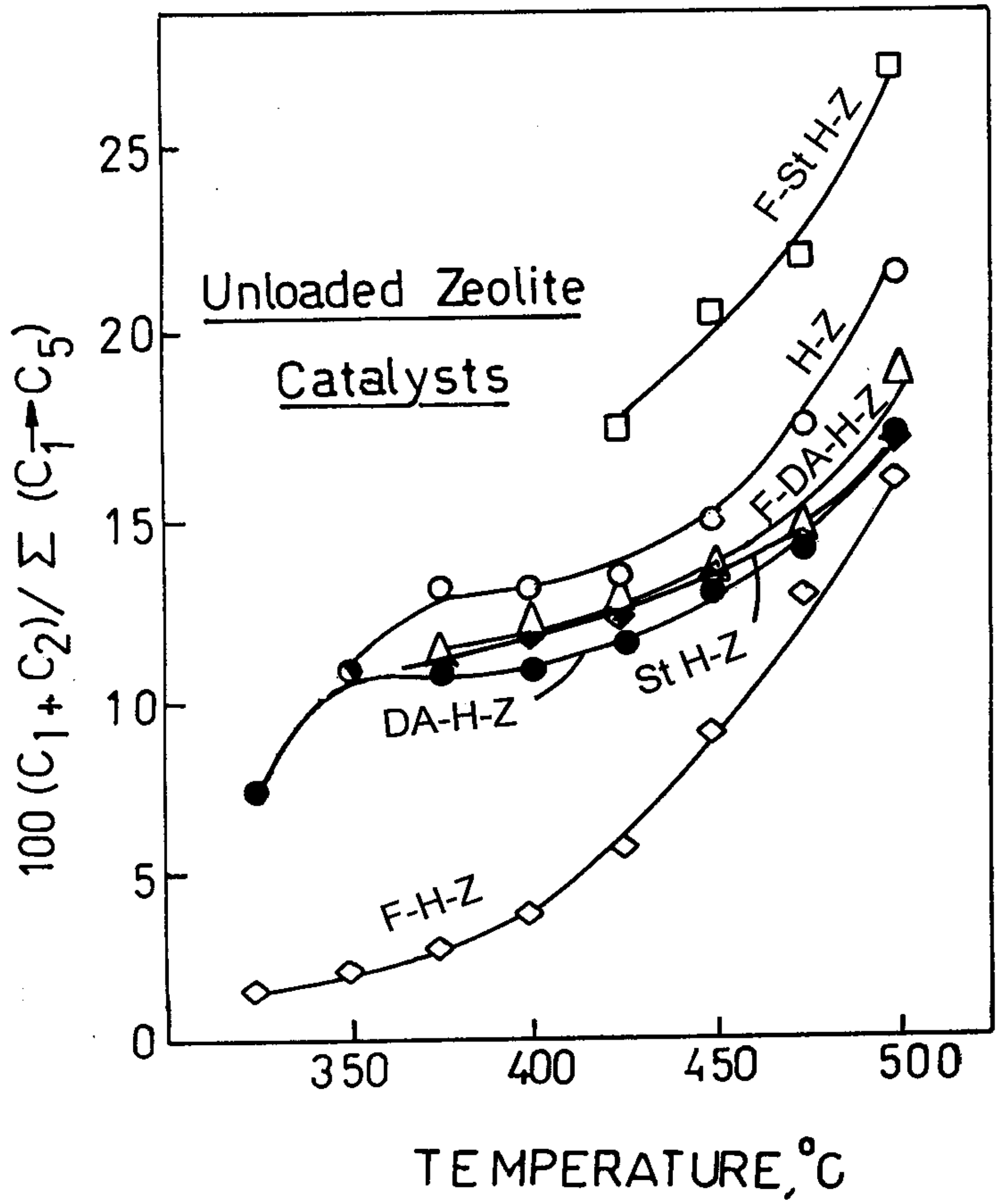

Fig. 2. C_1+C_2 in the hydrocracked product of n-hexane using the unloaded zeolite catalysts

$(C_1+C_2)100/\ \Sigma(C1\rightarrow C5)$ increases not only with increasing reaction temperature but also with the increase of the Pt content.

During the higher temperature range (425-500 °C), methylcyclopentane (MCP) is produced in very low percentages (0.5-1.3 %). However, cyclohexane and benzene do not appear in product.

3.1.2. Hydroconversion using Pt-loaded H-Z catalysts (Pt/H-Z):

Incorporation of Pt in H-ZSM-5 zeolite at concentrations of 0.15, 0.30 and 0.60 wt % gives 0.15 % Pt/H-Z, 0.30 % Pt/H-Z and 0.60 % Pt/H-Z catalysts, respectively. These catalysts are found to be greatly effective for enhancing the catalytic activity for n-hexane hydroconversion (Tables 2-4, Figs. 3-5).

For instance using the 0.15 % Pt/H-Z catalyst, n-hexane hydroconversion comprises 43.5-100 % at temperatures of 250-500 °C, respectively (Table 2). Using the 0.30 % Pt/H-Z and 0.60% Pt/H-Z catalysts, hydroconversions of 61.6-100 and 62.7-100 % are obtained at temperatures of 300-500 °C, respectively (Tables 3 and 4).

This enhancement is undoubtedly due to bifunctionality **[195]**, where Pt catalyses the dehydrogenation of the alkane which is then protonated at a Brönsted acid site yielding alkylcarbenium ion, which

Table 2 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.15 % Pt/ H-Z Catalyst

Component in Product, %	Reaction , Temperature, C°										
	250	275	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.0	0.2	1.1	2.4	4.3	6.8	9.8	13.5	18.9
Propane	0.0	0.0	0.0	2.0	10.8	21.5	35.4	47.5	50.5	50.5	47.3
Isobutane	0.0	0.0	0.0	0.2	0.6	3.9	4.3	4.5	4.7	4.4	3.6
n-Butane	0.0	0.0	0.0	0.5	1.7	4.8	7.8	9.9	9.3	8.3	6.5
Isopentane	0.0	0.0	0.0	0.4	1.2	1.8	2.8	2.7	1.4	1.0	0.5
n- Pentane	0.0	0.0	0.0	0.4	0.9	1.3	1.8	1.7	0.9	0.8	0.4
2,2- Dimethylbutane	0.0	0.0	0.0	0.6	1.5	2.3	2.3	1.1	0.2	0.0	0.0
Methylpentane + 2,3- Dimethylbutane	18.0	26.2	33.7	37.9	35.0	24.6	12.7	3.5	0.9	0.0	0.0
3- Methylpentane	25.5	33.7	34.5	30.1	23.5	15.8	8.1	2.0	0.8	0.0	0.0
n-Hexane	56.5	40.1	31.8	26.9	21.3	15.5	7.8	.3.1	1.1	0.0	0.0
Methylcyclopentane	0.0	0.0	0.0	0.8	1.1	0-9	0.6	0.2	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0	1.3	5.2	12.1	17.0	20.4	21.5	22.8
Hydrocracking %	0.0	0.0	0.0	3.7	16.3	35.7	56.4	73.1	76.6	78.5	77.2
Hydroisomerization %	43.5	59.9	68.2	68.6	60.0	42.7	23.1	6.6	1.9	0.0	0.0
Hydrocyclization %	0.0	0.0	0.0	0.8	2.4	6.1	12.7	17.2	20.4	21.5	22.8
Total Conversion	43.5	59.9	68.2	73.1	78.7	84.5	92.2	96.9	98.9	100	100
Hydrocracking Selectivity	0.0	0.0	0.0	5.1	20.7	42.2	61.2	75.4	77.5	78.5	77.2
Hydroisomerization selectivity	100	100	100	93.8	76.2	50.5	25.1	6.8	1.9	0.0	0.0
Dehydrocyclization Selectivity	0.0	0.0	0.0	1.1	3.1	7.2	13.8	17.8	20.6	21.5	22.8
Isobutane / n- Butane	0.0	0.0	0.0	0.4	0.35	0.81	0.55	0.45	0.5	0.53	0.55
Isopentane / n- Pentane	0.0	0.0	0.0	1.0	1.33	1.38	1.56	1.59	1.56	1.25	1.25

Table 3: Distribution of Reaction Products Through Hydroconversion of n- Hexane at Different Temperatures Using 0.30% Pt/ H-Z catalyst

Component in Product, %	Reaction, Temperature, C°								
	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.4	1.4	3.8	6.5	10.7	15.7	20.9	25.2
Propane	0.0	2.8	12.5	28.9	40.5	45.9	47.4	46.1	42.9
Isobutane	0.0	0.0	1.0	2.5	5.9	6.5	5.1	4.2	3.6
n-butane	0.0	0.5	2.2	4.6	9.7	11.0	8.7	7.0	5.7
Isopentane	0.0	1.1	2.1	3.5	4.2	2.6	0.8	0.0	0.0
n-Pentane	0.0	1.2	1.5	2.2	3.2	1.8	0.4	0.0	0.0
2,2-Dimethylbutane	0.0	1.0	2.1	3.0	2.0	0.0	0.0	0.0	0.0
2-Methylpentane + 2,3-Dimethylbutane	25.2	34.0	32.8	15.4	5.6	0.0	0.0	0.0	0.0
3-Methylpentane	36.4	31.0	23.1	11.1	2.7	0.0	0.0	0.0	0.0
n-Hexane	38.4	26.2	16.5	10.0	2.4	1.3	0.0	0.0	0.0
Methylcyclopentane	0.0	1.8	3.0	3.9	1.8	0.0	0.0	0.0	0.0
Benzene	0.0	0.0	1.8	11.1	15.8	20.2	21.9	21.8	22.6
Hydrocracking %	0.0	6.0	20.7	45.5	70.0	78.5	78.1	78..2	77.4
Hydroisomerization %	61.6	66.0	58.0	29.5	10.3	0.0	0.0	0.0	0.0
Hydrocyclization %	0.0	1.8	4.8	15.0	17.6	20.2	21.9	21.8	22.6
Total Conversion	61.6	73.8	83.5	90.0	97.6	98.7	100	100	100
Hydrocracking Selectivity	0.0	8.1	24.8	50.6	71.7	79.5	78.1	78.2	77.4
Hydroisomerization selectivity	100	89.4	69.5	32.8	10.6	0.0	0.0	0.0	0.0
Dehydrocyclization Selectivity	0.0	2.4	5.8	16.7	18.0	20.5	21.9	21.8	22.6
Isobutane / n-Butane	0.0	0.0	0.45	0.54	0.61	0.59	0.59	0.6	0.63
Isopentane / n-Pentane	0.0	0.09	1.4	1.59	1.31	1.44	2.0	0.0	0.0

Table 4: Distribution of Reaction Products Through Hydroconversion of n- Hexane at Different Temperatures Using 0.60% Pt/ H-Z catalyst

Component In Product, %	Reaction , Temperature, C°								
	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.3	1.1	2.5	4.9	9.7	14.4	20.9	25.2
Propane	0.3	2.3	5.2	13.9	29.4	40.1	42.0	39.5	37.0
Isobutane	0.1	0.4	2.1	3.4	3.3	3.3	2.5	2.5	2.0
n-Butane	0.3	0.7	3.4	6.4	7.0	7.0	5.0	4.0	2.0
Isopentane	0.3	1.2	3.4	4.8	5.4	3.6	1.4	0.6	0.3
n-Pentane	0.5	1.2	3.2	4.1	4.7	2.6	0.9	0.5	0.2
2,2-Dimethylbutane	0.0	0.9	2.2	3.4	2.6	1.0	0.3	0.1	0.2
2-Methylpentane + 2,3-Dimethylbutane	26.7	29.8	26.9	20.7	9.6	1.7	0.3	0.1	0.1
3-Methylpentane	34.5	32.0	24.9	15.6	7.0	1.1	0.4	0.1	0.1
n-Hexane	37.3	30.7	22.8	14.9	6.2	1.9	1.6	0.0	0.0
Methylcyclopentane	0.0	0.5	3.1	2.0	1.0	0.5	0.2	0.0	0.0
Benzene	0.0	0.0	1.7	8.3	18.9	27.5	31.0	32.5	32.9
Hydrocracking %	1.5	6.1	18.4	35.1	54.7	66.3	68.3	67.2	66.7
Hydroisomerization %	61.2	62.7	54.0	39.7	19.2	3.8	1.0	0.3	0.4
Hydrocyclization %	0.0	0.5	4.8	10.3	19.9	28.0	29.1	32.5	32.9
Total Conversion	62.7	69.3	77.2	85.1	93.8	98.1	98.4	100	100
Hydrocracking Selectivity	2.4	8.8	23.8	41.3	58.3	67.6	69.4	67.2	66.7
Hydroisomerization selectivity	97.6	90.5	70.0	46.7	20.5	3.9	1.0	0.3	0.4
Dehydrocyclization Selectivity	0.0	0.72	6.2	12.1	21.2	28.5	29.6	32.5	32.9
Isobutane / n-Butane	0.33	0.57	0.62	0.53	0.47	0.47	0.5	0.63	1.0
Isopentane / n-Pentane	0.6	1.0	1.06	1.17	1.15	1.38	1.56	1.2	1.5

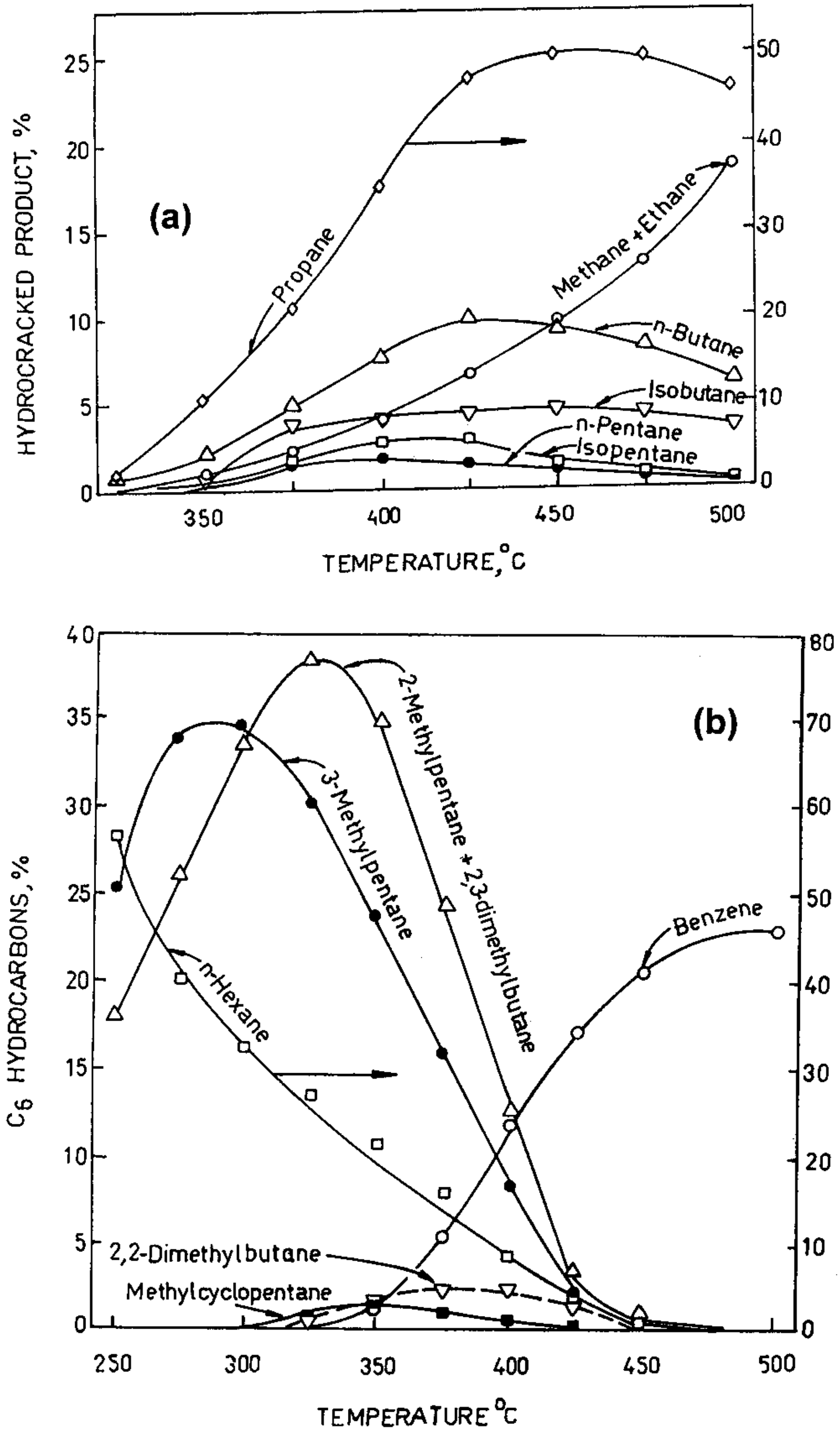

Fig. 3. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.15% Pt/H-Z catalyst

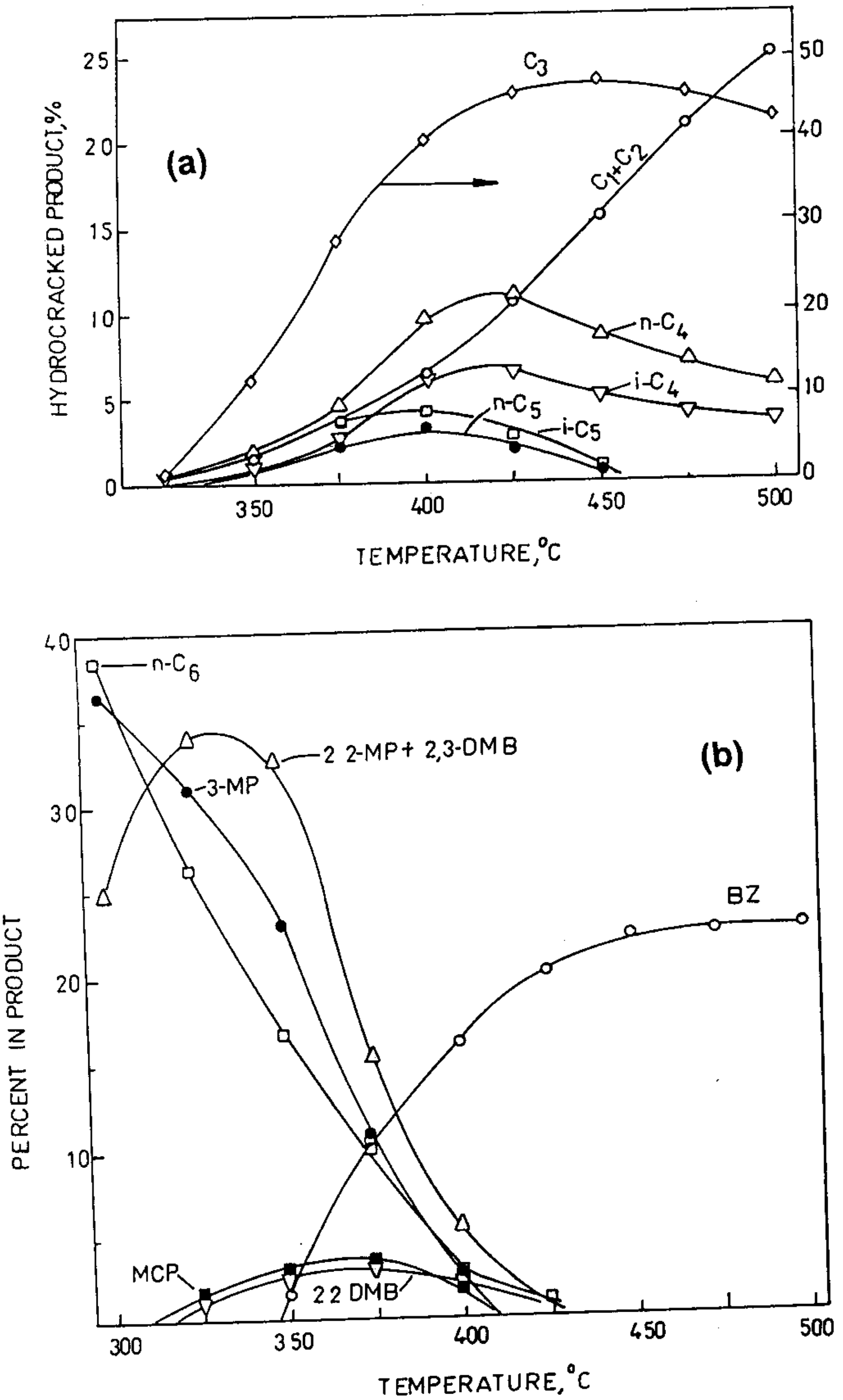

Fig. 4. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.30% Pt/H-Z catalyst

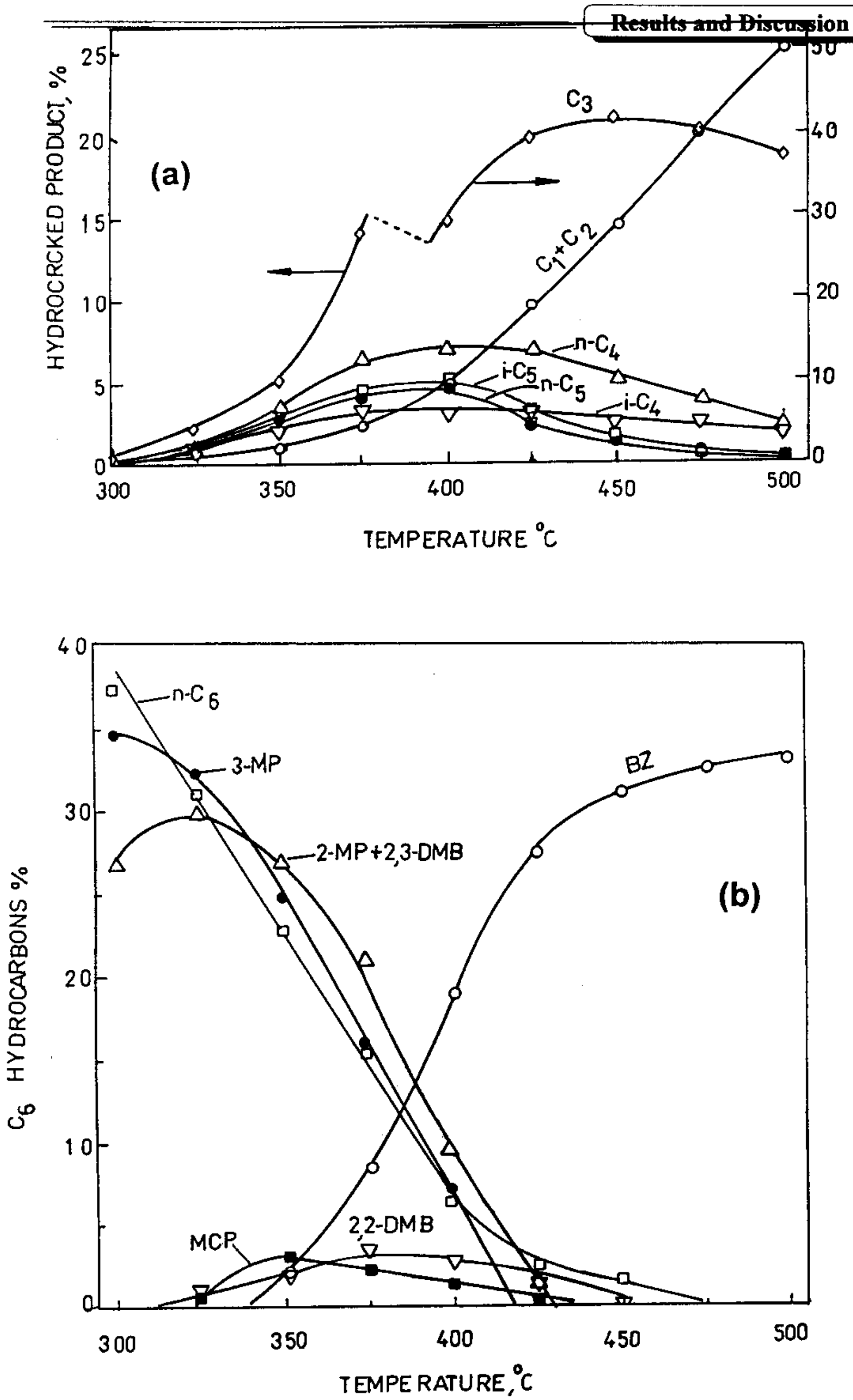

Fig. 5. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.60% Pt/H-Z catalyst

rearranges and/or crack. This ion migrates as an alkene to be hydrogenated on a metal site giving a saturated product **[196]**.

During the lower reaction temperature range, n-hexane hydro-isomerization seems to be the only reaction taking place in presence of the Pt/H-Z catalysts. Using the 0.15 % Pt/H-Z catalyst, isohexanes in product comprise 43.5 % at a temperature as low as 250 °C and reach a maximum of 68.6 % at 325 °C, beyond which they decline via a further increase of temperature. Using the 0.30% Pt and 0.60 % Pt/H-Z catalysts, isohexanes amount to 61.6 and 61.2 %, respectively, at 300 °C and increase with increasing the temperature to 325 °C to reach a maximum of 66.0 and 62.7 %, respectively. Beyond these maxima, isohexanes decrease with a further increase of temperature.

Comparing the data in Tables 1 and 2-4 shows that isohexanes which are as low as ≤ 1.0 % using the unloaded zeolite catalyst reach maxima of 62.7-68.6 % using the Pt/H-Z catalysts. This shows to what extent bifunctionality is of a prime importance for n-alkanes hydroisomerization. The metal has greatly inhibited the catalytic cracking activity at the lower reaction temperatures and directed its activity towards the skeletal rearrangement of n-hexane .

The largest hydroisomerization maximum (68.6 %) is achieved using the catalyst containing the lowest Pt concentration (0.15 %), whereas the lowest maximum (62.7 %) is accomplished using the catalyst containing the highest Pt content (0.60 %). The maximum hydrosomerization activities of the catalysts thus can be arranged in the order:

0.15 % Pt/H-Z > 0.30 % Pt/H-Z > 0.60 % Pt/H-Z

This order of activities is compatible with the number and strength of the acid sites in these catalysts (Fig. 6 and Table 5). Fig. 6 gives the temperature-programmed ammonia-desorption (TPD) curves obtained using a differential scanning calorimeter (DSC) as described by ***Aboul-Gheit*** **[190,191]**. Each TPD profile includes two endothermic peaks; a low-temperature (LT) and a high-temperature (HT) endothermic peak. The LT peak represents NH_3 desorption enthalpy from the weak acid sites in the catalyst, whereas the HT endothermic peak corresponds to the desorption of NH_3 from the strong acid sites, which are responsible for catalyzing the isomerization reaction under study. The data obtained from Fig. 7 and listed in Table 6, show that the unloaded zeolite contains the largest number of strong acid sites. The Pt/H-Z catalyst gives lower ΔH values; (Table 5), i.e., smaller numbers of acid sites, compared to the unloaded zeolite. Moreover, the number of acid sites in the Pt/H-Z catalysts decreases as the Pt content increases, i.e., the 0.60 Pt/H-Z catalyst possesses the lowest number of acid sites. This may indicate that Pt crystallites mask the acid sites and/ or exchange protons in this catalyst. The hydroconversion data indicate that the 0.15 % Pt/ H-Z catalyst contains optimum number and strength of acid sites combined with an optimum Pt content to attain maximum hydroisomerization of n-hexane.

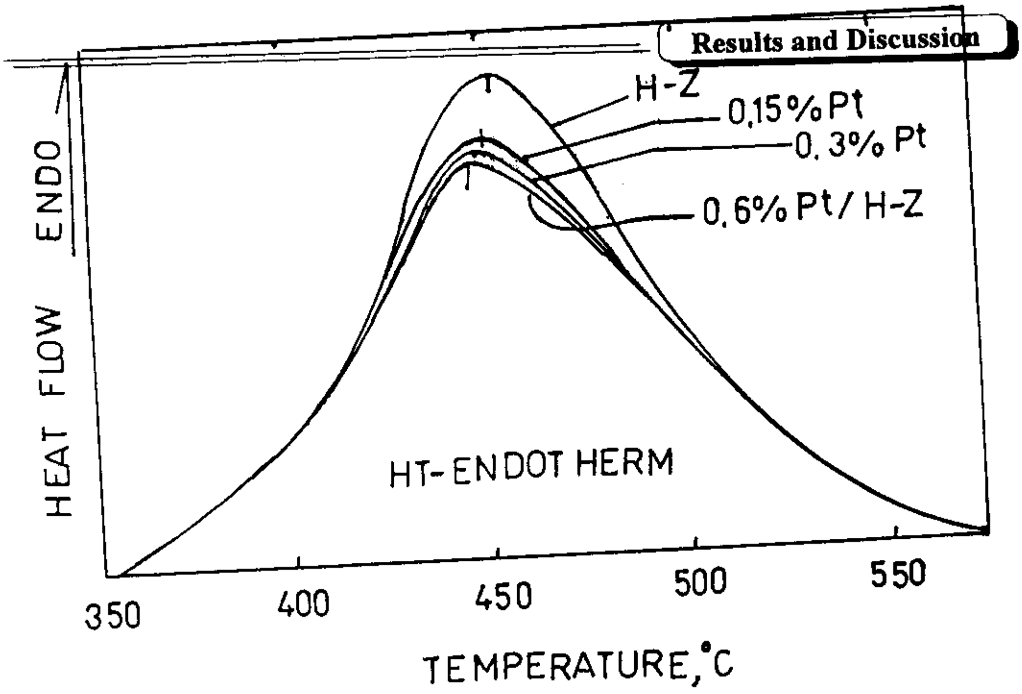

Fig. 6. TPD of ammonia from the strong acid sites (HT-endothermic peak) of H-Z and Pt/H-Z catalysts.

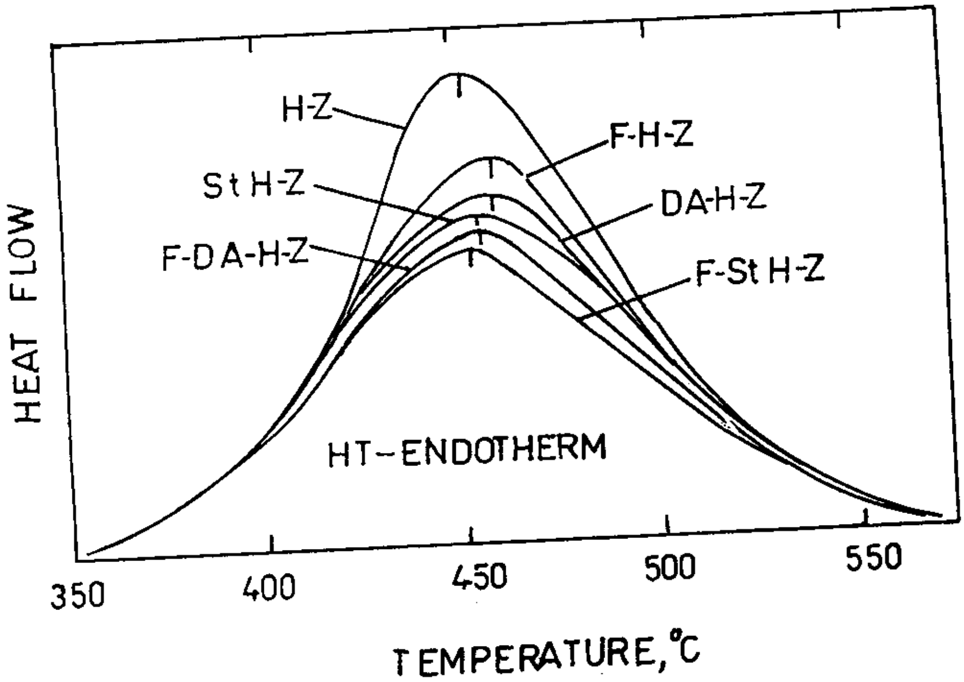

Fig. 7. TPD of ammonia from the strong acid sites (HT-endothermic peak) of H-Z and modified unloaded zeolite catalysts.

Table 5: NH_3 TPD and Pt- Dispersion in the Different Catalysts

Catalyst	NH_3 - TPD		Platinum Dispersion (H/Pt %)
	ΔH, Jg^{-1}	T max, °C	
0.15% Pt / H-Z	100.0	449.0	0.81
0.3 % Pt / H-Z	94.3	447.0	0.78
0.6 % Pt / H-Z	90.1	444.0	0.71
0.15% Pt / DA-Z	85.1	450.5	0.76
0.3 % Pt / DA-Z	82.0	448.5	0.72
0.6 % Pt / DA-Z	79.2	445.0	0.64
0.15% Pt / F-H-Z	97.9	451.5	0.73
0.3 % Pt / F-H-Z	91.8	449.5	0.68
0.6 % Pt / F-H-Z	87.1	446.0	0.61
St 0.15% Pt / H-Z	83.0	449.5	0.73
St 0.3 % Pt / H-Z	80.1	448.0	0.69
St 0.6 % Pt / H-Z	77.7	444.5	0.62
0.15% Pt / F-DA-Z	75.3	450.0	0.68
0.3 % Pt / F-DA-Z	71.1	448.0	0.64
0.6 % Pt / F-DA-Z	66.8	445.0	0.55
0.15% Pt / F-St-Z	70.8	448.5	0.57
0.3 % Pt / F-St-Z	66.0	446.0	0.53
0.6 % Pt / F-St-Z	61.4	443.0	0.43

Table 6 : NH_3 - Temperature Programmed Desorption (TPD) for the Modified Unloaded Zeolite Catalysts

Catalyst	NH_3-desorption, ΔH, Jg^{-1}	Peak temperature, °C	Acid sites(*) decrease, %
H-Z	115.5	452.0	—
DA-H-Z	98.5	456.0	14.7
F-H-Z	104.1	457.0	9.9
St H-Z	93.2	453.0	19.3
F-DA-H-Z	81.5	454.0	29.4
F-St H-Z	77.4	452.5	32.9

(*) decrease via modifications: DA, F, St, F+DA, F+St

The HT-endothermic peak temperature, which characterizes the acid sites strength in the catalysts is highest for the unloaded H-Z and lowest for the 0.60% Pt / H-Z catalyst (Tables 5 and 6). The acid sites number and strength in the catalysts under study can be arranged in the order:

H-Z > 0.15 % Pt/H-Z > 0.3 % Pt/H-Z > 0.6 % Pt/H-Z

This indicates that both orders of acid sites number and strength in the Pt/ H-Z catalysts are compatible with the order of the hydroisomerization maxima using these catalysts. Hydrocracking of n-hexane reaches 66.7-77.4 % at a temperature of 500°C. The highest hydrocracking activity is achieved using the 0.30 % Pt/ H-Z catalyst. Nevertheless, the 0.6 % Pt/ H-Z catalyst exhibits a lower hydrocracking activity during the higher temperature range, which may be attributed to the lower acid sites number and strength (Fig. 6 and Table 5).

The largest individual hydrocracked component on all catalysts is propane, which implies the preference of central bond rupture. The curves representing propane in product (Figs. 1, 3-5 and Tables 1-4) show that this hydrocarbon is susceptible to undergo secondary hydrocracking reactions at higher temperatures. Using the 0.15, 0.30 and 0.60 % Pt/H-Z catalysts, maximum yield of propane in product amounts to 50.5, 47.4 and 42.0 %, respectively, at a temperature of 450°C; beyond this temperature propane production declines by a further increase of temperature.

$C_1$and C_2 are considered undesirable hydrocracked components. To judge whether hydrocracking tends to be central or peripheral, a correlation of the percentage of C_1+C_2 components in the total hydrocracked product Σ ($C_1 \rightarrow C_5$) is examined (Fig. 8). The unloaded zeolite (H-Z catalyst) is the most active for directing toward peripheral hydrocracking up to a reaction temperature of 425°C. However beyond 425°C, this catalyst is still more active than the 0.15 % Pt/H-Z catalyst for C_1+C_2 production, whereas it is less active than the 0.30 and 0.60 % Pt/H-Z catalysts for peripheral cracking. Beyond 425°C, C_1+C_2 formation is attributed to hydrogenolysis. Hydrogenolysis takes place principally on the Pt crystallites rather than on acid sites. The higher acceleration of C_1+C_2 formation over the 0.60 wt % Pt containing catalyst at temperatures of 450-500°C substantiates the role of Pt content for enhancing hydrogenolysis. In the hydroconversion of n-heptane **[193]**, it is recognized that hydrogenolysis is favoured by the presence of large Pt particles.

Methylcyclopentane (MCP) is a product of low significance using the catalysts under study. Its maximum formation amounts to 1.1, 3.9 and 3.1 % using the 0.15%, 0.30% and 0.60 % Pt/H-Z catalysts, respectively. However, benzene which starts formation at 350°C on all Pt/H-Z catalysts, is significantly increased with increasing temperature up to 450°C to reach 20.4, 21.9 and 31.0 % on these catalysts, respectively (Figs. 3-5), indicating that Pt content in the catalyst has a significant role in benzene production. Although cyclohexane is theoretically an

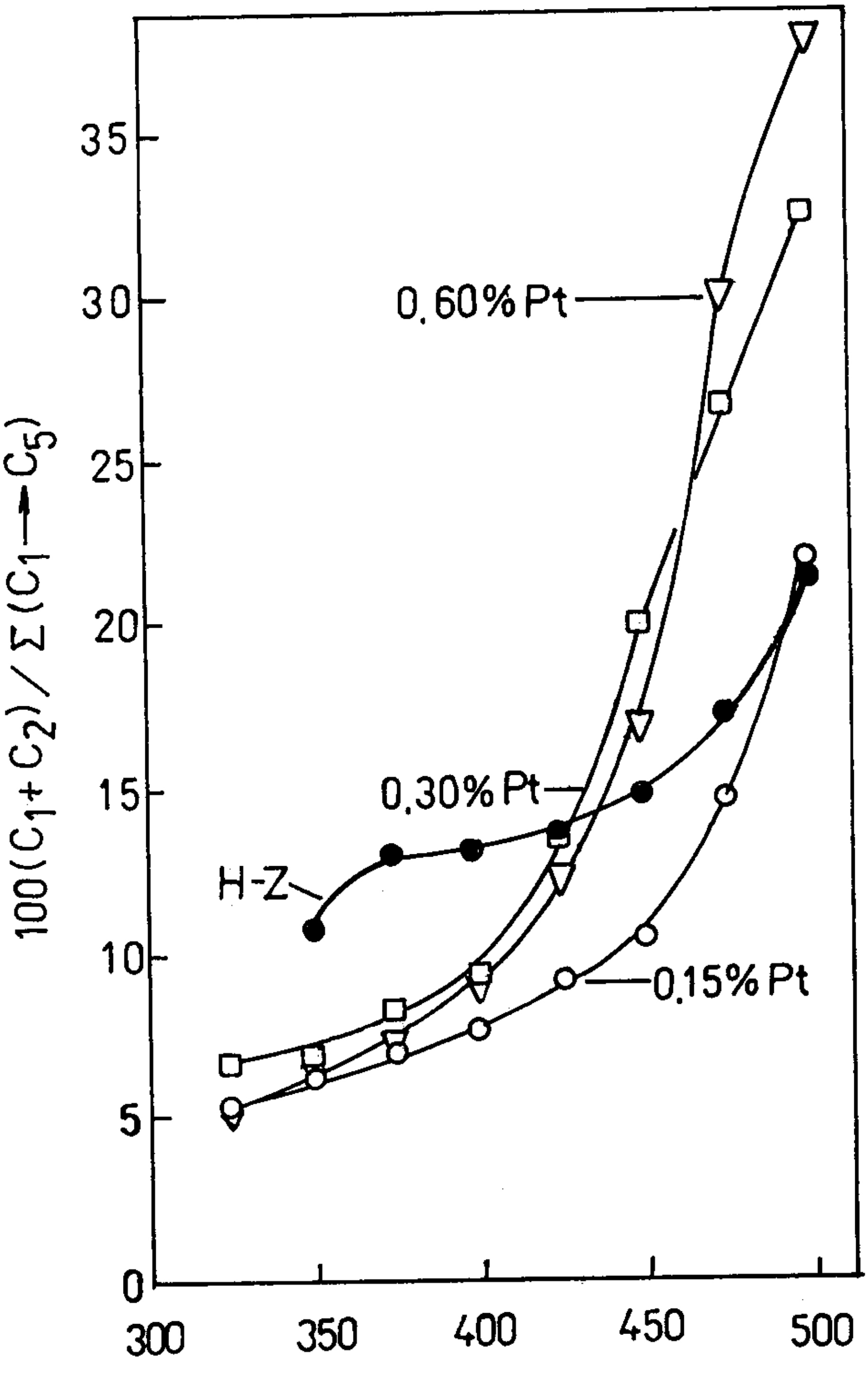

Fig. 8. C_1+C_2 in the hydrocracked product of n-hexane using the H-Z and Pt/H-Z catalysts.

intermediate during the transformation of n-hexane to benzene, cyclohexane has not been detected in the product using all Pt/H-Z catalysts. It may thus be assumed that cyclohexane is formed but directly dehydrogenated to benzene while still absorbed on the catalyst. Since benzene is absent in the product using the unloaded H-Z catalyst, dehydrocyclization can evidently be assumed to depend primarily on Pt.

Although dehydrocylization of alkanes is an endothermic reaction, it is evident (Figs. 3-5) that its rate of increase with increasing temperature does not conform with the Arrhenius assumption beyond 450°C. Beyond this temperature, the rate of benzene formation slows down with a further increase of temperature, which may be attributed to the relatively stronger adsorption of the formed benzene molecules due to their relatively stronger basicity. Stronger adsorption will also affect the rate of diffusion of benzene molecules along the channels of H-Z zeolite.

Fig. 9 shows the change of the ratio of the percentages of 3-methylpentane (3-MP) and 2,2-dimethylbutane (2,2-DMB) in the hexanes fraction in product relative to those in the thermodynamic equilibrium (Y/Y_e) at respective reaction temperatures. The curves show that 3-MP ratio decreases in general with increasing reaction temperature, whereas 2,2-DMB increases more significantly up to a temperature of 425°C. The ratio of 3-MP in product using the 0.3 % Pt/ H-Z catalyst is the lowest ratio compared to the two other catalysts, whereas the ratio of 2,2-DMB

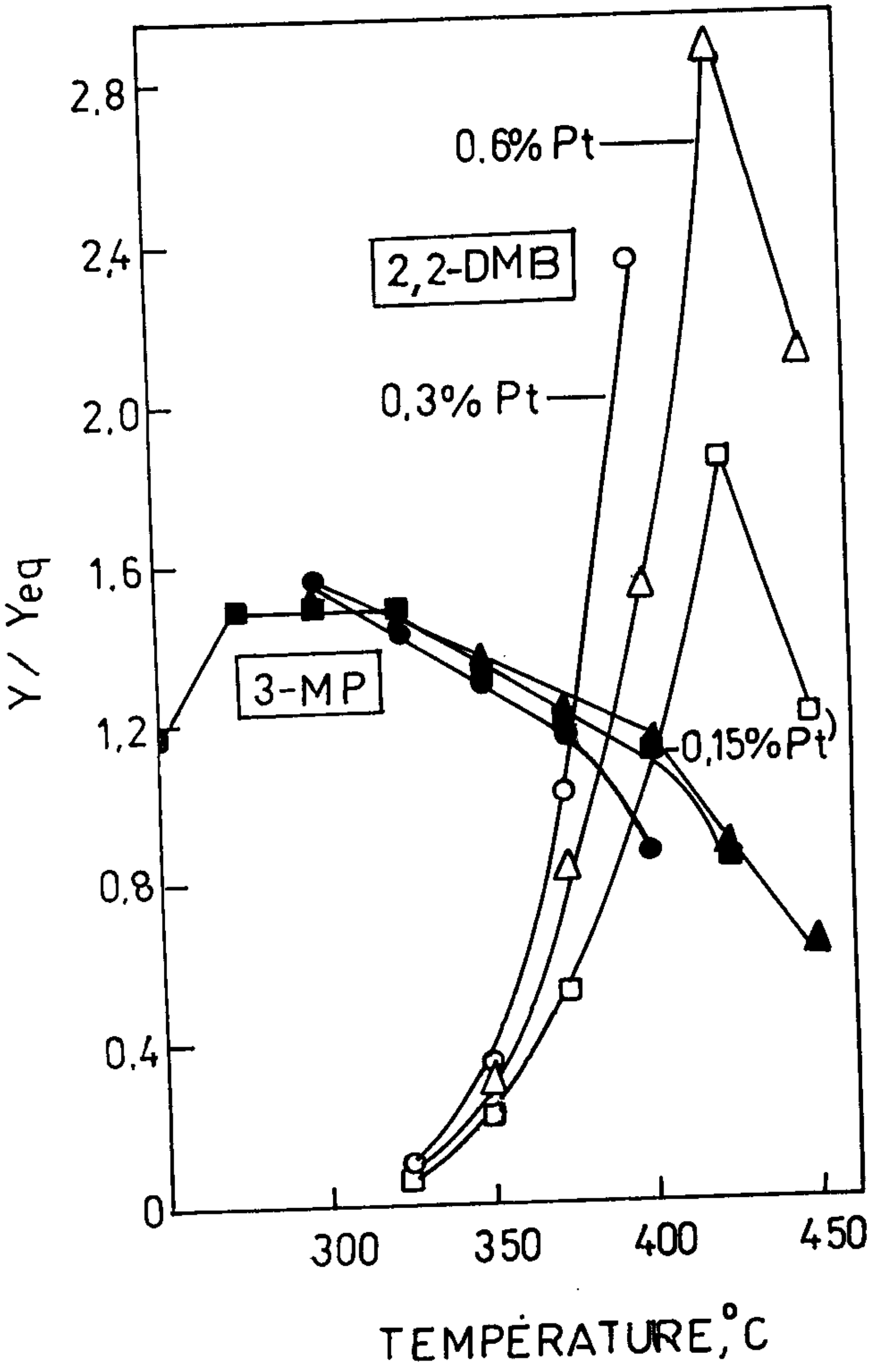

Fig. 9. 3-MP and 2,2-DMB in the hydroconversion product of n-hexane relative to their equilibrium concentrations (Y/Y_{eq}) at different reaction temperatures using the H-Z catalyst

is increased as temperature increases. The hydroisomerization reaction is maximized during the low temperature range (Fig. 4).

3.2. n-Hexane Hydroconversion Using Catalysts Containing H-Z Dealuminated with EDTA (DA-H-Z Catalyst)

3.2.1. Using Unloaded DA-H-Z Catalyst

The catalytic activity of the unloaded DA-H-Z catalyst compared to that of the unloaded H-Z catalyst is shown in Figs.10 and 1, respectively.

The DA-H-Z catalyst is less active at temperatures below 425°C than the mother H-Z zeolite catalyst, but more active at temperatures higher than 450°C. The difference in acidities of these zeolites may be responsible for this difference in activity. Fig. 7 shows that number of acid sites in the DA-H-Z catalyst is lower than in the H-Z catalyst, since protons which are attached to Al^{3+} as charge compensating cations are removed together with Al removal during the dealumination of H-Z.

Hydrocracking is the major reaction over the unloaded DA-H-Z and H-Z catalysts; on the former catalyst, the hytdrocracking selectivities range between 86.7and 100 % at temperatures ranging between 325 and 500°C, respectively, whereas using the H-Z catalyst, the hydrocracking selectivities range between 100 and 96.5 %, respectively. A comparison

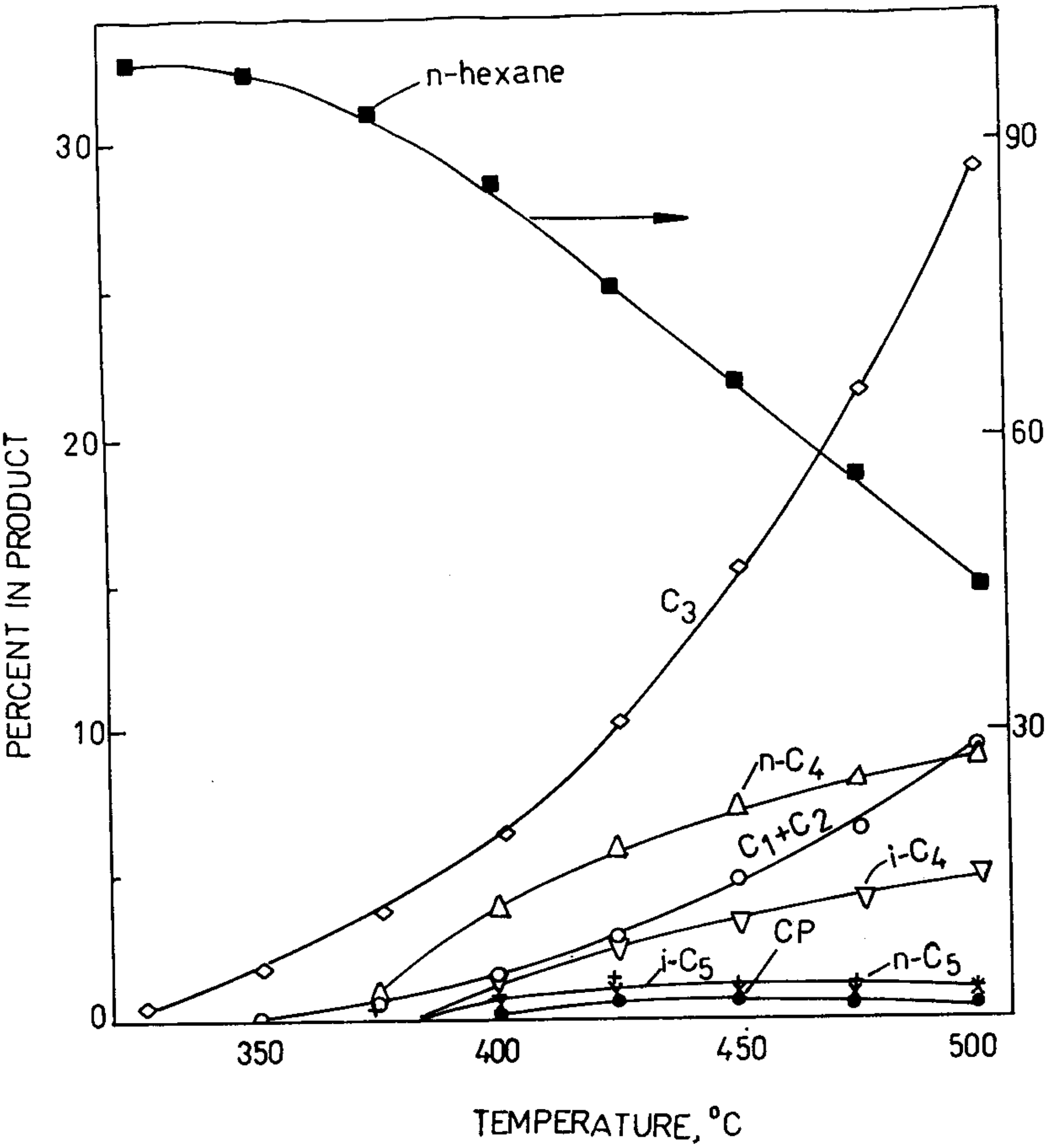

Fig. 10. Hydroconversion products of n-hexane using the DA-H-Z Catalyst.

of the hydrocracked components; methane + ethane, propane, butanes and pentanes in the product at a reaction temperature of 500°C, using the DA-H-Z and H-Z catalysts may be more informative. These values amount to 9.5, 29.0, 14.1 and 2.4 %, respectively, over the former catalyst (Table 7), and 7.7, 14.9, 11.2 and 2.4 %, respectively, over the latter catalyst (Table 1) . These values show that the dealuminated zeolite catalyst is more selective for central bond rupture than the virgin H-ZSM-5 zeolite (H-Z catalyst). The somewhat stronger acidity of DA-H-Z catalyst than the H-Z catalyst coupled with a lower number of acid sites (Fig. 7) may have contributed to the centering of the hydrocracking action on the hexane molecule.

Hydroisomerization of n-hexane to isohexanes is completely inactive using the unloaded DA-H-Z catalyst. Cyclization of n-hexane to cyclohexane and MCP as well as its dehydrocyclization to benzene are also inactive reactions over this catalyst. Nevertheless, methyl-cyclopentane is found in product in very low percentages (0.2-0.5 %).

3.2.2. Using Pt/ DA-H-Z catalysts

It is interesting to compare the hydroconversion of n-hexane using Pt/ DA-H-Z and Pt/ H-Z catalysts as well as to compare the effect of changing the Pt content in these catalysts between 0.15 and 0.6 % Pt (Table 8-10 and 2-4 and Figs. 11-13 and 3-5, respectively).

Table 7 : Distribution of Reaction Products Through Hydroconversion of n- Hexane at Different Temperatures Using DA-H-Z Catalyst.

Component in Product, %	Reaction , Temperature, C°							
	325	350	375	400	425	450	475	500
Methane + Ethane	0.1	0.3	0.7	1.6	2.8	4.8	6.5	9.5
Propane	0.8	1.9	3.8	6.5	10.2	15.5	21.5	29.0
Isobutane	0.1	0.2	0.5	1.5	2.5	3.5	4.2	5.0
n-Butane	0.3	0.4	1.1	3.8	6.0	7.4	8.4	9.1
Isopentane	0.0	0.0	0.1	0.5	1.1	1.1	1.3	1.2
n-Pentane	0.0	0.0	0.2	0.7	1.4	1.3	1.3	1.2
2,2-Dimethylbutane	0.0	0.0	0.1	0.3	0.5	0.7	0.6	0.7
2-Methylpentane + 2,3-Dimethylbutane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
n-Hexane	98.5	97.0	93.3	84.9	75.0	65.7	56.2	44.3
Methylcyclopentane	0.2	0.2	0.2	0.2	0.55	0.0	0.0	0.0
Hydrocracking %	1.3	2.8	6.5	14.9	24.5	34.3	43.8	55.7
Hydroisomerization %	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrocyclization %	0.2	0.2	0.2	0.2	0.5	0.0	0.0	0.0
Total Conversion	1.5	3.0	6.7	15.1	25.0	34.3	43.3	55.7
Hydrocracking Selectivity	86.7	93.3	97.0	98.7	98.0	100	100	100
Hydroisomerization selectivity	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Dehydrocyclization Selectivity	13.3	6.7	3.0	1.3	2.0	0.0	0.0	0.0
Isobutane / n-Butane	0.33	0.5	0.45	0.39	0.42	0.47	0.5	0.55
Isopentane / n-Pentane	0.0	0.0	0.5	0.71	0.79	0.85	1.0	1.0

Table 8: Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.15 Pt % / DA-H-Z Catalyst.

Components in Product, %	Reaction Temperature, C°									
	275	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.1	1.0	3.2	5.3	6.4	8.9	11.7	14.4
Propane	0.0	0.0	3.4	9.6	27.0	42.5	49.9	50.2	50.5	50.3
Isobutane	0.0	0.0	0.1	1.3	2.7	4.9	5.9	6.3	5.6	4.5
n-Butane	0.0	0.0	0.2	2.7	7.0	10.2	11.2	11.0	10.0	9.0
Isopentane	0.0	0.0	0.0	0.4	2.0	3.5	4.0	2.3	1.3	0.6
n-Pentane	0.0	0.0	0.0	0.2	1.5	2.2	3.0	1.3	0.5	0.4
2,2-Dimethylbutane	0.0	0.0	1.0	2.3	2.5	1.9	0.0	0.0	0.0	0.0
2-Methylpentane + 2,3-Dimethylbutane	30.7	37.0	40.4	36.5	23.2	9.2	3.0	1.3	0.5	0.0
3-Methylpentane	31.1	29.5	27.3	23.0	13.0	6.3	2.5	0.7	0.0	0.0
n-Hexane	38.2	33.5	27.5	23.0	16.3	10.1	6.4	5.0	3.5	2.8
Methylcyclopentane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0	1.6	4.0	7.7	13.0	16.4	18.0
Hydrocracking %	0.0	0.0	3.8	15.2	43.4	68.5	80.4	80.0	79.6	79.2
Hydroisomerization %	61.8	66.5	68.7	61.8	38.7	17.4	5.5	2.0	0.5	0.0
Hydrocyclization %	0.0	0.0	0.0	0.0	1.6	4.0	7.7	13.0	16.4	18.0
Total Conversion	61.8	66.5	72.5	77.0	83.7	89.9	93.6	95.0	96.5	97.2
Hydrocracking Selectivity	0.0	0.0	5.2	19.7	51.9	76.2	85.9	84.2	82.5	81.5
Hydroisomerization selectivity	100	100	94.8	80.3	46.2	19.4	5.9	2.1	0.5	0.0
Dehydrocyclization Selectivity	0.0	0.0	0.0	0.0	1.9	4.5	8.2	13.7	17.0	18.5
Isobutane / n-Butane	0.0	0.0	0.5	0.48	0.39	0.48	0.53	0.57	0.56	0.5
sopentane / n-Pentane	0.0	0.0	0.0	2.0	0.75	1.59	1.33	1.77	2.6	1.5

Table 9 : Distribution of Reaction Products Through Hydroconversion of n - Hexane at Different Temperatures Using 0.30 Pt % / DA-H-Z Catalyst.

Components in Product, %	Reaction Temperature, C°									
	275	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.4	0.8	2.5	4.3	6.1	8.2	12.1	19.5
Propane	0.0	0.0	1.2	9.0	22.2	37.7	43.9	48.3	47.5	46.5
Isobutane	0.0	0.0	0.2	0.4	1.4	2.8	3.8	4.5	4.2	3.5
n-Butane	0.0	0.0	0.4	0.8	4.3	7.7	8.9	9.2	9.0	7.5
Isopentane	0.0	0.0	0.0	0.7	1.3	2.4	2.3	1.9	1.5	0.6
n-Pentane	0.0	0.0	0.0	0.7	0.8	1.5	1.7	1.5	1.2	0.4
2,2-Dimethylbutane	0.0	0.0	1.7	2.0	2.4	1.9	1.4	0.0	0.0	0.0
2-Methylpentane + 2,3-Dimethylbutane	31.0	37.0	40.5	37.7	27.4	13.0	6.5	3.3	2.0	0.8
3-Methylpentane	29.0	32.8	29.6	25.6	17.7	8.1	4.0	1.9	0.5	0.0
n-Hexane	40.0	30.2	25.0	19.9	15.0	9.7	7.6	5.5	4.5	2.5
Methylcyclopentane	0.0	0.0	1.0	1.4	1.6	1.3	0.0	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	1.0	3.4	9.6	13.8	15.7	17.5	18.7
Hydrocracking %	0.0	0.0	2.2	12.4	32.5	56.4	66.7	73.6	75.5	78.0
Hydroisomerization %	60.0	69.8	71.8	65.3	47.5	23.0	11.9	5.2	2.5	0.8
Hydrocyclization %	0.0	0.0	1.0	2.4	5.0	10.9	13.8	15.7	17.5	18.7
Total Conversion	60.0	69.8	75.0	80.1	85.0	90.3	92.4	94.5	95.5	97.5
Hydrocracking Selectivity	0.0	0.0	2.9	15.5	38.2	62.5	72.2	77.9	79.1	80.0
Hydroisomerization selectivity	100	100	95.7	81.5	55.9	25.5	12.9	5.5	2.6	0.8
Dehydrocyclization Selectivity	0.0	0.0	1.3	3.0	5.9	12.1	14.9	16.6	18.3	19.2
Isobutane / n-Butane	0.0	0.0	0.5	0.5	0.33	0.36	0.43	0.49	0.47	0.47
Isopentane / n-Pentane	0.0	0.0	0.0	1.0	1.63	1.6	1.35	1.27	1.25	1.5

Table 10 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.60 % Pt/ DA- H-Z Catalyst.

Components In Product, %	Reaction Temperature, C°									
	275	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.4	1.4	3.4	4.8	7.4	12.8	20.2	28.4
Propane	0.0	0.5	1.8	7.1	15.6	31.5	44.5	45.9	43.3	38.5
Isobutane	0.0	0.2	0.3	0.7	1.5	3.3	4.5	4.9	4.2	3.3
n-Butane	0.0	0.5	0.7	1.5	4.0	7.2	9.0	8.1	6.6	4.8
Isopentane	0.0	0.5	0.8	1.9	2.6	3.8	2.9	1.9	1.3	0.7
n-Pentane	0..0	0.0	0.8	1.3	1.9	2.9	2.1	1.4	1.2	0.5
2,2-Dimethylbutane	0.0	0.0	0.5	1.7	3.2	2.8	1.4	0.8	0.5	0.0
2-Methylpentane + 2,3-Dimethylbutane	20.0	31.6	40.5	37.0	28.4	15.1	4.8	1.8	1.0	0.7
3-Methylpentane	30.0	33.5	29.2	23.5	18.0	12.5	6.5	1.4	0.4	0.0
n-Hexane	50.0	33.2	24.4	17.0	11.5	6.0	2.2	1.9	1.5	1.2
Methylcyclopentane	0.0	0.0	0.6	5.7	5.4	1.5	0.0	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	1.2	4.5	8.6	14.7	19.1	19.8	21.9
Hydrocracking %	0.0	1.7	4.8	13.9	29.0	53.5	70.4	75.0	76.8	76.2
Hydroisomerization %	50.0	65.1	70.2	62.2	49.6	30.4	12.7	4.0	1.9	0.7
Hydrocyclization %	0.0	0.0	0.6	6.9	9.9	10.1	14.7	19.1	19.8	21.9
Total Conversion	50.0	66.8	75.6	83.0	88.5	94.0	97.8	98.1	98.5	98.8
Hydrocracking Selectivity	0.0	2.5	6.4	16.8	32.8	56.9	72.0	76.5	78.0	77.1
Hydroisomerization selectivity	100	97.5	92.9	74.9	56.1	32.3	13.0	4.1	1.9	0.7
Dehydrocyclization Selectivity	0.0	0.0	0.8	8.3	11.2	10.8	15.0	19.5	20.1	22.2
Isobutane / n-Butane	0.0	0.4	0.43	0.27	0.38	0.46	0.5	0.6	0.64	0.69
Isopentane /n-Pentane	0.0	----	1.0	1.46	1.37	1.31	1.38	1.36	1.08	1.4

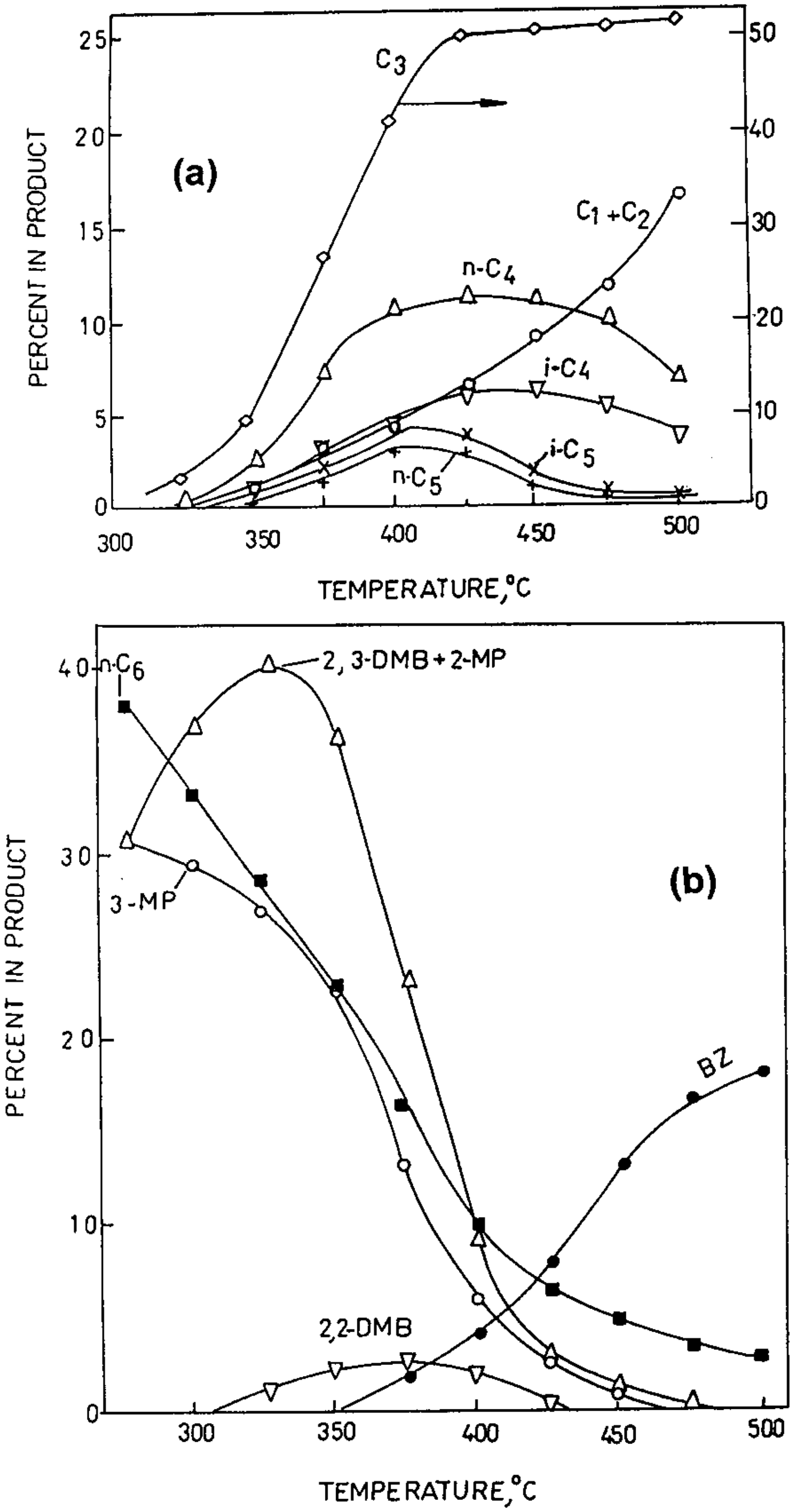

Fig. 11. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.15% Pt/DA-H-Z catalyst

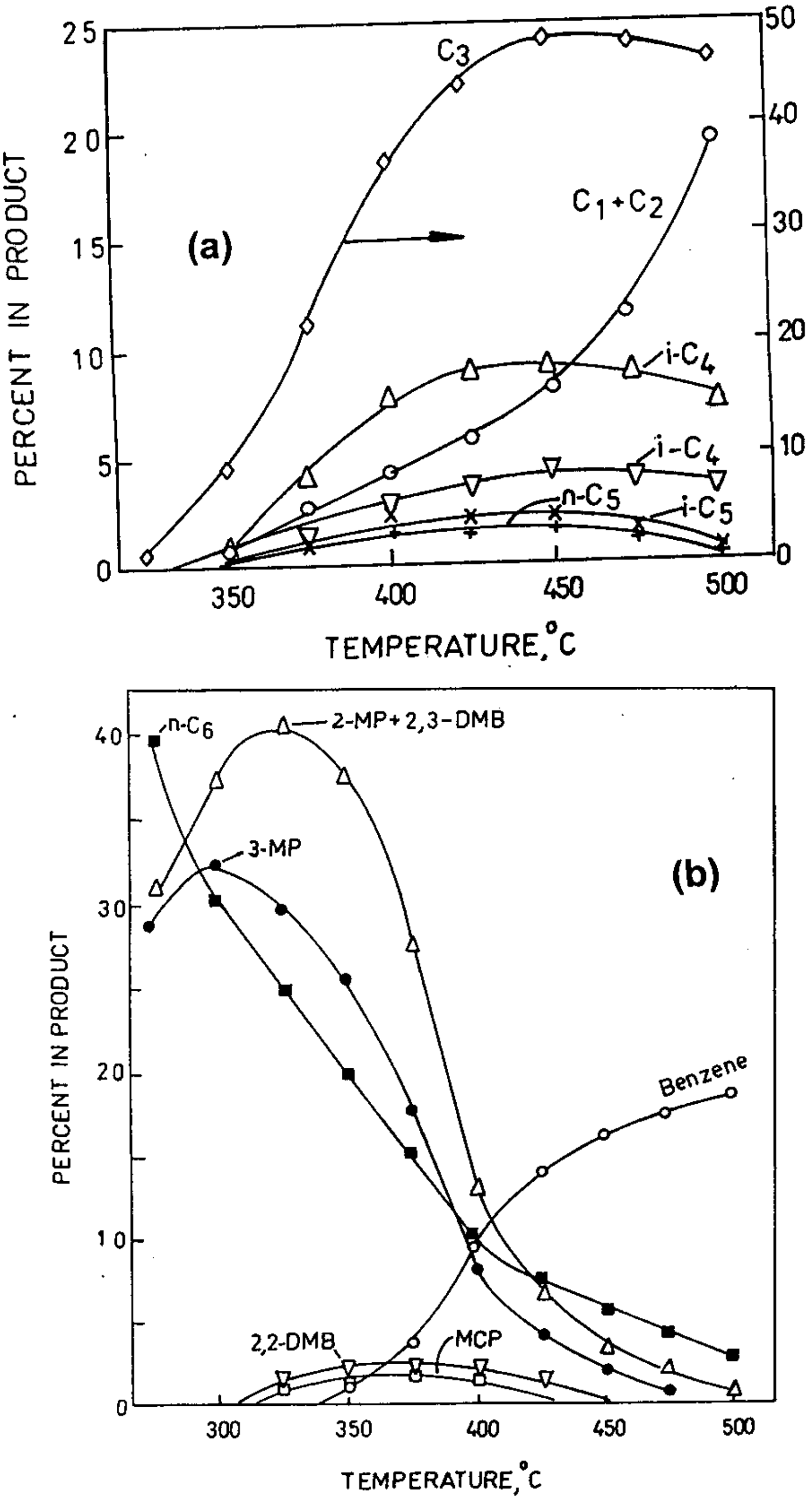

Fig. 12. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.30% Pt/DA-H-Z catalyst.

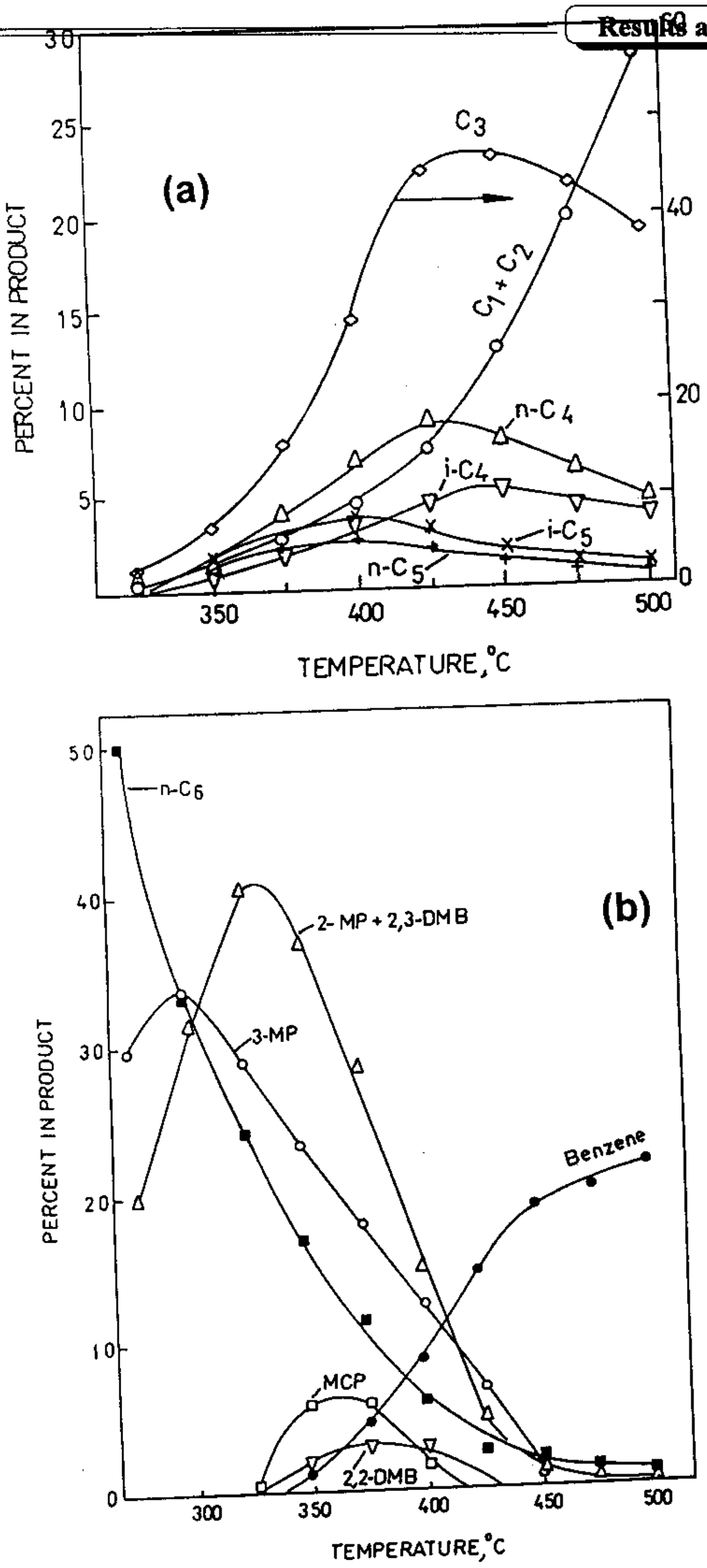

Fig. 13. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.60% Pt/DA-H-Z catalyst.

The maximum hydroisomerization level is considered a hydroconversion parameter of prime importance in the upgrading of light naphtha for the purpose of octane number improving. Using the 0.15 % Pt/DA-H-Z and 0.15 % Pt/H-Z catalysts, the maximum isohexane levels are almost equal, i.e., ~ 68.5% between 300 and 325°C, whereas using the catalysts containing 0.30 and 0.60 % Pt, the isomers levels using the DA-H-Z zeolite supported catalysts are higher than using the H-Z zeolite supported catalysts. Using the 0.30 and 0.60 % Pt supported on DA-H-Z catalysts, isohexanes maxima amount to 72.0 and 70.0 %, respectively, at a temperature of 325°C, whereas using the 0.30 and 0.60 % Pt supported on H-Z catalysts, these isomers maxima amount to 66.0 and 62.5 %, respectively, at temperatures of 325 and 300°C, respectively. Summarizing the comparison of the maximum isohexanes levels in product using the Pt/DA-H-Z catalysts, the order of catalytic activities according to Pt content is as follows:

0.30 % Pt/DA-H-Z > 0.60 % Pt/DA-H-Z > 0.15 % Pt/DA-H-Z

Although the 0.15 % Pt/ DA-H-Z catalyst (Fig. 11 and Table 8) possesses a higher acid sites number and strength than the 0.30 and 0.60% Pt-containing catalysts of this series (Figs. 12 and 13 and Tables 9 and 10), it gives the lowest isohexanes maximum. Moreover, the dispersion of Pt (Table 5) in the 0.15 % Pt/ DA-H-Z catalyst is higher than in those containing 0.3 and 0.6 % Pt. This may indicate that neither acid sites nor Pt dispersion in the zeolite dealuminated using EDTA, are controlling the hydroisomerization level. However, this level is controlled by the acid sites nature and Pt dispersion in the catalysts supported on the mother H-Z zeolite as mentioned above. It may be assumed that an optimum Pt content is a principal controlling component for the hydroisomerization maximum level irrespective of the number and strength of acid sites acquired by the zeolite support. Moreover, the Pt dispersion extent in the catalysts supported on EDTA-dealuminated H-Z zeolite plays a controlling role. ***Blomsma et al.*** **[195]** indicate that optimum balance and intimacy or synergism between the two catalytic functions constituting bifunctionality are controlling the hydroisomerization activity in catalysts containing Pt and/or Pd supported on ß-zeolite. Moreover, most of the industrial catalysts used in hydroisomerization and catalytic reforming of naphtha contain 0.30-0.40 wt % Pt. The Pt/DA-H-Z and Pt/H-Z catalysts, under study, exhibit varying hydrocracking (Fig. 14) and hydroisomerization (Fig. 15) tendencies as a result of incorporating varying Pt contents. Fig. 14 shows that the hydrocracking activity of the 0.15 % Pt/DA-H-Z catalyst is higher than that of the 0.15 % Pt/H-Z catalyst at temperatures > 350°C, whereas the hydrocracking activity using the 0.30 % Pt/DA-H-Z catalyst is lower than that of the 0.30 % Pt/H-Z catalyst at all reaction temperatures. Moreover, the hydrocracking activity of the 0.6 % Pt/DA-H-Z catalyst is lower than that on the 0.60 % Pt/ H-Z catalyst at temperatures < 400 °C, but higher at temperatures > 400 °C.

On the other hand using the 0.15 % Pt/DA-H-Z and 0.15 % Pt/H-Z catalysts, hydroisomerization is indifferent at temperatures < 350 °C; however, at temperatures > 350 °C, the activity of 0.15 % Pt/DA-H-Z

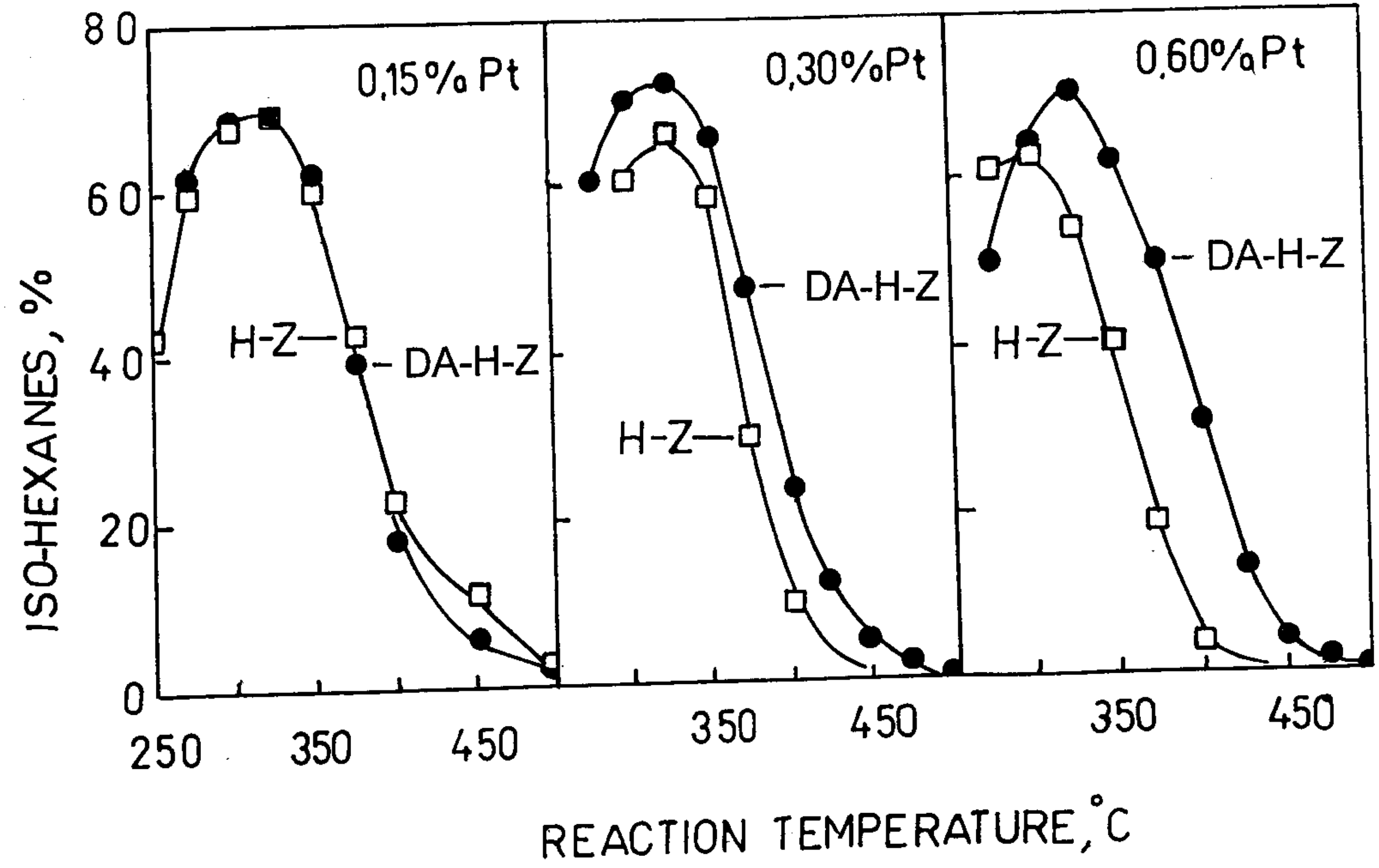

Fig. 15. Comparison of the Hydroisomerization activities of the Pt/H-Z and Pt/DA-H-Z catalysts.

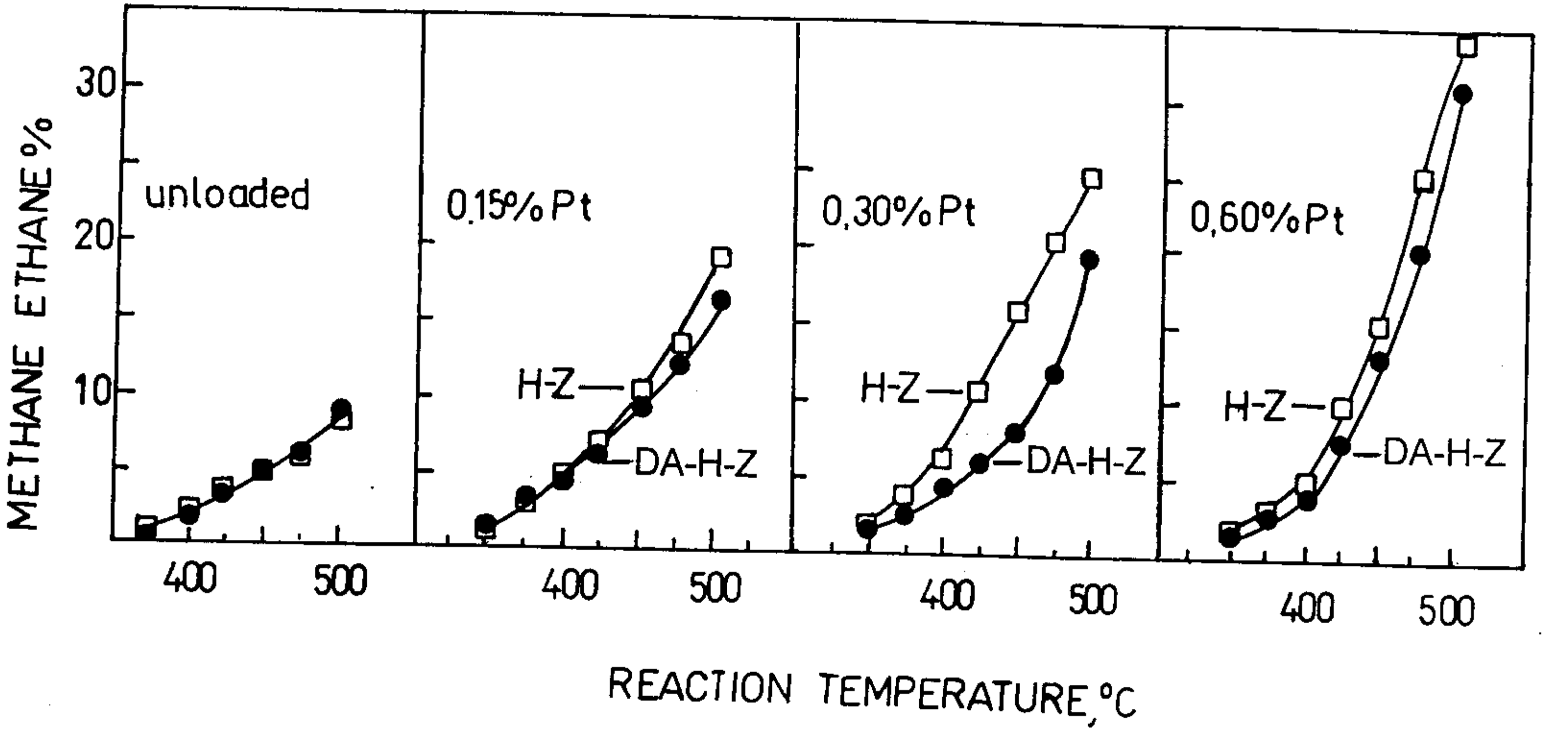

Fig. 16. Comparison of the C_1+C_2 production in the hydroconversion product using the Pt/H-Z and Pt/DA-H-Z catalysts.

different on the catalysts containing 0.15 % Pt (Fig. 16), whereas on the catalysts containing 0.30 and 0.60 % Pt, these hydrocarbons are higher on the H-Z-supported catalysts than on the DA-H-Z-supported catalysts. In general, these hydrocarbons increase in product as the Pt content in the catalyst increases. Although the acid sites number and strength decrease as the Pt content increases (Fig. 6 and Table 5), the C_1+C_2 increase, indicating the contributing action of the metal crystallites to hydrogenolysis (Fig. 17), since the latter reaction is confined to metal.

To get more information on the quality of the hydrocracked product concerning C-C bond rupture position, the distribution of C_1 up to C_5 components have been calculated and given in Tables 11 and 12. These data show that propane production using the Pt/ DA-H-Z catalysts can be arranged in the order:

0.30 % Pt/DA-H-Z > 0.15 % Pt/DA-H-Z > 0.60 % Pt/DA-H-Z

whereas using Pt/ H-Z catalysts the order is:

0.15% Pt/ H-Z > 0.30% Pt/ H-Z > 0.60% Pt/ H-Z.

These orders indicate that acid site number and strength in the Pt/ H-Z catalysts, together with Pt dispersion in the H-Z support may be activity-controlling, whereas in case of the Pt/ DA-H-Z catalysts, the metal/acid sites balance may be more effective for the control of C-C bond rupture.

Benzene formation via hydrocyclization of n-hexane using the Pt/ DA-H-Z and Pt/ H-Z catalysts is depicted in Fig. 18. The dimension of the benzene molecule is close to the channel dimension of H-ZSM-5

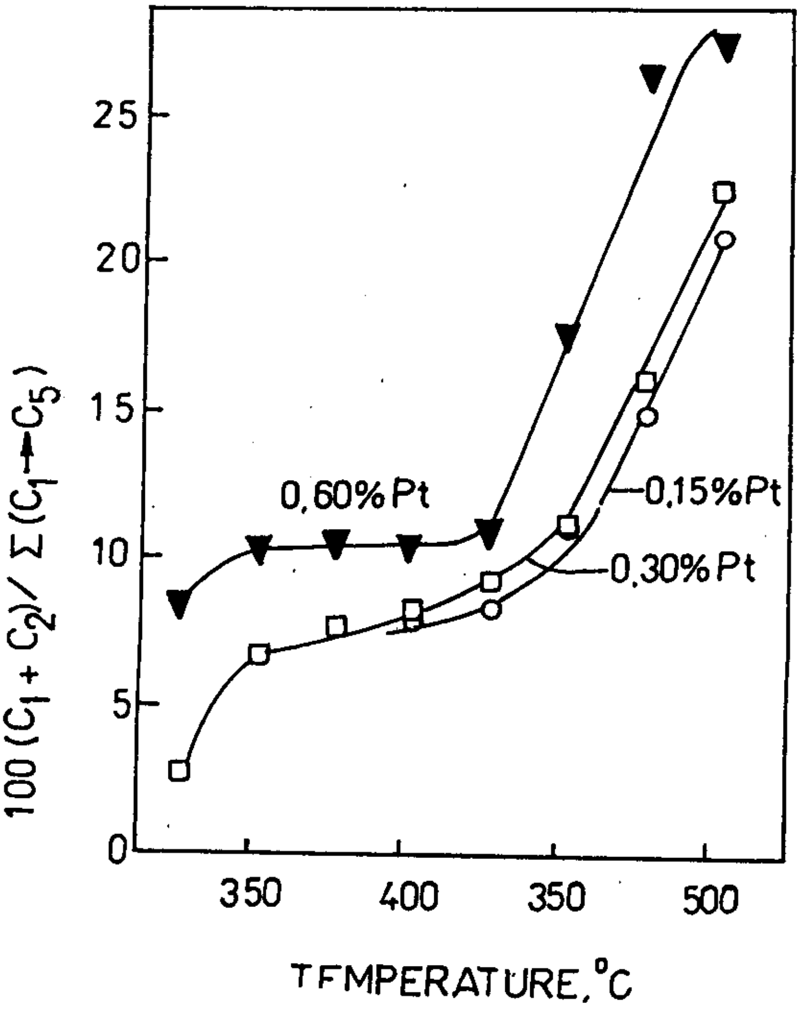

Fig. 17. C_1+C_2 in the hydrocracked product of n-hexane using the Pt/DA-H-Z catalysts.

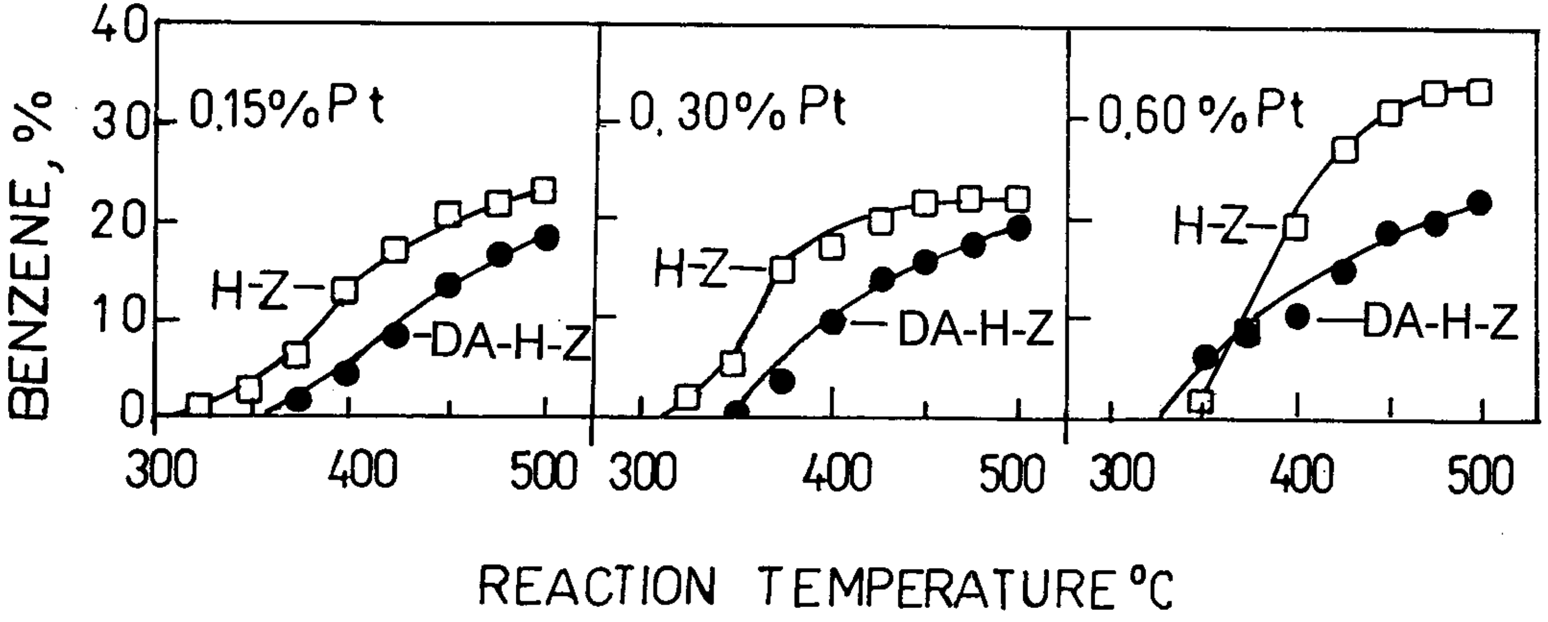

Fig. 18. Comparison of benzene in the hydroconversion product using the Pt/H-Z and Pt/DA-H-Z catalysts.

Table 11: Carbon Number Distribution ($C_1 \rightarrow C_5$) of the Individual Hydrocracked Products Using the H-Z catalysts

Catalyst: 0.15% Pt/ H-Z

Components	Temperature, °C							
	325	350	375	400	425	450	475	500
c_1+c_2	5.4	6.7	6.7	7.6	9.3	12.8	17.2	24.5
c_3	54.1	66.3	60.2	62.7	65.0	65.9	64.3	61.3
i-c_4+n-C_4	18.9	14.1	24.4	21.5	19.7	18.3	16.2	13.0
i-c_5+n-C_5	21.6	12.9	8.7	8.2	6.0	3.0	2.3	1.2

Catalyst: 0.30% Pt/H-Z

Components	Temperature, °C							
	325	350	375	400	425	450	475	500
c_1+c_2	6.7	6.8	8.4	9.3	13.6	20.1	26.7	32.6
c_3	46.7	60.4	63.5	57.8	58.5	60.7	59.0	55.4
i-c_4+n-C_4	8.3	15.5	15.6	22.3	22.3	17.7	14.3	12.0
i-c_5+n-C_5	38.3	17.3	12.5	10.6	5.6	1.5	0.0	0.0

Catalyst: 0.60% Pt/H-Z

Components	Temperature, °C								
	300	325	350	375	400	425	450	475	500
c_1+c_2	o.o	4.9	6.0	7.1	9.0	14.6	21.1	29.9	37.8
c_3	20	37.7	28.3	39.6	53.7	60.5	61.5	58.8	55.5
i-c_4+n-C_4	26.7	18.0	29.9	27.9	18.8	15.5	11.0	9.7	5.0
i-c_5+n-C_5	53.3	39.4	35.9	25.4	18.5	9.4	3.4	1.6	0.7

Table 12: Carbon Number Distribution ($C_1 \rightarrow C_5$) of the Individual Hydrocracked Products Using the DA-H-Z catalysts

Catalyst: 0.15% Pt/DA-H-Z

Components	Temperature, °C							
	325	350	375	400	425	450	475	500
c_1+c_2	2.6	6.6	7.4	7.8	8.0	11.1	14.7	18.2
c_3	89.5	63.2	62.2	62.2	62.1	62.8	63.4	63.5
i-c_4+n-C_4	7.9	26.3	22.4	22.0	21.3	21.6	19.6	17.0
i-c_5+n-C_5	0.0	4.0	8.1	8.0	8.7	4.5	2.3	1.3

Catalyst:0.30 % Pt/DA-H-Z

Components	Temperature, °C							
	325	350	375	400	425	450	475	500
c_1+c_2	18.2	6.5	7.8	7.6	9.2	11.1	16.0	25.0
c_3	54.6	72.6	68.3	66.8	65.8	65.6	62.9	95.6
i-c_4+n-C_4	27.3	9.7	17.5	18.6	19.0	18.6	17.5	14.1
i-c_5+n-C_5	0.0	11.3	6.5	6.9	6.0	4.6	3.6	1.3

Catalyst: 0.60% Pt/DA-H-Z

Components	Temperature, °C								
	300	325	350	375	400	425	450	475	500
c_1+c_2	0.0	8.3	10.1	11.7	9.0	14.6	17.1	26.3	37.3
c_3	29.4	37.5	51.1	53.8	53.7	60.5	61.2	56.4	50.5
i-c_4+n-C_4	41.2	20.8	15.8	19.0	18.8	15.5	17.3	14.0	10.6
i-c_5+n-C_5	29.4	33.4	23.0	15.5	18.5	9.4	4.4	3.3	1.6

zeolite, hence, it is suggested that benzene is formed in the wider channel intersections of this zeolite. This view may be supported by the finding of ***Lercher*** and ***Rumplmayr*** [197] who have found that pyridine, which possesses approximately the dimensions of benzene, can adsorb only in the intersections of the channels in ZSM-5 zeolites.

Nevertheless, using the DA-H-Z supported catalyst, benzene production is found to be, in general, lower than using the corresponding H-Z supported catalyst although the channels in DA-H-Z catalyst are wider than those in the H-Z catalyst. Hence, the channel dimension can not be the activity controlling parameter. The DA-H-Z zeolite supported catalysts are more hydrophobic than those containing H-Z zeolite as a support **[198]**.

Benzene which is more polar than the other hydrocarbon species in the vicinity of the catalytic sites should be less strongly adsorbed on the more hydrophobic zeolite-containing catalysts (Pt/DA-H-Z) compared to the more hydrophilic H-Z-containing catalysts. Since the adsorption strength of a product is an important criterion for directing the reaction towards the formation of this product, it can be assumed that formation of benzene over the H-Z-supported catalysts should be logically higher than using the DA-H-Z- supported catalyst.

The increase of Pt content in the Pt/ DA-H-Z and Pt/ H-Z catalysts, increases benzene production since dehydrocyclization of alkanes is a metal site reaction. Using the 0.15, 0.30 and 0.60 % Pt-containing catalysts supported on DA-H-Z zeolite, benzene production at 450°C amounts to 13.0, 15.7 and 19.1 % using the H-Z supported catalysts benzene amounts to 20.4, 21.9 and 31.0 %, respectively.

On the other hand, methylcyclopentane (MCP) has not been detected in the product using the 0.15 % Pt/DA-H-Z catalyst at all reaction temperatures. However, using the 0.30 % Pt/DA-H-Z catalyst, MCP amounts to 1.0 - 1.6 %, but using the 0.60 % Pt/DA-H-Z catalyst this hydrocarbon reaches 5.7 %in product. Again, using the 0.15, 0.30 and 0.60 % Pt/H-Z catalysts, MCP reaches 1.1, 3.9 and 3.1 %, respectively. However, cyclohexane has not been detected in the reaction product using all H-Z and DA-H-Z containing catalysts, which may be attributed to its fast dehydrogenation.

The ratio of 3-MP and 2,2-DMB realive to their thermodynamic equilibrium values indicates (Fig. 19) that the highest values of both isomers can be obtained at most reaction temperatures using the 0.60 % Pt/DA-H-Z catalyst. However, 2,2-DMB increases considerably relative to its equilibrium values as temperature increases, whereas 3-MP decreases using the 0.15 and 0.30 % Pt/DA-H-Z catalysts.

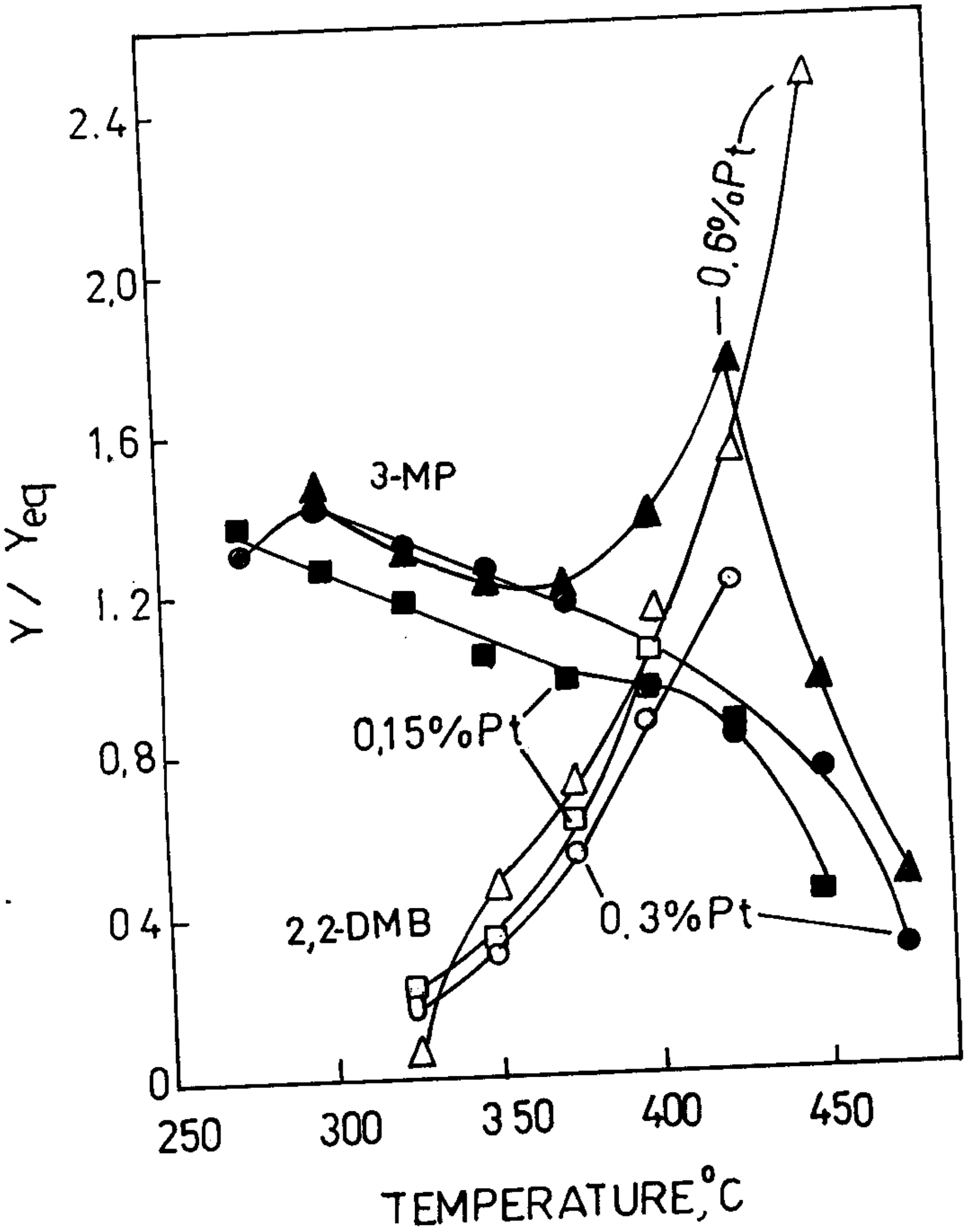

Fig. 19. 3-MP and 2,2-DMB in the hydroconversion product of n-hexane relative to their equilibrium concentrations (Y/Y_{eq}) at different reaction temperatures using the DA-H-Z catalyst

3.3. n-Hexane Hydroconversion Using Fluorinated H- ZSM-5 Containing Catalysts.

3.3.1. Using Unloaded F-H-Z Catalyst

From recent studies carried out in this laboratory on fluorinated catalysts **[199, 200]**, it has been found that a fluorine content of 3.0 wt % gives optimum hydroconversion activities, hence, this fluorine content is used in preparing the fluorinated catalysts under study. Like other catalysts, unloaded with Pt, the hydroconversion activity using the F-H-Z catalyst is found to be mainly hydrocracking (Table 13 and Fig. 20). Nevertheless, hexane hydroconversion is significantly higher on the F-H-Z catalyst than on the mother H-Z catalyst, i.e., 33.1-49.4 % on the former catalyst as compared to 1.8 - 36.2 % on the latter catalyst at temperatures of 350-500°C, respectively. This significant enhancement of activity is attributed to a significant increase of the strength of Brönsted acid sites in the F-H-Z catalyst due to the replacement of some surface -OH groups by F, whereby proton dilution is achieved on the zeolite surface, thus, decreasing the interaction of neighboring protons, and hence the remaining protons will be more strongly acidic. This is evident in Fig.7 and Table 6 , where the curves obtained for NH3-TPD show a lower ammonia desorption enthalpy (smaller number of acid sites) but a higher peak temperature in case of the F-H-Z zeolite (104.1 Jg^{-1}; 457°C) than in case of the H-Z zeolite (115.5 Jg^{-1};452°C).

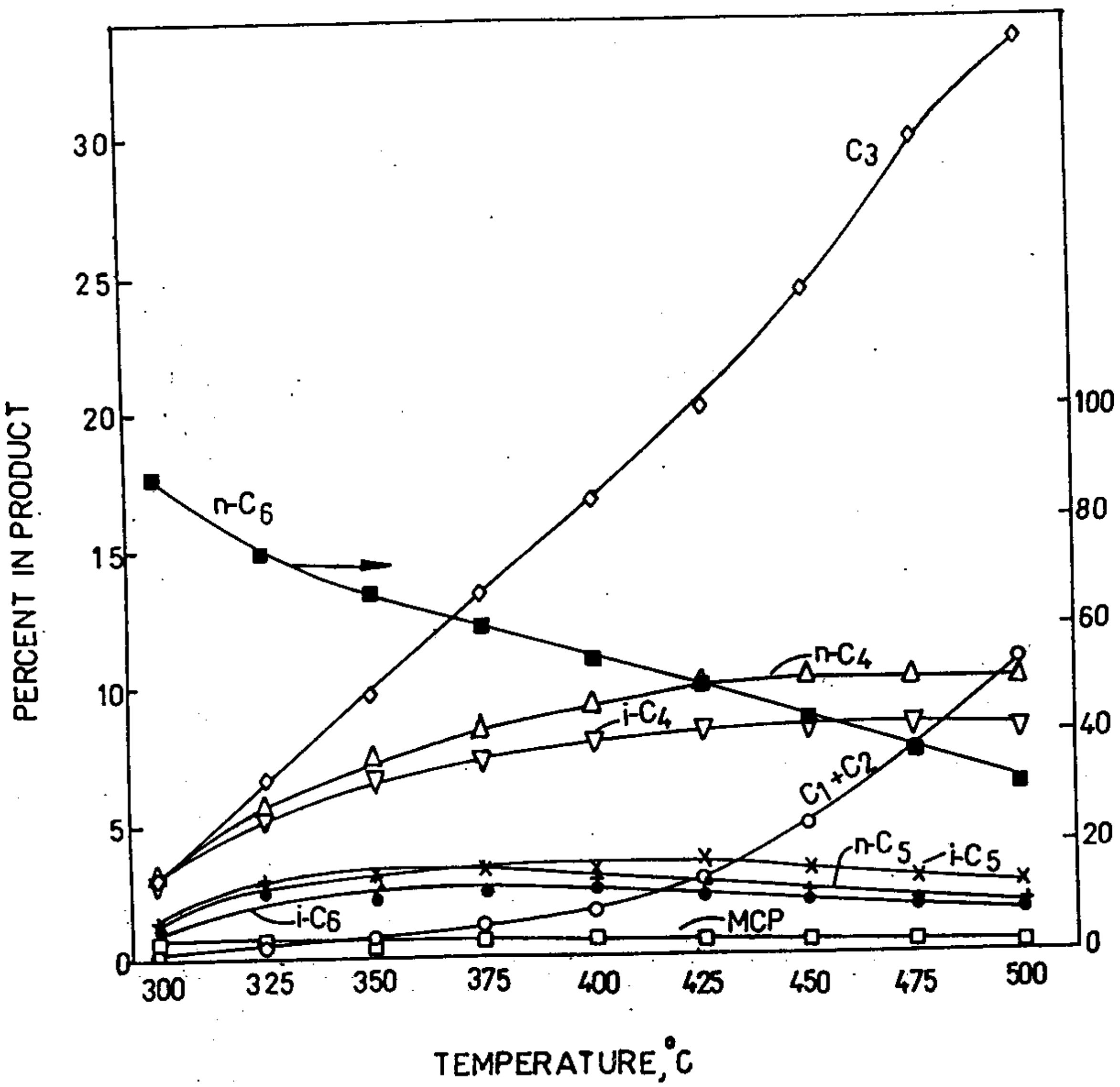

Fig. 20. Hydroconversion products of n-hexane using the F-H-Z Catalyst.

Table 13 : Distribution of n- Hexane Hydroconversion Products at Different Temperatures Using F-H-Z Catalyst .

Component in Product, %	Reaction , Temperature, C°								
	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.1	0.4	0.7	1.1	1.7	2.8	4.8	7.6	10.9
Propane	2.7	6.6	9. 7	13.4	16.8	21.1	24.4	29.8	33.4
Isobutane	2.7	5.1	6.4	7.1	7.6	8.2	8.4	8.3	8.1
n-Butane	3.1	5.6	7.4	8.4	9.3	9.8	10.3	10.2	10.2
Isopentane	1.2	2.5	3.0	3.2	3.3	3.3	3.2	2.8	2.6
n-Pentane	1.3	2.7	3.2	3.2	3.0	2.7	2.4	1.8	1.5
Σ iC$_6$'s	1.1	2.4	2.3	2.3	2.4	2.2	2.1	1.7	1.6
n-Hexane	87.1	73.9	66.9	60.7	55.3	49.1	43.3	36.9	30.6
Methylcyclopentane	0.7	0.8	0.4	06	0.6	0.5	0.5	0.4	0.3
Benzene	0.0	0.0	0.0	0.0	0.0	0.3	0.6	0.5	0.8
Hydrocracking %	11.1	22.9	30.4	36.4	41.7	47.9	53.5	60.5	66.7
Hydroisomerization %	1.1	2.4	2.3	2.3	2.4	2.2	2.1	1.7	1.6
Hydrocyclization %	0.7	0.8	0.4	0.6	0.6	0.8	1.1	0.9	1.1
Total Conversion	12.9	26.1	33.1	39.3	44.7	50.9	56.7	63.1	49.4
Hydrocracking Selectivity	89.2	87.7	91.8	92.6	93.3	94.1	94.4	95.9	96.1
Hydroisomerization selectivity	8.5	9.2	6.0	5.9	5.4	4.3	3.7	2.7	2.3
Dehydrocyclization Selectivity	5.4	3.1	1.2	1.5	1.3	1.6	1.9	1.4	1.6
Isobutane / n-Butane	0.87	0.91	0.86	0.85	0.82	0.84	0.82	0.81	0.79
Isopentane / n-Pentane	0.92	0.93	0.94	1..0	1.1	1.2	1.3	1.6	1..7

However, the hydrocracking selectivity approaches 100 % on both catalysts at all temperatures. However, using the F-H-Z catalyst, hydrocracking is less terminal compared to that using the H-Z catalyst. The percentage of methane + ethane in the hydrocracked product, $(C_1 + C_2)100/\sum(C_1 \rightarrow C_5)$, ranges between 2.3 and 16.0 % using the F-H-Z catalyst, compared to 11.1 - 21.3 % using the H-Z catalyst at temperatures of 350 - 500 °C, respectively (Fig. 2). Nevertheless, Fig. 2 also shows that $(C_1 + C_2)$ fraction in the cracked product is lowest using the F-H-Z catalyst compared to all other catalysts.

3.3.2. Using Pt/ F-H-Z Catalysts

To evaluate the role of fluorine in the Pt containing H-Z catalysts, such evaluation has to be relative to the unfluorinated version. In general, hydroconversion of n-hexane is moderately inhibited after F introduction. Hydroconversion amounts to 37.5-89.8 %, 53.2-89.5 % and 36.5-95.3 % using the 0.15 % Pt (Table 14 and Fig. 21), 0.30 % Pt (Table 15 and Fig. 22), and 0.60 % Pt/F-H-Z (Table 16 and Fig. 23) catalysts at temperatures of 300-450°, respectively, compared to 68.2-98.9 %, 61.6 -100 % and 62.7-98.4 %, using the respective Pt/ H-Z catalysts (Tables 2-4). This inhibition of n-hexane hydroconversion is chiefly attributed to the inhibition of the hydrocracking activity as a result of decreasing the number of strong acid sites after F introduction (compare Tables 5 and 6). Fluorine replaces a number of surface -OH groups in the zeolite, thus reducing the number of Brönsted acid sites which are known to be principally responsible for the C-C bond breaking **[201-203]**.

Table 14: Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.15 % Pt/ F-H-Z Catalyst.

Component in Product, %	Reaction , Temperature, C°								
	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.1	0.3	0.8	1.7	2.8	4.4	5.4
Propane	0.0	0.2	1.0	3.3	11.0	27.5	37.7	44.4	50.0
Isobutane	0.0	0.0	0.3	0.6	1.8	2.2	2.5	3.0	2.8
n-Butane	0.0	0.0	0.5	1.2	3.2	4.3	5.5	6.6	6.7
Isopentane	0.0	0.0	0.6	0.9	1.5	1.6	1.6	1.5	1.2
n-Pentane	0.0	0.0	0.5	0.8	1.3	1.3	1.4	1.2	0.9
2,2-Dimethylbutane	0.0	0.0	0.5	1.1	1.8	2.0	1.8	1.6	1.1
2-Methylpentane + 2,3-Dimethylbutane	14.0	22.6	26.9	31.4	26.0	19.5	13.9	8.5	5.8
3-Methylpentane	23.5	31.8	32.0	27.8	22.9	15.0	9.9	5.6	3.7
n-Hexane	62.5	45.4	37.6	29.3	23.2	15.5	10.2	6.5	3.7
Methylcyclopentane	0.0	0.0	0.0	1.2	2.8	1.9	1.5	1.1	0.6
Benzene	0.0	0.0	0.0	2.1	3.7	7.5	11.2	15.6	18.1
Hydrocracking %	0.0	0.2	3.0	7.1	19.6	38.6	51.5	61.1	67.0
Hydroisomerization %	37.5	54.4	59.4	60.3	50.7	36.5	25.6	15.7	10.6
Hydrocyclization %	0.0	0.0	0.0	3.3	6.5	9.4	12.7	16.7	18.7
Total Conversion	37.5	54.6	62.4	70.7	76.8	84.5	89.8	93.5	96.3
Hydrocracking Selectivity	0.0	0.4	4.8	10.0	25.5	45.7	57.4	65.4	69.6
Hydroisomerization selectivity	100	99.6	95.2	85.3	66.0	43.2	28.5	16.8	11.0
Dehydrocyclization Selectivity	0.0	0.0	0.0	4.7	8.5	11.1	14.1	17.9	19.4
Isobutane / n-Butane	0.0	0.0	0.6	0.5	0.56	0.51	0.45	0.45	0.42
Isopentane / n-Pentane	0.0	0.0	1.2	1.13	1.15	1.23	1.14	1.25	1.33

Table 15 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.30 % Pt/F-H-Z Catalyst.

Component in Product, %	Reaction , Temperature, C°								
	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.1	0.3	0.9	2.6	3.4	4.0	4.4
Propane	0.0	0.3	1.2	4.1	13.9	27.8	46.3	54.1	58.0
Isobutane	0.0	0.1	0.2	0.4	1.0	3.0	2.9	3.2	3.2
n-Butane	0.0	0.2	0.3	0.8	1.5	5.0	6.4	6.4	7.0
Isopentane	0.0	0.0	0.2	1.7	0.4	1.5	1.3	1.5	2.0
n-Pentane	0.0	0.0	0.0	0.4	0.3	1.0	0.8	1.1	1.4
2,2-Dimethylbutane	0.0	0.0	0.5	1.3	2.1	1.8	1.4	0.7	0.5
2-Methylpentane + 2,3-Dimethylbutane	23.9	30.8	34.5	35.7	32.1	19.3	10.4	5.9	2.5
3-Methylpentane	29.3	32.7	30.5	26.4	21.6	14.0	6.5	3.6	1.5
n-Hexane	46.8	35.9	30.7	26.3	21.7	15.3	10.5	5.9	2.6
Methylcyclopentane	0.0	0.0	1.8	1.4	1.0	1.1	0.8	0.4	0.4
Benzene	0.0	0.0	0.0	1.2	3.5	7.6	9.3	13.2	16.5
Hydrocracking %	0.0	0.6	2.0	7.7	18.0	40.9	61.1	70.3	76.0
Hydroisomerization %	53.2	63.5	65.5	63.4	55.8	35.1	18.3	10.2	4.5
Hydrocyclization %	0.0	0.0	1.8	2.6	4.5	8.7	10.1	13.6	16.9
Total Conversion	53.2	64.1	69.3	73.7	78.3	84.7	89.5	94.1	97.4
Hydrocracking Selectivity	0.0	0.9	2.9	10.5	23.0	48.3	68.3	74.7	78.0
Hydroisomerization selectivity	100	99.1	94.5	86.0	71.3	41.4	20.5	10.8	4.6
Dehydrocyclization Selectivity	0.0	0.0	2.6	3.5	5.8	10.3	11.3	14.5	17.4
Isobutane / n-Butane	0.0	0.5	0.67	0.5	0.67	0.6	0.45	0.5	0.46
Isopentane / n-Pentane	0.0	0.0	0.0	4.25	1.33	1.5	1.63	1.36	1.4

Table 16 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.60 % Pt/F-H-Z Catalyst

Component in Product, %	Reaction , Temperature, C$^{\circ}$								
	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.1	0.4	1.4	3.0	8.0	6.7	9.7	11.7
Propane	0.3	1.8	6.4	23.1	41.1	51.5	56.6	59.3	61.1
Isobutane	0.0	0.1	0.9	1.9	3.3	3.9	5.2	4.8	3.5
n-Butane	0.0	0.3	1.4	4.0	7.8	11.5	13.0	10.2	6.5
Isopentane	0.0	0.1	0.5	1.8	2.8	2.6	1.7	1.1	0.3
n-Pentane	0.0	0.1	0.5	1.4	2.0	1.8	1.2	0.7	0.2
2,2-Dimethylbutane	0.0	0.5	1.0	1.6	1.5	0.8	0.3	0.2	0.1
2-Methylpentane + 2,3-Dimethylbutane	19.4	26.6	29.4	23.2	13.3	4.9	1.7	0.6	0.1
3-Methylpentane	16.8	18.2	19.0	14.9	8.5	3.0	1.8	0.4	0.0
n-Hexane	63.5	51.8	39.9	25.1	13.5	6.8	4.7	2.9	3.6
Methylcyclopentane	0.0	0.4	0.4	0.6	0.5	0.3	0.1	0.0	0.0
Benzene	0.0	0.0	0.2	1.0	2.7	4.9	7.0	10.1	12.9
Hydrocracking %	0.3	2.5	10.1	33.6	60.0	79.3	84.4	85.8	83.3
Hydroisomerization %	36.2	45.3	49.4	39.7	23.3	8.7	3.8	1.2	0.2
Hydrocyclization %	0.0	0.4	0.6	1.6	3.2	5.2	7.1	10.1	12.9
Total Conversion	36.5	48.2	60.1	74.9	86.5	93.2	95.3	97.1	96.4
Hydrocracking Selectivity	0.8	5.2	16.8	44.9	69.4	85.1	88.6	88.4	86.4
Hydroisomerization selectivity	99.2	94.0	82.2	53.0	26.9	9.3	4.0	1.2	0.2
Dehydrocyclization Selectivity	0.0	0.8	1.0	2.1	3.7	5.6	7.5	10.4	13.4
Isobutane / n-Butane	0.0	0.33	0.64	0.48	0.42	0.34	0.4	0.47	0.54
Isopentane / n-Pentane	0.0	1.0	1.0	1.29	1.4	1.44	1.42	1.57	1.5

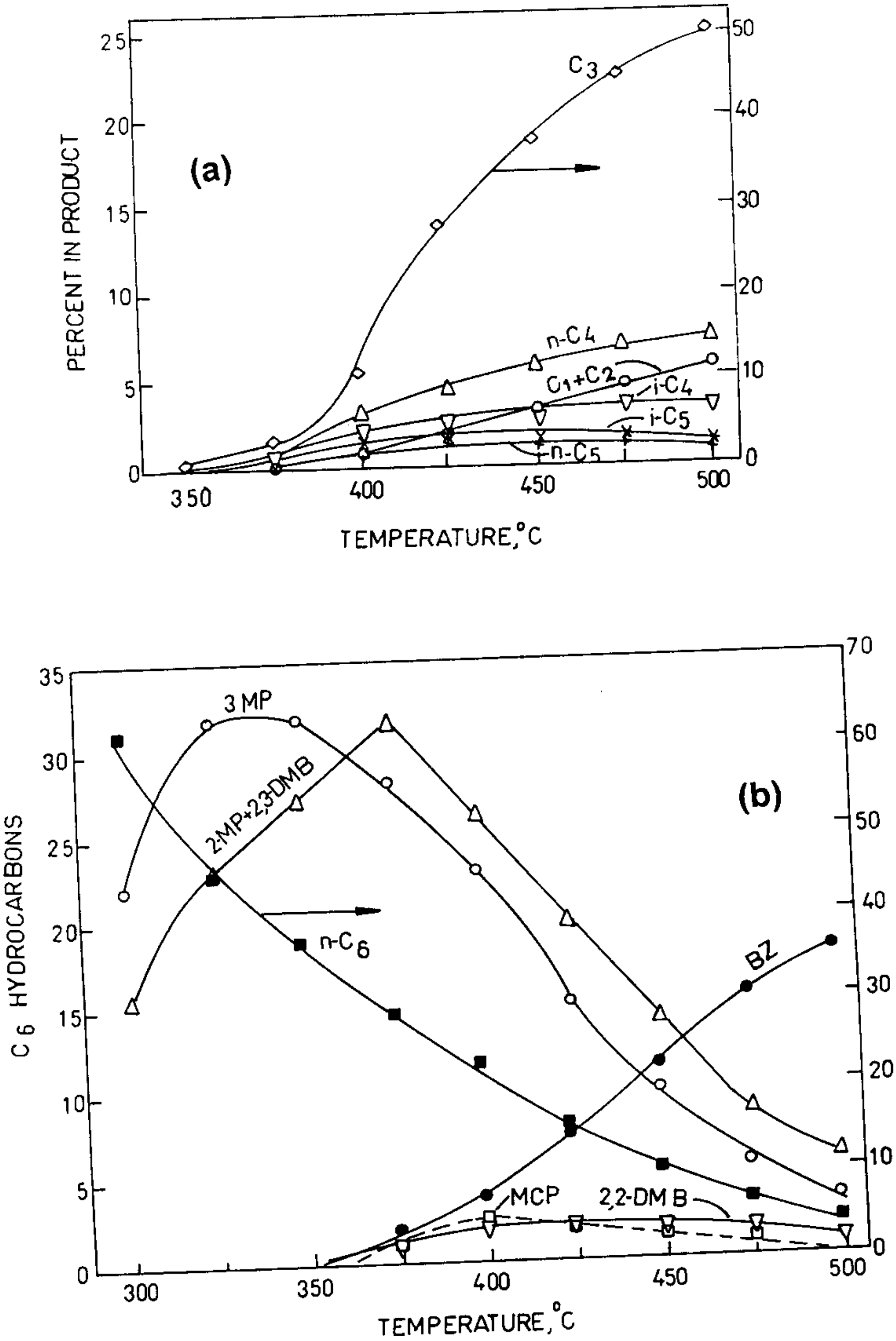

Fig. 21. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.15% Pt/F-H-Z catalyst

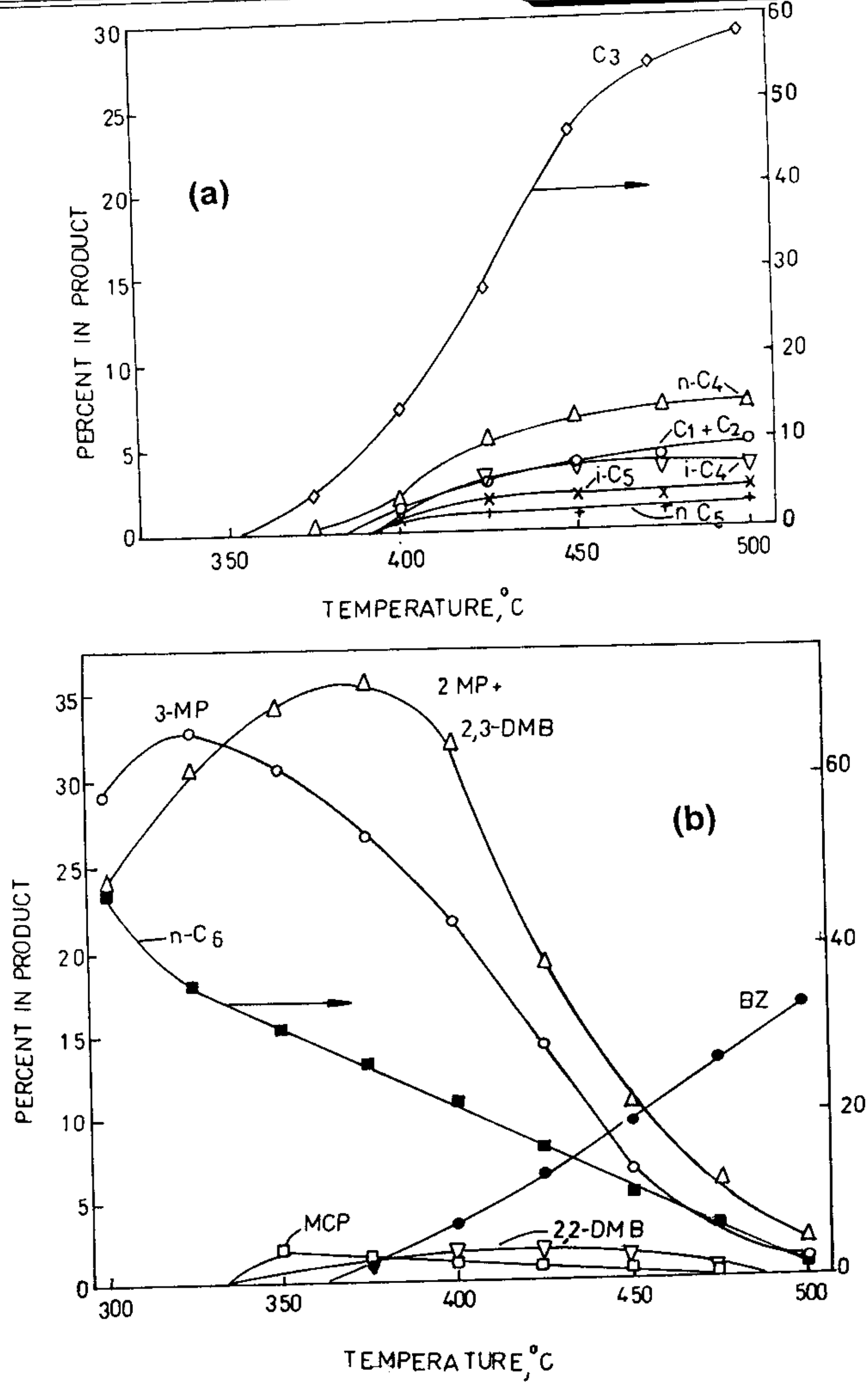

Fig. 22. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.30% Pt/F-H-Z catalyst.

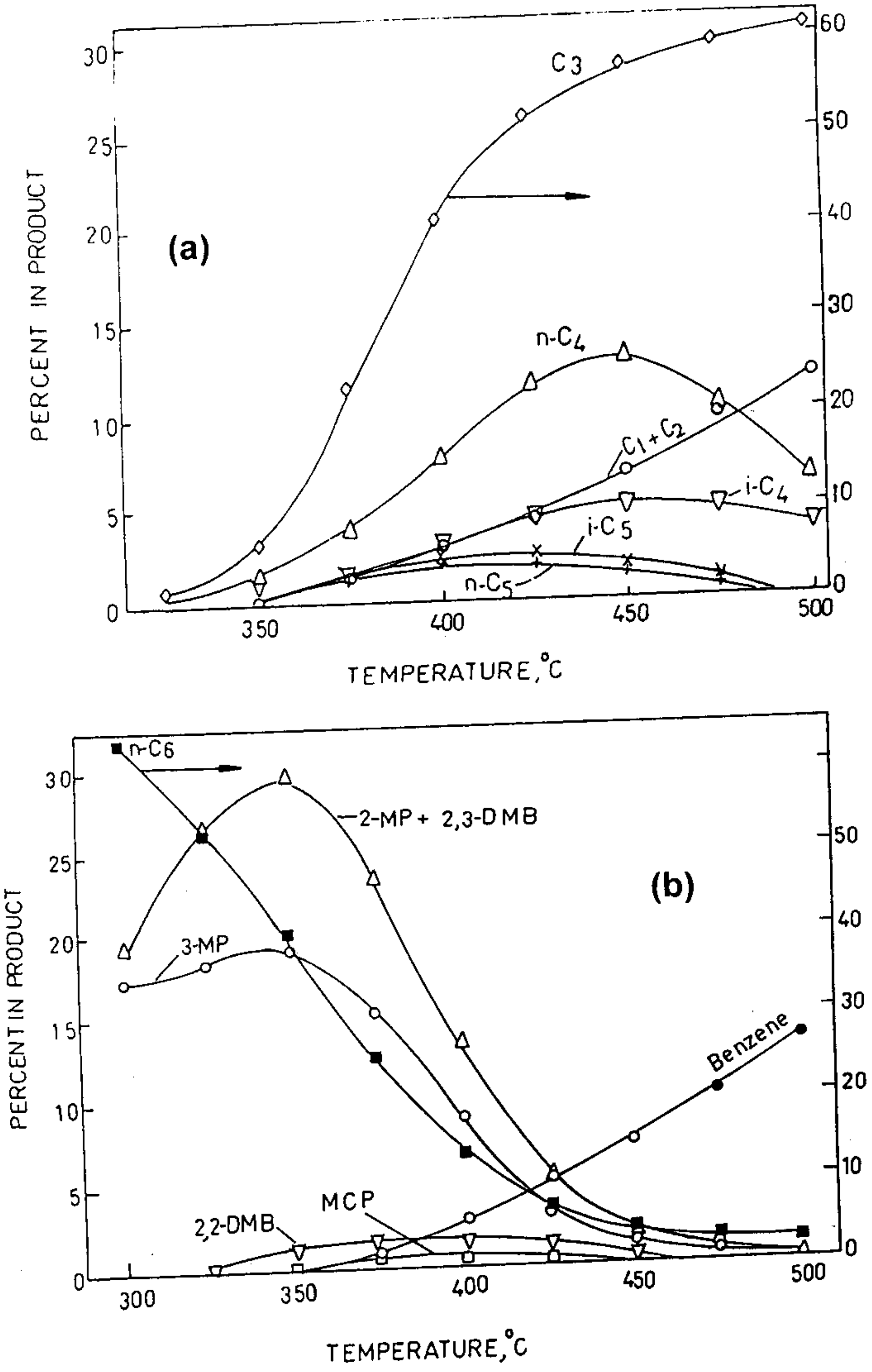

Fig. 23. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.60% Pt/F-H-Z catalyst.

Furthermore, F introduction appears to have increased the hydrophobicity of the catalysts which also results in inhibiting the dehydrocyclization of n-hexane to benzene. Using the 0.15, 0.30 and 0.60 % Pt/FH-Z catalysts, benzene in product amounts to 3.7-18.1 %, 3.5-16.5 % and 2.7-12.9 % at temperatures of 400-500 °C, respectively, as compared to 12.1-22.8 %, 15.8-22.6 % and 18.9-32.9 %, respectively, using the respective Pt/H-Z versions. The combined effect of inhibiting both hydrocracking and dehydrocyclization reactions has increased the hydroisomerization selectivities of the F-promoted catalysts. For instance, isomerization selectivities of 100.0-66.0%, 100.0-71.3 % and 99.2-26.9 %, are obtained using the 0.15 % Pt, 0.30 % Pt and 0.60 % Pt/F-H-Z catalysts (Tables 14-16), respectively, at temperatures of 300-400 °C, compared to 100-25.1%, 100-10.6 % and 97.6-20.5 % respectively, (Tables 2-4) using the respective Pt/H-Z catalysts.

Correlation of the percentage of methane + ethane in the hydrocracked product, $(C_1 + C_2)100 / \sum(C_1 \rightarrow C_5)$, using the Pt/F-H-Z and Pt/H-Z catalysts, simply compares the terminal hydrocracking efficiencies of these two series of catalysts (Figs. 24 and 8). A significant inhibition of terminal hydrocracking is observed via fluorine inclusion in the catalysts. Using the 0.15 % Pt, 0.30 % Pt and 0.60 % Pt/F-H-Z catalysts, the percentage of C_1+C_2 in the hydrocracked product amounts to 3.3-8.1 %, 3.9-5.8 % and 4.0-14.0 % at temperatures of 350-500 °C, respectively, compared to 6.7-22.5 %, 6.8-32.6 % and 6.0-37.8 %, respectively, using the respective Pt/H-Z catalysts.

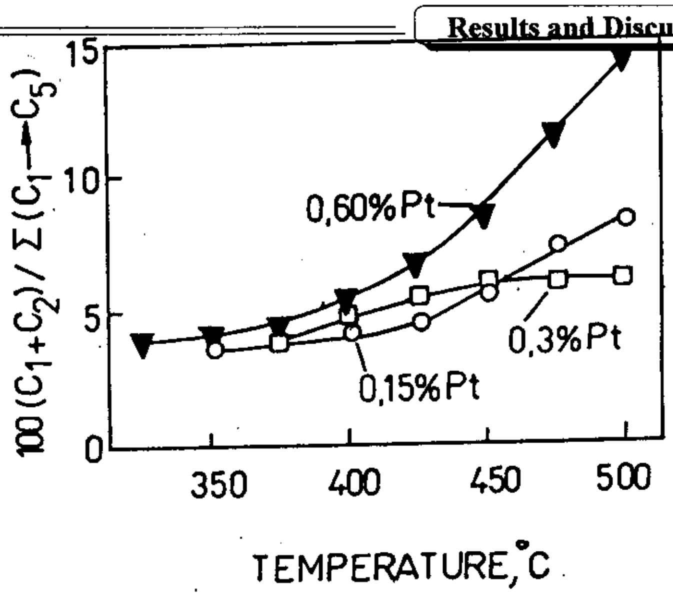

Fig. 24. C_1+C_2 in the hydrocracked product of n-hexane using the Pt/F-H-Z catalysts.

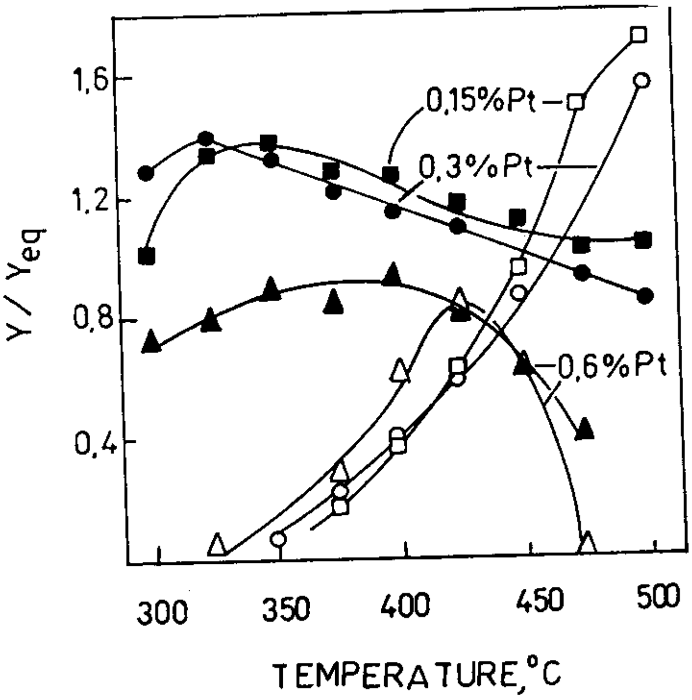

Fig. 25. 3-MP and 2,2-DMB in the hydroconversion product of n-hexane relative to their equilibrium concentrations (Y/Y_{eq}) at different reaction temperatures using the Pt/F-H-Z catalyst

The 3-MP values in product relative to those in the thermodynamic equilibrium (Fig. 25) are highest using the 0.15% Pt-containing catalyst and lowest over the 0.60% Pt-containing catalyst. However, the ratios of 2,2-DMB are highest using the 0.60% Pt-containing catalyst and lowest using the 0.15% Pt-containing catalyst (at low temperatures). The variation of the ratios is most clear using the 0.60% Pt-containing catalyst. 2,2-DMB appears to require higher Pt content than 3-MP up to a temperature of 425 °C.

3.4. Hyrdoconversion of n-Hexane Using Steamed H-ZSM-5 Zeolite Containing Catalysts

3.4.1. Using Unloaded Steamed H-ZSM-5 Zeolite Catalyst (St H-Z Catalyst)

Comparing the data in Table 17 and Fig. 26 with those in Table 1 and Fig. 1 shows that hydrothermal treatment (steam treatment) of H-ZSM-5 zeolite results in some decrease of its hydroconversion activity. Neither isomerization nor cyclization products appear in the reaction product using the St H-Z zeolite catalyst. Although the hydrocracking selectivity is 100 % all over the temperature range investigated, yet the hydrocracking activity exhibits some decrease. Hydrocracked products amount to 6.6-32.6 % at temperatures of 400-475 °C respectively, using the St H-Z catalyst compared to 19.7-34.0 % respectively, using the untreated H-Z zeolite catalyst. However although methane + ethane in product amount to 0.2-6.5 % and propane amounts to 1.3-27.0 % at

Table 17 : Distribution of Reaction Products Through Hydroconversion of n- Hexane at Different Temperatures Using St-H-Z Catalyst.

Component in Producti, %	Reaction , Temperature, C°						
	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.2	0.8	1.8	3.1	4.5	6.5
Propane	0.5	1.3	4.2	8.0	13.0	19.0	27.0
Isobutane	0.0	0.3	0.3	0.9	1.7	2.2	0.0
n-Butane	0.0	0.0	1.3	2.6	3.9	4.9	1.5
Isopentane	0.0	0.0	0.0	0.4	1.0	1.1	1.8
n-Pentane	0.0	0.0	0.0	0.4	1.0	0.9	1.7
2,2-Dimethylbutane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
2-Methylpentane + 2,3-Dimethylbutane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-Methylpentane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
n-Hexane	99.5	98.2	93.4	85.9	0.0	0.0	0.0
Methylcyclopentane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrocracking %	0.5	1.8	6.6	14.1	23.7	32.6	38.5
Hydroisomerization %	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrocyclization %	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Conversion	0.5	1.8	6.6	14.1	23.7	32.6	38.5
Hydrocracking Selectivity	100	100	100	100	100	100	100
Hydroisomerization selectivity	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Dehydrocyclization Selectivity	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Isobutane / n-Butane	0.0	0.0	0.23	0.35	0.44	0.45	0.0
Isopentane / n-Pentane	0.0	0.0	0.0	1.0	1.0	1.22	1.06

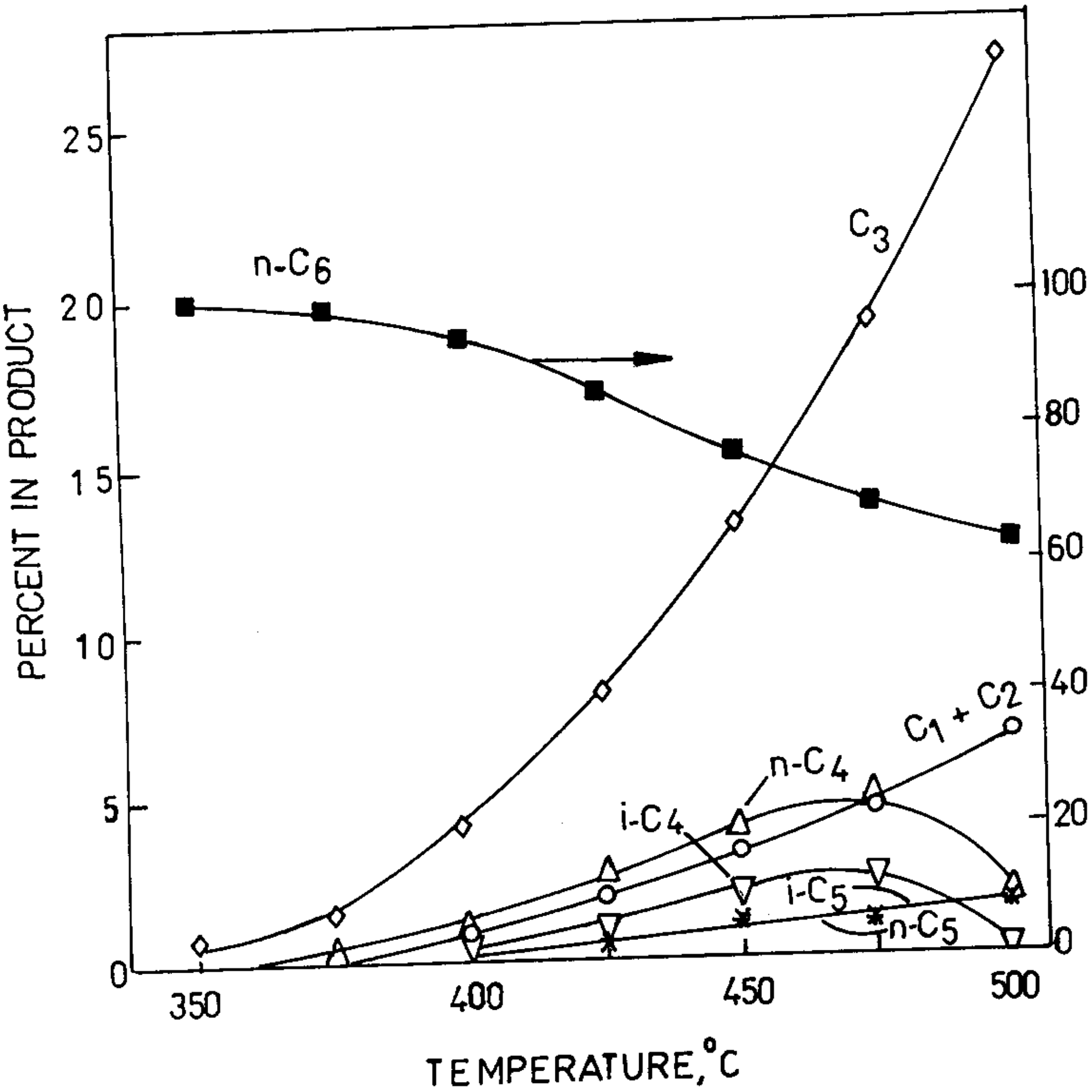

Fig. 26. Hydroconversion products of n-hexane using the St H-Z Catalyst.

temperatures of 375-500 °C, respectively, these hydrocarbons, i.e., C_1+C_2 amount to 1.2-7.7 % and propane amount to 5.4-14.9 % using the H-Z catalyst. This indicates that steam-treatment of the zeolite enhances central splitting of n-hexane to propane, particularly at higher temperatures.

In the hydrocracked products using the St H-Z catalyst, the i-C_4/n-C_4 ratio ranges between o.23 and 0.45, showing insignificant variation from the corresponding values using the unsteamed H-Z version (0.27-0.49) (Tables 17 and 1). However, i-C_5/n-C_5 ratios of 1.0-1.22 using the St H-Z catalysts are obtained as compared to ratios of 0.67-0.87 using the unsteamed catalyst. These data may show slight improvement of hexane hydroisomerizing activity of H-Z zeolite via steam treatment.

3.4.2. Steamed Pt/ H-ZSM-5 Catalysts (Pt/St H-Z Catalyst)

In these catalysts, Pt incorporation has preceded the steam treatment. So the extent of stability of the Pt- H-Z catalysts against steaming show that steaming is effective in decreasing the hydroconversion activities of the Pt/ H-Z catalysts at all Pt concentrations (compare Tables 18-20 with Tables 3-5, respectively). Steam-treatment of the 0.15 % Pt/H-Z catalyst (Figs. 27and 28), 0.30 % Pt/H-Z (Figs. 29 and 30) and 0.60 % Pt/H-Z (Figs. 31 and 32) catalysts gives n-hexane hydroconversion of 36.1-82.5 %, 33.8-90.5 % and 42.6-94.1 %, respectively, at reaction temperatures between 300 and 500 °C, compared to 68.2-100 %, 61.6-100 and 62.7-100 %, respectively, using the corresponding untreated Pt/H-Z catalysts.

Table 18 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using **St 0.15% Pt/H-Z** ***Catalyst.***

Component In Product, %	Reaction, Temperature, C°										
	250	275	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.0	0.7	1.5	2.9	4.5	6.6	8.4	10.7	12.0
Propane	00.	0.0	1.9	4.4	7.9	13.3	21.0	26.0	28.2	29.0	29.0
Isobutane	0.0	0.0	0.5	1.2	1.9	4.1	5.8	8.1	9.1	9.0	8.5
n-Butane	0.0	0.0	0.7	2.0	3.5	6.0	9.5	12.4	13.8	13.5	13.0
Isopentane	0.0	0.0	0.0	0.7	1.6	2.5	4.0	4.5	3.5	2.5	1.2
n-Pentane	0.0	0.0	0.0	0.6	1.4	3.1	3.6	3.3	2.7	2.0	1.3
2,2-Dimethylbutane	0.0	0.0	0.0	1.1	1.7	2.1	1.9	1.2	0.0	0.0	0.0
2-Methylpentane + 2,3-Dimethylbutane	4.9	11.5	17.1	20.8	21.3	17.8	13.0	8.4	4.5	2.5	2.0
3-Methylpentane	5.5	10.0	13.5	16.1	16.8	13.9	9.8	5.7	2.8	1.3	0.5
n-Hexane	89.6	78.5	63.9	50.4	40.4	32.4	25.7	20.3	18.2	17.5	17.5
Methylcyclopentane	0.0	0.0	2.4	2.0	2.0	2.0	1.9	1.2	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	3.5	8.8	12.0	15.0
Hydrocracking %	0.0	0.0	3.1	9.6	17.8	31.9	48.4	60.9	65.7	66.7	65.0
Hydroisomerization %	10.4	21.5	30.6	38.0	39.8	33.8	24.7	15.3	7.3	3.8	2.5
Hydrocyclization %	0.0	0.0	2.4	2.0	2.0	1.9	1.2	3.5	8.8	12.0	15.0
Total Conversion	10.4	21.5	36.1	49.6	59.6	67.6	74.3	79.7	81.8	82.5	82.5
Hydrocracking Selectivity	0.0	0.0	8.6	19.4	29.9	47.2	65.1	76.4	80.3	80.9	78.8
Hydroisomerization selectivity	100	100	84.8	76.6	66.8	50.0	33.2	19.2	8.9	4.6	3.0
Dehydrocyclization Selectivity	0.0	0.0	6.7	4.0	3.4	2.8	1.6	4.4	10.8	14.6	18.2
Isobutane / n-Butane	0.0	0.0	0.71	0.6	0.54	0.68	0.61	0.65	0.66	0.67	0.65
Isopentane / n-Pentane	0.0	0.0	0.0	1.17	1.14	0.81	1.11	1.36	1.3	1.25	0.92

Table 19 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using St 0.30% Pt/H-Z *Catalyst.*

Component In Production %	Reaction , Temperature, C°										
	250	275	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.3	0.8	1.7	3.4	5.2	7.8	9.3	11.5	14.5
Propane	0.0	0.7	2.3	5.5	9.9	17.8	25.6	31.5	34.0	36.1	37.6
Isobutane	0.0	0.0	0.0	1.4	2.9	5.6	7.2	9.7	10.7	10.1	8.5
n-Butane	0.0	0.5	0.9	2.3	4.9	9.1	12.0	14.8	15.2	14.1	12.0
Isopentane	0.0	0.0	0.0	1.0	2.7	4.7	5.5	5.5	4.8	4.2	1.5
n-Pentane	0.0	0.0	0.0	0.9	2.2	4.0	4.0	3.7	3.5	2.5	0.7
2,2-Dimethylbutane	0.0	0.0	0.4	0.9	1.5	1.9	2.0	1.5	0.5	0.0	0.0
2-Methylpentane + 2,3-Dimethylbutane	2.5	9.8	16.5	19.8	20.5	15.7	10.5	5.0	2.0	0.0	0.0
3-Methylpentane	3.6	7.8	12.0	14.7	15.5	11.9	7.5	3.5	1.3	0.0	0.0
n-Hexane	93.9	81.2	66.2	51.3	36.8	24.2	18.0	13.5	10.2	9.0	9.5
Methylcyclopentane	0.0	0.0	1.4	1.4	1.4	1.7	1.3	0.0	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	1.2	3.5	8.5	12.5	15.7
Hydrocracking %	0.0	1.2	3.5	11.9	24.3	44.6	59.5	73.0	77.5	78.5	74.8
Hydroisomerization %	6.1	17.6	28.9	35.4	37.5	29.5	20.0	10.0	3.8	0.0	0.0
Hydrocyclization %	0.0	0.0	1.4	1.4	1.4	1.7	2.5	3.5	8.5	12.5	15.7
Total Conversion	6.1	18.8	33.8	48.7	63.2	75.8	82.0	86.5	89.8	91.0	90.5
Hydrocracking Selectivity	0.0	6.3	10.4	24.4	38.5	58.8	72.6	84.4	86.3	86.3	82.7
Hydroisomerization selectivity	100	93.6	85.5	72.7	59.3	38.9	24.4	11.6	4.2	0.0	0.0
Dehydrocyclization Selectivity	0.0	0.0	4.1	2.9	2.2	2.2	3.1	4.1	9.5	13.7	17.4
Isobutane / n-Butane	0.0	0.0	0.0	0.61	0.59	0.62	0.6	0.66	0.7	0.72	0.71
Isopentane / n-Pentane	0.0	0.0	0.0	1.11	1.23	1.18	1.38	1.49	1.37	1.68	0.21

Table 20 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using* St 0.60% Pt/H-Z *Catalyst

Component in Product, %	Reaction , Temperature,C°										
	250	275	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.2	0.6	1.7	3.0	4.7	6.6	9.4	13.0	16.5
Propane	0.0	0.4	2.2	4.6	10.4	16.0	23.3	29.5	36.0	33.8	30.3
Isobutane	0.0	0.0	0.6	1.3	2.7	4.6	7.3	9.6	10.0	10.2	8.0
n-Butane	0.0	0.0	0.7	2.0	4.6	7.6	11.6	13.8	15.0	14.7	11.4
Isopentane	0.0	0.0	0.0	0.9	2.3	4.3	5.6	5.2	3.4	2.3	1.3
n-Pentane	0.0	0.0	0.0	0.7	1.9	3.8	4.6	4.1	2.4	1.5	1.0
2,2-Dimethylbutane	0.0	0.0	0.7	1.2	2.0	2.7	2.3	1.3	0.0	0.0	0.0
2-Methylpentane + 2,3-Dimethylbutane	7.8	16.4	20.2	22.6	22.7	18.2	12.0	5.3	2.1	1.0	0.0
3-Methylpentane	8.7	13.8	16.2	17.2	17.2	13.8	8.7	3.8	1.2	0.3	0.0
n-Hexane	83.5	69.4	57.4	46.7	32.9	24.4	17.2	14.0	9.4	6.9	5.9
Methylcyclopentane	0.0	0.0	1.8	2.2	1.6	1.6	1.2	1.1	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	1.5	5.7	11.1	14.5	17.5
Toluene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	1.8	8.1
Hydrocracking %	0.0	0.4	3.7	10.1	23.6	39.3	57.1	68.8	76.2	75.5	68.5
Hydroisomerization %	16.5	30.2	37.1	41.0	41.9	34.7	23.0	10.4	3.3	1.3	0.0
Hydrocyclization %	0.0	0.0	1.8	2.2	1.6	1.6	2.7	6.8	11.1	16.3	25.6
Total Conversion	16.5	30.6	42.6	53.3	67.1	75.6	82.8	86.0	90.6	93.1	94.1
Hydrocracking Selectivity	0.0	1.3	8.7	18.9	35.2	52.0	69.0	80.0	84.1	81.1	72.8
Hydroisomerization selectivity	100	98.7	87.1	76.9	62.4	45.9	27.8	12.1	3.6	1.4	0.0
Dehydrocyclization Selectivity	0.0	0.0	4.2	4.1	2.4	2.1	3.3	7.9	12.3	17.5	27.2
Isobutane / n-Butane	0.0	0.0	0.86	0.65	0.59	0.61	0.63	0.7	0.67	0.69	0.7
Isopentane / n-Pentane	0.0	0.0	0.0	1.29	1.21	1.13	1.22	1.27	1.42	1.53	1.3

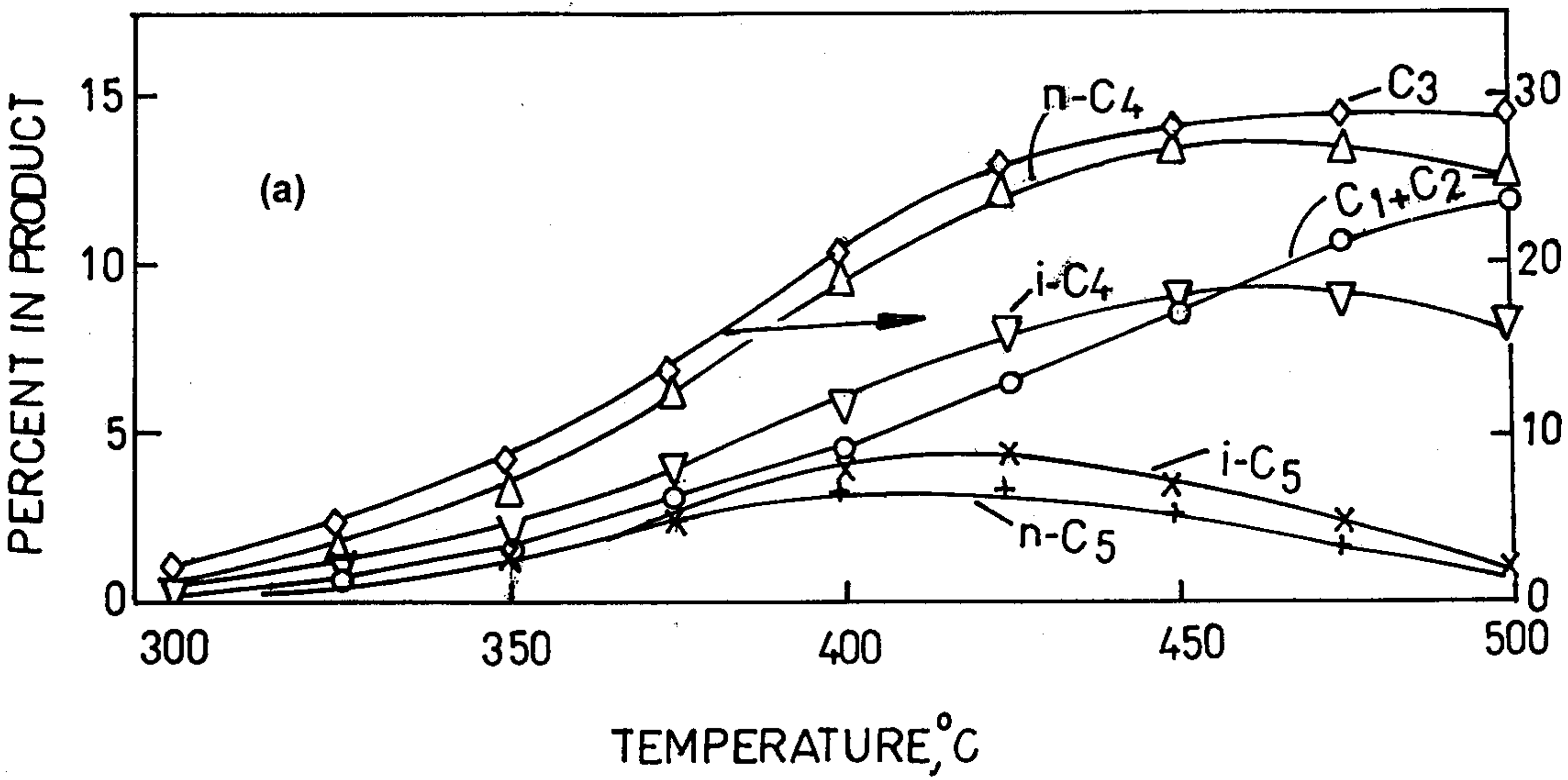

Fig. 27. Hydrocracked components in the hydroconversion product of n-hexane using the St 0.15 % Pt/ H-Z catalyst

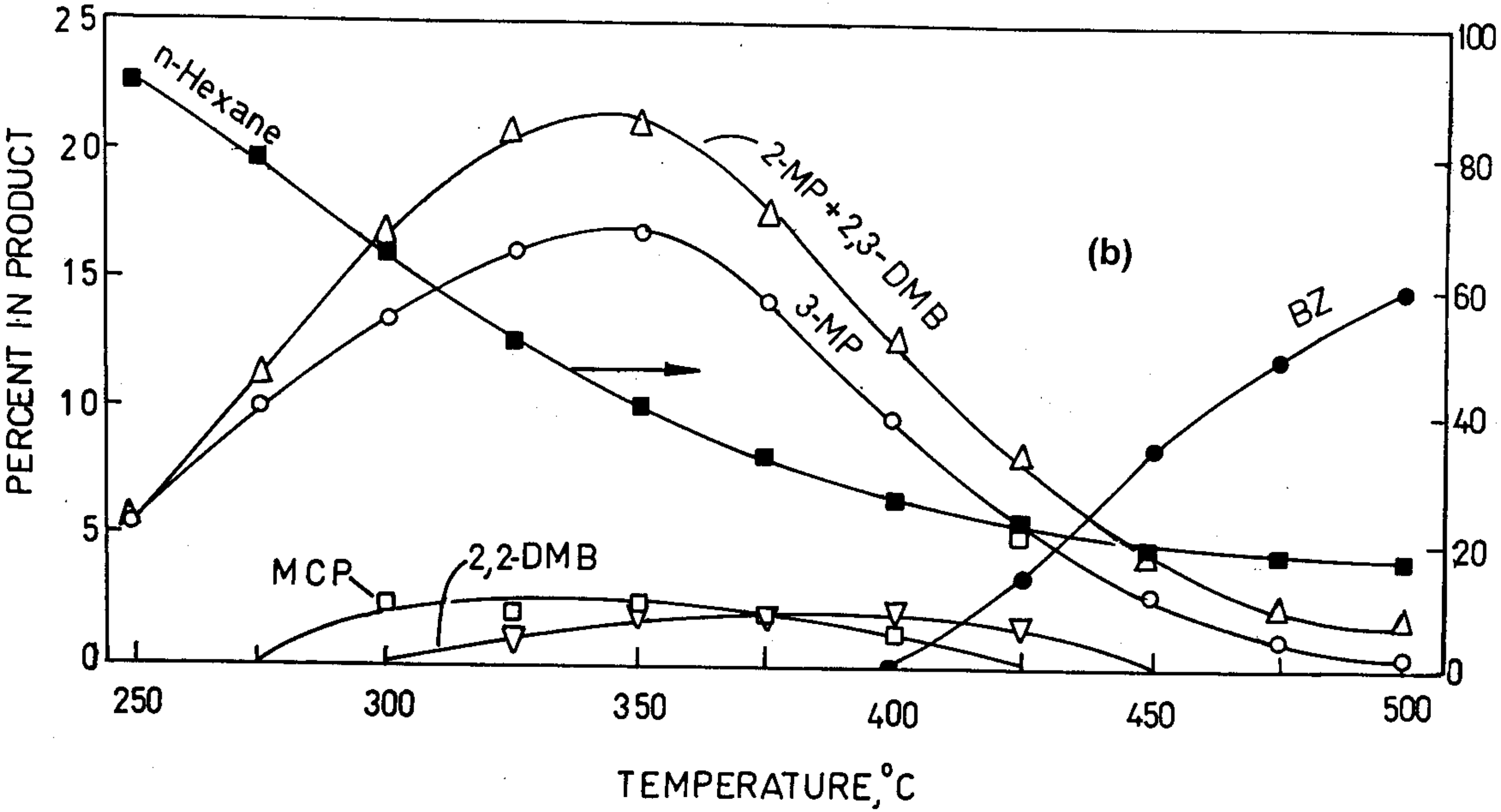

Fig. 28. C_6 components in the hydroconversion product of n-hexane using the St 0.15% Pt/ H-Z catalyst

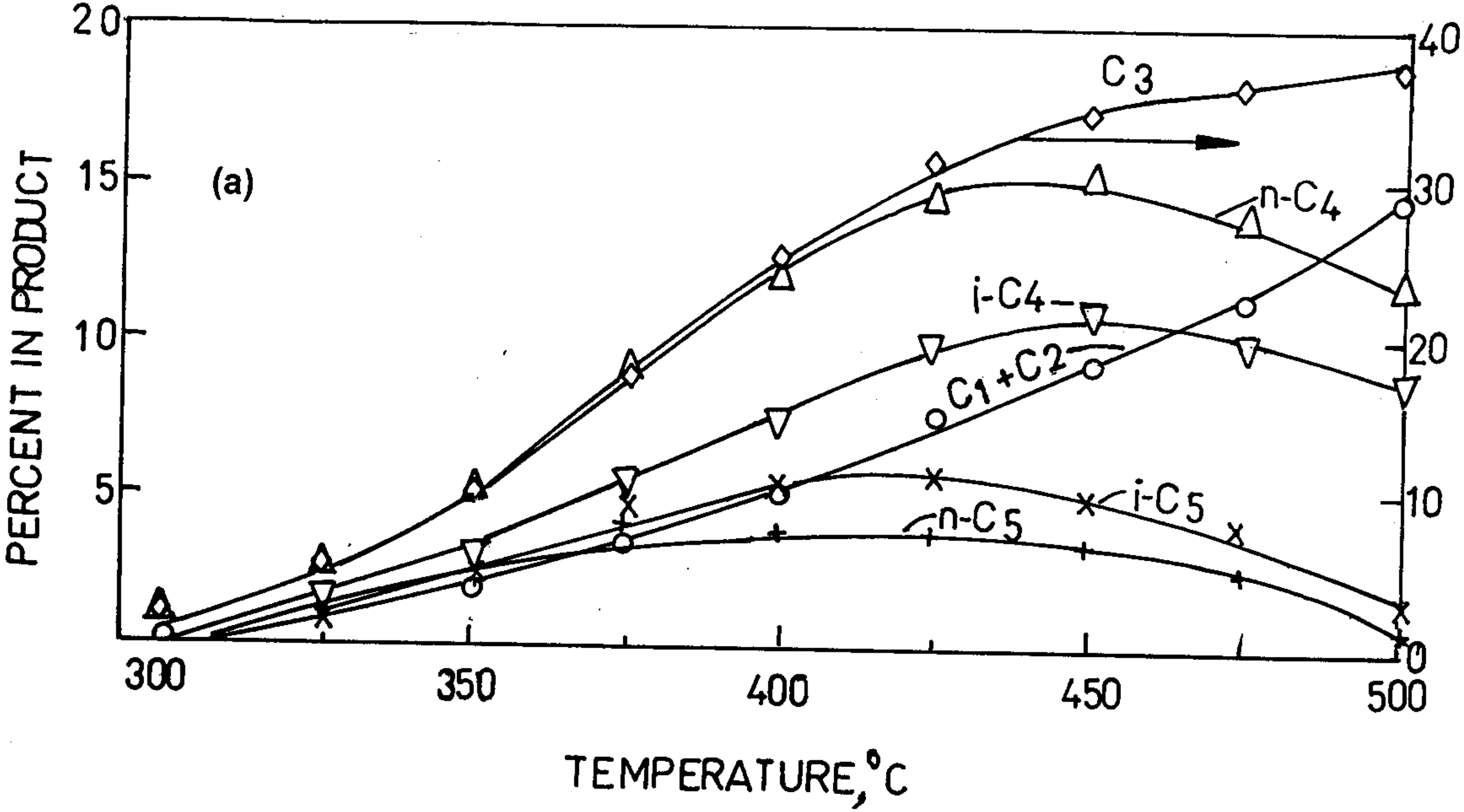

Fig. 29. Hydrocracked components in the hydroconversion product of n-hexane using the St 0.30 % Pt/ H-Z catalyst

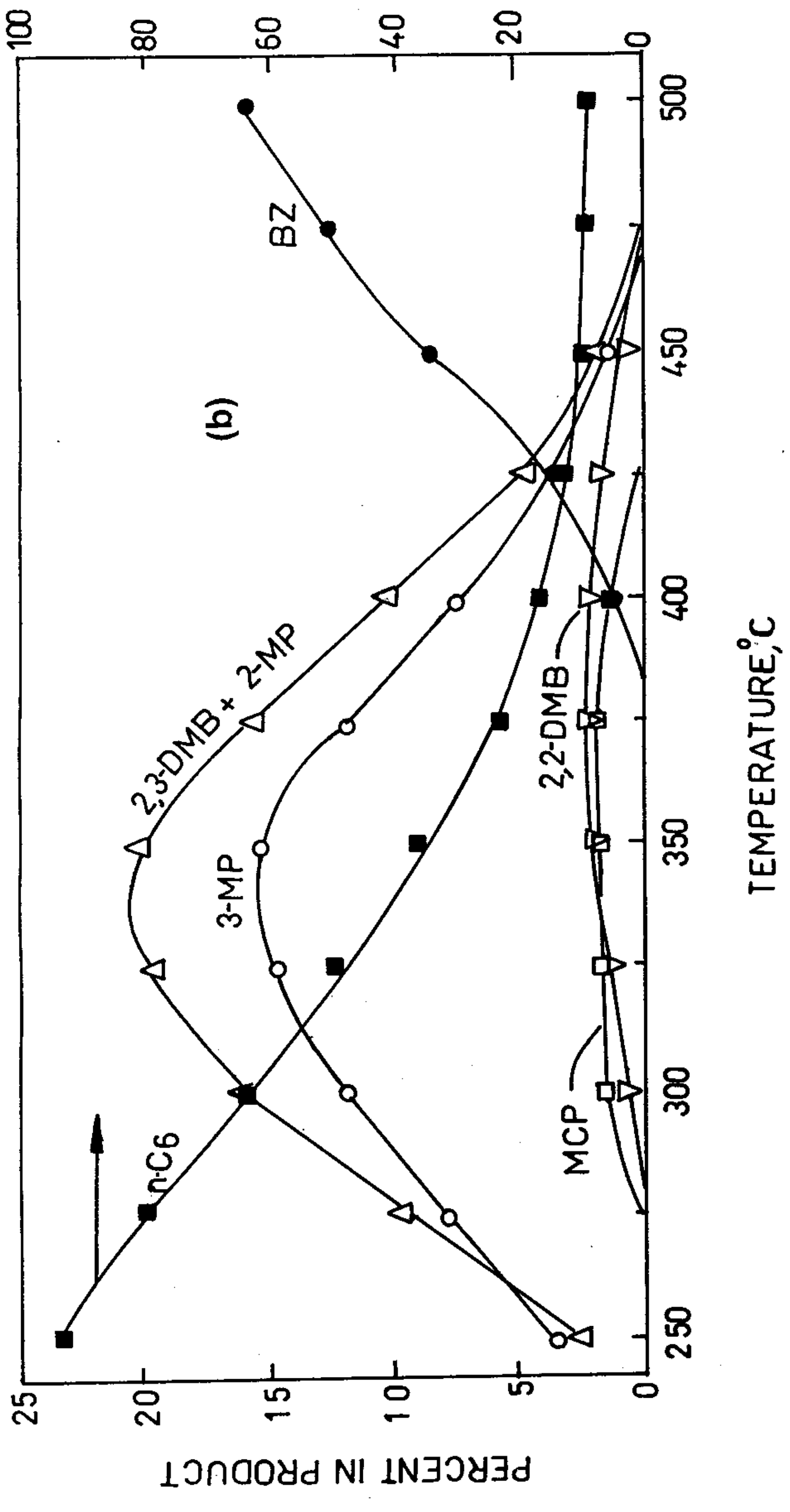

Fig. 30. C_6 components in the hydroconversion product of n-hexane using the St 0.30% Pt/ H-Z catalyst

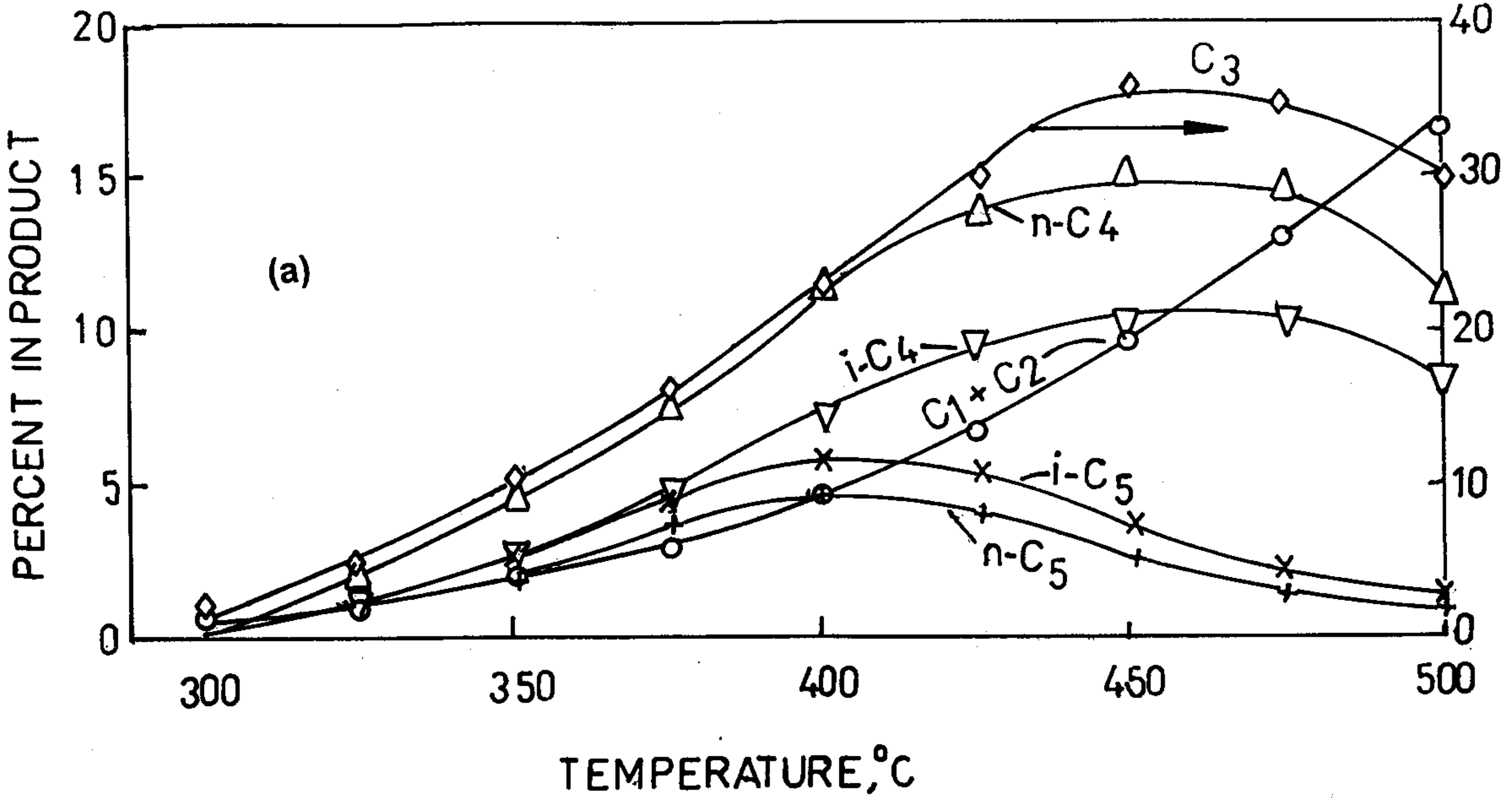

Fig. 31. Hydrocracked components in the hydroconversion product of n-hexane using the St 0.60 % Pt/ H-Z catalyst

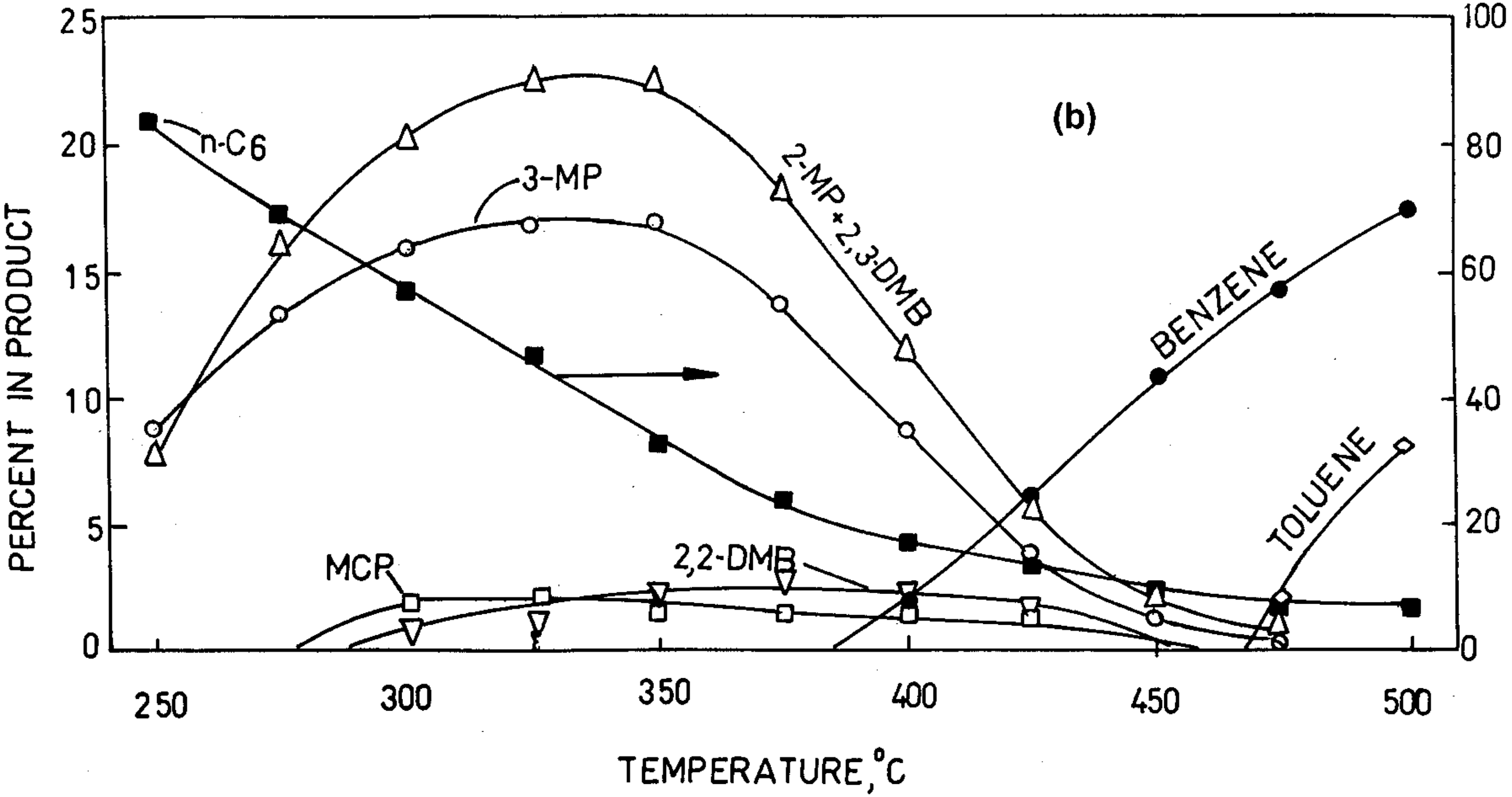

Fig. 32. C_6 components in the hydroconversion product of n-hexane using the St 0.60% Pt/ H-Z catalyst

Using the St Pt/H-Z catalysts the hydroisomerization maxima amount to 39.8, 37.5 and 41.9 %, respectively, at a reaction temperature of 350 °C, compared to significantly higher maxima of 68.6, 66.0 and 62.7 % using the corresponding Pt/ H-Z catalysts, respectively, at a reaction temperature of 325 °C, i.e., steaming has not only decreased the level of these isomers maxima but also raised the temperature at which these maxima take place (Tables 18-20 and Figs. 27-32).

Benzene cannot be formed using the unloaded St H-Z catalyst, whereas after Pt incorporation in this zeolite, benzene formation takes place and increases with temperature. Using the St Pt/H-Z catalysts, benzene is significantly lower than using the corresponding Pt/H-Z catalysts. Benzene reaches its maximum formation of 15.0, 15.7 and 17.5 % at 500 °C using the St 0.15%, 0.30% and 0.60% Pt/H-Z catalysts, respectively, compared to 22.8, 22.6 and 32.9 %, respectively, using the corresponding Pt/H-Z catalysts. This reflects the hydrophobic nature of the steamed zeolite catalysts, since steaming results in hydrothermal dealumination of the zeolite, but the removed Al from the framework remains in non-framework positions in the zeolite channels and cages. The Si/Al ratio of the steamed H-Z catalyst (Table 21) is not significantly lower than that of the mother H-Z zeolite, which indicates that most of the Al removed from the framework is still contained in the steamed zeolite. Both neutral and ionic Al species have been identified by several authors **[97,201,202]** in the hydrothermally-treated zeolites.

Table 21: **Si / Al Ratio for the Unloaded H-Z Zeolite and its Modified Versions**

Catalysts	Si / Al Ratio	Si / Al increase, %
H-Z	24.0	--
DA-H-Z	31.3	30.4
F-H-Z	27.7	15.4
St H-Z	28.0	16.7
F-DA-H-Z	36.5	52.1
F-St H-Z	32.5	36.7

Toluene also appears in the product of n-hexane hydroconversion using the St 0.60 % Pt/H-Z catalyst at higher temperatures; it amounts to 1.8-8.1 % at temperatures of 475-500 °C, respectively. Since toluene does not appear in the reaction product using the Pt/DA-H-Z catalysts, which have been dealuminated using EDTA and possessing higher Si/Al ratios than those treated with steam, it can be assumed that the Al species deposited in the channels of the St 0.60 % Pt/H-Z catalyst may be responsible for the formation of toluene. Toluene may be formed via alkylation of the formed benzene, while it is still adsorbed on the catalyst via methyl group transfer reaction. The methyl groups are formed via hydrogenolysis of n-hexane, in relatively larger percentages, on the higher Pt-containing catalysts. Hydrogenolysis is an active reaction over Pt crystallites; therefore, it seems logic that toluene is formed over the catalyst containing o.60 % Pt only but not on the catalysts containing 0.15 or 0.30 % Pt.

The extent of hydrocracking using the St Pt/H-Z catalysts do not significantly differ from that using the corresponding untreated Pt/H-Z catalysts. The hydrocracking selectivities using the steamed catalysts is higher than those using the unsteamed catalysts. The hydrocracking selectivities reach maxima of 80.9, 86.3 and 84.1 % using the steamed 0.15, 0.30 and 0.60 % Pt containing catalysts, compared to values of 77.5, 79.0 and 69.4 % using the corresponding Pt/H-Z catalysts. Steam-treatment may have created some strong Brönsted acid sites as assumed by ***Mirodatos et al.*** **[128].**

Moreover, benzene in product using the steam-treated 0.15, 0.30 and 0.60 % Pt/ H-Z catalysts is also lower than using the corresponding unsteamed Pt/ H-Z catalysts. Using the steamed catalysts, benzene amounts to 15.0, 15.7 and 25.6 %, respectively, at a temperature of 500 °C, whereas using the corresponding unsteamed catalysts, benzene in the product reaches 22.8, 22.6 and 32.9 %, respectively. The decrease of benzene production after steam-treatment of the catalysts is most probably due to increasing the hydrophobic character of the zeolite. Although a portion of Al is removed outside the channels of the zeolite, yet another portion remains in these channels in the form of non-framework oxo-aluminium species $(AlO)^{+}_{p}$ **[128]**. Data in the preceding part show that dealumination via EDTA treatment has greatly enhanced n-hexane hydroisomerization activity and selectivity (Fig. 15), whereas steam-treatment, which also results in framework dealumination, has, on the contrary, significantly inhibited the isomerization activities and selectivities of the catalyst. An important reason for this inhibition is attributed to a significant decrease of Pt dispersion, (Table 5) which results in significant agglomeration of the Pt crystallites; thus deteriorating the proper action of bifunctionality and intimacy **[195]**. Another reason for the decrease of the hydroisomerization activity and selectivity is the presnce of some non-framework amorphous Al species in the zeolitic channels and cages of the St Pt/H-Z catalysts.

The hydrocracking activity of the St Pt/H-Z catalysts for producing C_1+C_2 components in the hydrocracked product do not greatly differ (Fig. 33) via changing the Pt content from 0.15% Pt to 0.60%. Only using the 0.60% Pt-containing catalyst the C_1+C_2 component increases with a relatively higher rate at temperatures from 450 to 500°C. This also indicates activated hydrogenolysis.

Nevertheless, the ratio of i-C_4/n-C_4 in the product using the St Pt/H-Z catalysts (Table 18-20) is higher than that using the unsteamed versions (Table 2-4) and also higher than using the catalyst versions wherein the zeolite is dealuminated by EDTA (Tables 8-10). This may indicate that the C_6 isomers formed on the St Pt/ H-Z catalysts are rapidly cracked to produce higher iso-butane/n-butane ratios. This may also indicate that some oxo-aluminium species of higher acidity strength **[128]** are formed in the channels and cages of the St Pt/H-Z catalysts.

The Y/Ye values obtained for 3-MP and 2,2-DMB (Fig. 34) increase with temperature up to a maximum, beyond which they decrease with a further increase of temperature. At lower temperatures, 3-MP is significantly higher than 2,2-DMB. The maxima of these isohexanes take place at 350 and 450°C, respectively. In general, this ratio is in the order 0.60 % Pt > 0.15 % Pt > 0.30 % Pt at least up to a temperature of 350°C. This indicates that a higher Pt content of 0.60% does not cause restriction of the formation of these components.

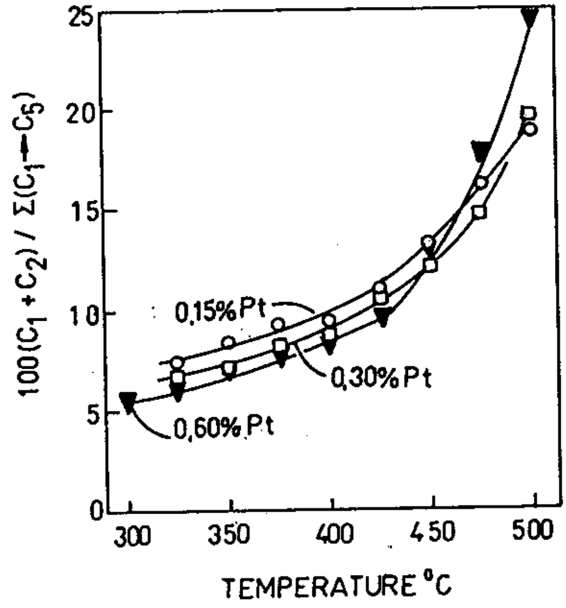

Fig. 33. C_1+C_2 in the hydrocracked product of n-hexane using the St Pt/H-Z catalysts.

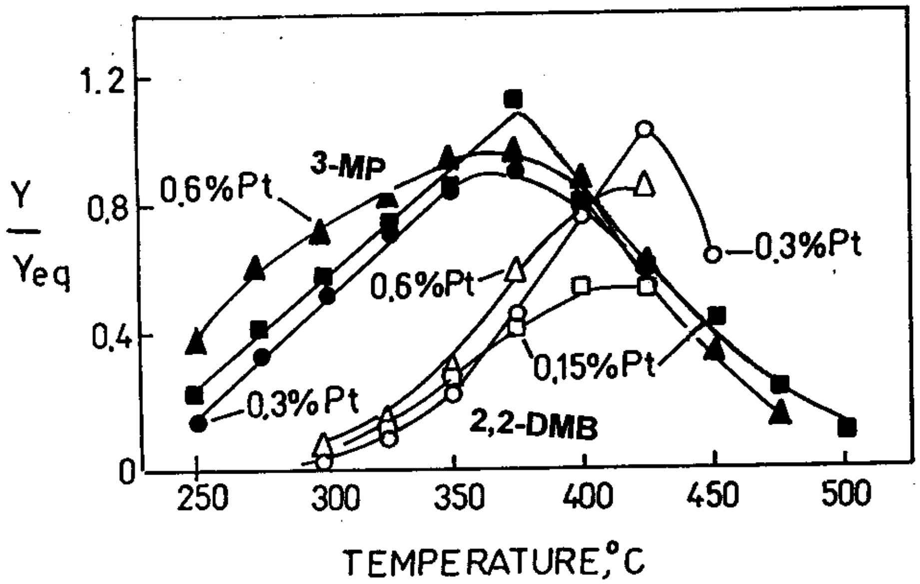

Fig. 34. 3-MP and 2,2-DMB in the hydroconversion product of n-hexane relative to their equilibrium concentrations (Y/Y_{eq}) at different reaction temperatures using theSt Pt/H-Z catalyst

n-Hexane Hydroconversion Using F-DA-H-Z Containing Catalysts

3.5.1. Correlation of Catalysts Treated with EDTA, F and with Both Treatments

Each of the dealuminating procedures, EDTA or F treatment, gives enhancement of n-hexane hydroconversion. Using the mother H-Z catalyst, hydroconversion products comprise 1.8-36.2% between temperatures of 350 and 500°C, respectively, compared to 3.0-55.7% (Table 7) and 33.1-49.4% (Table 13) respectively, using the DA-H-Z and F-H-Z catalysts, respectively.

On the other hand, combination of the two above mentioned treatments together, i.e., EDTA treatment followed by fluorination, the catalyst obtained (F-DA-H-Z) exhibits a lower activity (1.1-36.8%) (Table 22 and Fig. 35) than using the F-H-Z and DA-H-Z catalysts for n-hexane hydroconversion. This conversion level is lower than using either F-H-Z or DA-H-Z but, rather close to the activity level using the untreated H-Z catalyst. The greater activation of the F-H-Z catalyst than the DA-H-Z catalyst can be attributed to the larger number of strong acid sites, since the TPD-profiles obtained using differential scanning calorimetry show that ammonia-desorption enthalpy from the acid sites of F-H-Z and DA-H-Z amount to 104.1 and 98.5 Jg^{-1}, respectively and the HT-peak temperatures for ammonia-desorption are, respectively, 457 and 456°C (Fig.7and Table6) compared to 452°C using the H-Z catalyst..

Table 22 : Distribution of Reaction Products Through Hydroconversion of n- Hexane at Different Temperatures Using F-DA-H-Z Catalyst

Component in Products %	Reaction , Temperature, C°						
	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.6	1.5	2.5	3.8	5.1	7.0
Propane	0.8	3.0	7.0	10.7	14.8	18.1	19.9
Isobutane	0.0	0.4	1.0	1.6	2.1	2.8	2.4
n-Butane	0.2	1.0	2.2	3.7	5.2	6.3	5.4
Isopentane	0.0	0.1	0.2	0.3	0.6	0.7	0.6
n-Pentane	0.1	0.1	0.4	0.6	1.0	1.1	0.9
2,2- Dimethylbutane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Cyclopentane	0.0	0.0	0.2	0.3	0.4	0.5	0.6
2-Methylpentane + 2,3-Dimethylbutane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
3-Methylpentane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
n-Hexane	98.9	94.8	87.8	80.3	72.1	65.4	63.2
Methylcyclopentane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrocracking %	1.1	5.2	12.5	19.7	27.9	34.6	36.8
Hydroisomerization %	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Hydrocyclization %	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total Conversion	1.1	5.2	12.5	19.7	27.9	34.6	36.8
Hydrocracking Selectivity	100	100	100	100	100	100	100
Hydroisomerization selectivity	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Dehydrocyclization Selectivity	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Isobutane / n-Butane	0.0	0.40	0.45	0.43	0.4	0.44	0.44
Isopentane / n-Pentane	0.0	1.0	0.5	0.5	0.6	0.64	0.67

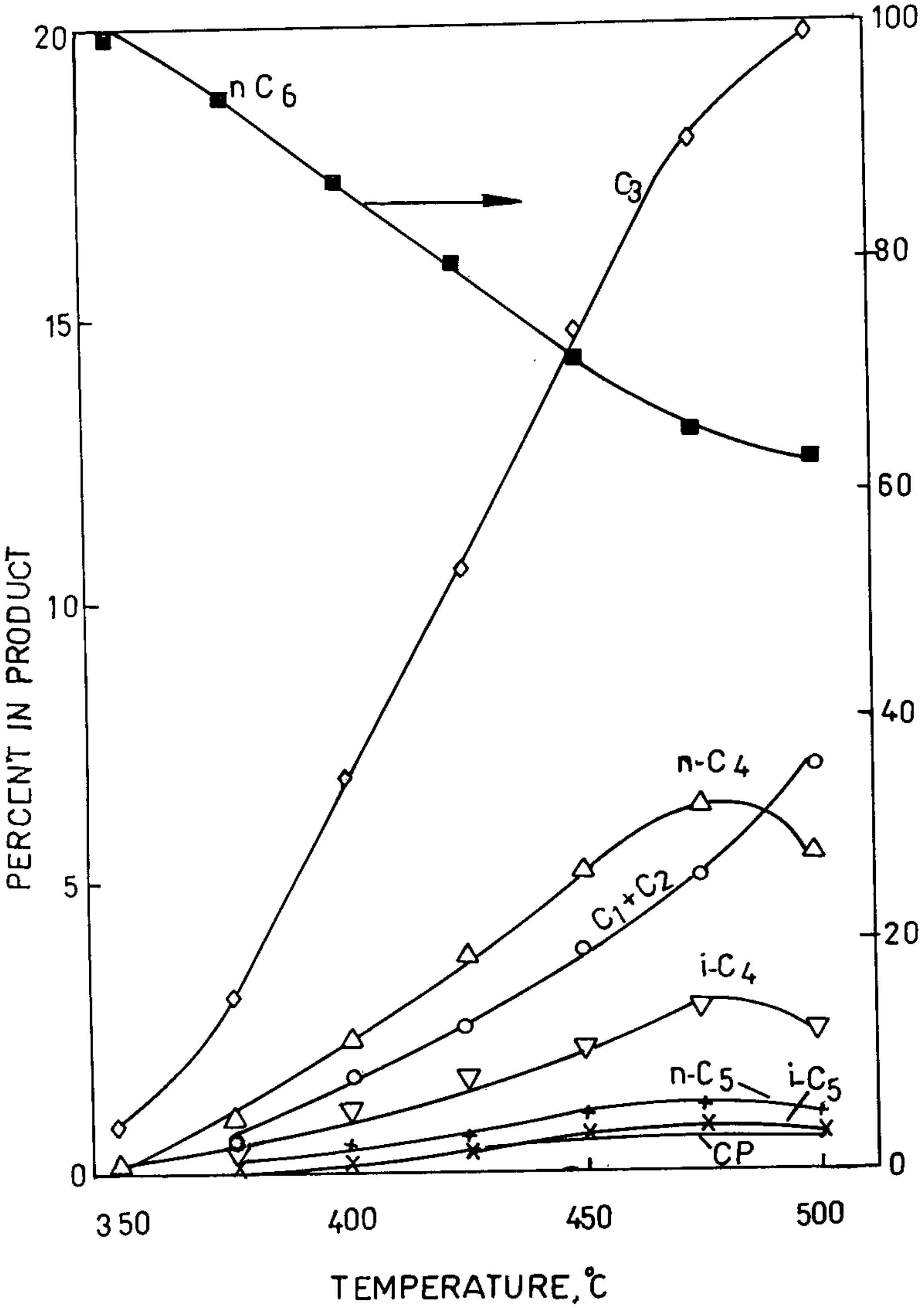

Fig. 35. Hydroconversion products of n-hexane using the F-DA-H-Z Catalyst.

Although the hydroconversion levels using the mother H-Z catalyst and its double-treated version (F-DA-H-Z) are almost equal, the former catalyst acquires a larger number of strong acid sites (ammonia-desorption ΔH equals 115.5 vs. 81.5 Jg^{-1} (Table 6) using the latter catalyst), whereas these strong acid sites are relatively stronger in the latter catalyst than in the former (peak temperature is 452 °C for H-Z and 454 °C for the F-DA-H-Z catalyst). It is to be pointed out that the principal or even the sole reaction on these catalysts is hydrocracking. However, hydroisomerization and aromatization reactions are completely absent.

3.5.2. Hydroconversion of n-Hexane Using the Pt/F-DA-H-Z Catalysts

The Pt- loaded F-DA-H-Z catalysts containing 0.15% Pt (Table 23 and Fig. 36), 0.30% Pt (Table 24 and Fig. 37) and 0.60% Pt (Table 25 and Fig. 38) show significant lower hydroconversion activities than the corresponding Pt/DA-H-Z and Pt/F-H-Z catalysts. Comparing the catalysts containing 0.15% Pt supported on F-DA-H-Z, H-Z, DA-H-Z and F-H-Z, hydroconversions of 34.2-80.3%, 68.2-100%, 66.5-97.2 and 12.9-69.4%, respectively, are obtained at reaction temperatures of 300-500 °C, respectively. This indicates that the 0.15% Pt containing catalysts can be arranged according to their hydroconversion activities as follows:

Table 23 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.15% Pt/ F-DA- H-Z Catalyst.

Component in Product, %	Reaction , Temperature, C°								
	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.2	0.5	1.5	2.5	3.5	4.9	5.6
Propane	0.0	0.7	2.7	8.4	19.0	32.0	37.9	40.4	41.0
Isobutane	0.0	0.0	0.3	0.6	1.5	1.5	2.0	3.2	4.0
n-Butane	0.0	0.0	0.5	1.3	2.8	3.7	5.3	6.5	7.4
Isopentane	0.0	0.0	0.0	0.4	0.6	0.7	1.2	1.1	1.0
n-Pentane	0.0	0.0	0.0	0.3	0.5	0.6	1.0	0.9	0.8
2,2-Dimethylbutane	0.0	0.0	0.3	0.6	1.6	1.3	1.3	1.3	1.0
2-Methylpentane + 2,3-Dimethylbutane	15.7	24.1	29.0	29.0	24.5	17.2	10.4	7.0	5.1
3-Methylpentane	18.5	22.9	24.2	22.2	16.8	11.6	6.7	4.0	3.1
n-Hexane	65.8	52.3	42.8	34.9	28.0	23.5	21.8	20.2	19.7
Methylcyclopentane	0.0	0.0	0.0	0.8	0.8	0.8	0.8	0.8	1.0
Benzene	0.0	0.0	0.0	1.0	2.4	4.6	8.1	9.7	10.3
Hydrocracking %	0.0	0.7	3.7	11.5	25.9	41.0	50.9	57.0	59.8
Hydroisomerization %	34.2	47.0	53.5	51.8	42.9	30.1	18.4	12.3	9.2
Hydrocyclization %	0.0	0.0	0.0	1.8	3.2	5.4	8.9	10.5	11.3
Total Conversion	34.2	47.7	57.2	65.1	72.0	76.5	78.2	79.8	80.3
Hydrocracking Selectivity	0.0	1.5	6.5	17.7	36.0	53.6	65.1	71.4	74.4
Hydroisomerization selectivity	100	98.5	93.5	79.6	59.6	39.4	23.5	15.4	11.5
Dehydrocyclization Selectivity	0.0	0.0	0.0	2.7	4.4	7.0	11.4	13.2	14.1
Isobutane / n-Butane	0.0	0.0	0.6	0.46	0.54	0.41	0.38	0.57	0.54
Isopentane / n-Pentane	0.0	0.0	0.0	1.33	1.2	1.17	1.2	1.22	1.25

Table 24 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.30 % Pt/ F-DA- H-Z Catalyst.

Component in Products %	Reaction , Temperature, C°									
	275	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.2	0.5	1.7	2.8	4.5	6.3	7.5	9.7
Propane	0.0	0.6	2.7	8.5	24.4	34.7	40.0	43.9	48.7	49.0
Isobutane	0.0	0.0	0.2	0.6	1.8	2.9	3.8	4.5	5.0	5.0
n-Butane	0.0	0.0	0.3	1.5	4.2	6.9	9.5	10.0	9.8	9.5
Isopentane	0.0	0.0	0.0	0.6	1.7	2.4	2.2	1.7	1.1	0.6
n-Pentane	0.0	0.0	0.0	0.5	1.3	2.0	1.8	1.4	1.1	0.6
2,2-Dimethylbutane	0.0	0.0	0.8	0.9	1.0	0.8	0.5	0.5	0.4	0.0
2-Methylpentane + 2,3-Dimethylbutane	14.0	24.0	29.5	29.0	22.5	15.0	9.2	5.0	2.0	0.0
3-Methylpentane	16.5	18.7	21.0	21.3	15.5	10.0	6.0	3.3	1.3	0.0
n-Hexane	69.5	57.3	45.3	36.0	24.6	20.0	17.5	16.7	15.0	14.6
Methylcyclopentane	0.0	0.0	0.0	0.6	0.5	0.7	1.6	1.7	0.0	0.0
Benzene	0.0	0.0	0.0	0.0	0.8	1.8	3.7	5.0	8.1	11.5
Hydrocracking %	0.0	0.6	3.4	12.2	35.1	51.7	61.8	67.8	73.2	74.4
Hydroisomerization %	30.5	42.7	51.3	51.2	39.0	25.8	15.7	8.8	3.7	0.0
Hydrocyclization %	0.0	0.0	0.0	0.6	1.3	2.5	5.0	6.7	8.1	11.0
Total Conversion	30.5	43.3	54.7	64.0	75.4	80.0	82.5	83.3	85.0	85.4
Hydrocracking Selectivity	0.0	1.4	6.2	19.1	46.6	64.6	74.9	81.4	86.1	87.1
Hydroisomerization selectivity	100	98.6	93.8	80.0	51.7	32.3	19.0	10.6	4.4	0.0
Dehydrocyclization Selectivity	0.0	0.0	0.0	0.9	1.7	3.1	6.1	8.0	9.5	12.9
Isobutane / n-Butane	0.0	0.0	0.67	0.4	0.43	0.42	0.4	0.45	0.51	0.53
Isopentane / n-Pentane	0.0	0.0	0.0	1.2	1.3	1.2	1.2	1.21	1.0	1.0

Table 25 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.60 % Pt/ F-DA-H-Z Catalyst

Component In Product, %	Reaction , Temperature, C°									
	275	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.0	1.0	1.9	3.5	5.0	6.5	8.5	11.4
Propane	0.0	0.7	3.5	9.0	23.1	38.0	46.0	50.0	51.9	51.5
Isobutane	0.0	0.0	0.0	0.8	1.9	3.5	3.9	4.3	4.8	5.0
n-Butane	0.0	0.0	0.3	1.8	5.0	9.5	11.0	11.3	10.8	10.0
Isopentane	0.0	0.0	0.0	0.8	1.9	2.9	2.7	2.0	0.8	0.5
n-Pentane	0.0	0.0	0.0	0.3	1.3	2.0	2.0	1.5	0.7	0.4
2,2-Dimethylbutane	0.0	0.0	0.6	1.3	1.5	1.1	0.8	0.2	0.0	0.0
2-Methylpentane + 2,3-Dimethylbutane	15.0	24.8	29.5	28.0	22.0	12.0	6.0	3.0	1.0	0.0
3-Methylpentane	16.5	18.3	20.0	20.0	13.7	7.4	3.5	1.5	0.4	0.0
n-Hexane	68.5	56.2	46.1	36.7	25.9	16.8	12.8	10.0	8.9	7.7
Methylcyclopentane	0.0	0.0	0.0	0.3	0.5	0.4	0.3	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0	1.3	2.9	6.0	9.7	12.2	13.5
Hydrocracking %	0.0	0.7	3.8	13.7	35.1	59.4	70.6	75.6	77.5	78.8
Hydroisomerization %	31.5	43.1	50.1	49.3	37.2	20.5	10.3	4.7	1.4	0.0
Hydrocyclization %	0.0	0.0	0.0	0.3	1.8	3.3	6.3	9.7	12.2	13.5
Total Conversion	31.5	43.8	53.9	63.3	74.1	83.2	87.2	90.0	91.1	92.3
Hydrocracking Selectivity	0.0	1.6	7.0	21.6	47.4	71.4	81.0	84.0	85.1	85.4
Hydroisomerization selectivity	100	98.4	93.0	77.9	50.2	24.6	11.8	5.2	1.5	0.0
Dehydrocyclization Selectivity	0.0	0.0	0.0	0.5	2.4	4.0	7.2	10.8	13.4	14.6
Isobutane / n-Butane	0.0	0.0	0.0	0.44	0.38	0.37	0.35	0.38	0.44	0.5
Isopentane / n-Pentane	0.0	0.0	0.0	2.67	1.46	1.45	1.35	1.33	1.14	1.25

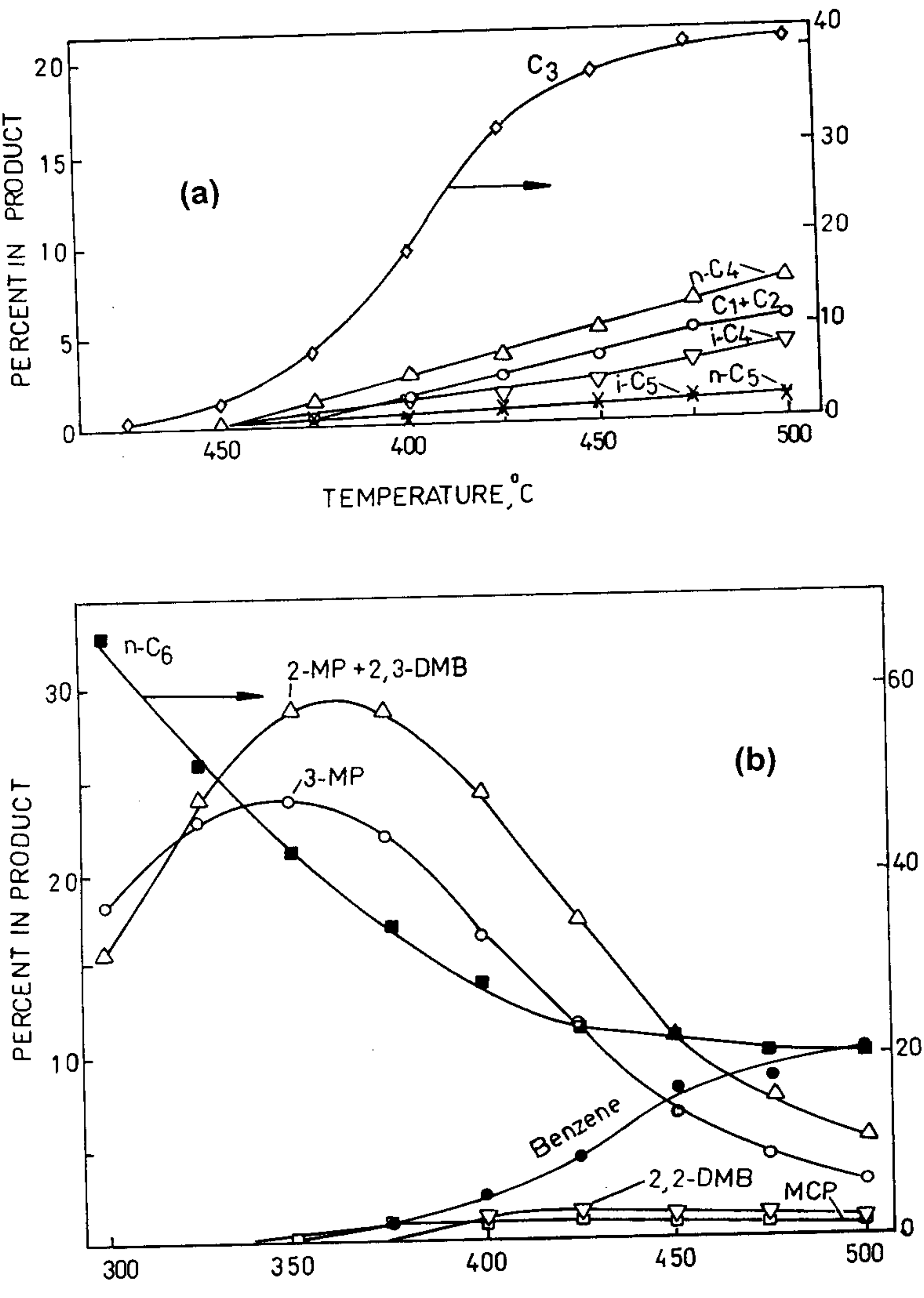

Fig. 36. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.15% Pt/F-DA-H-Z catalyst

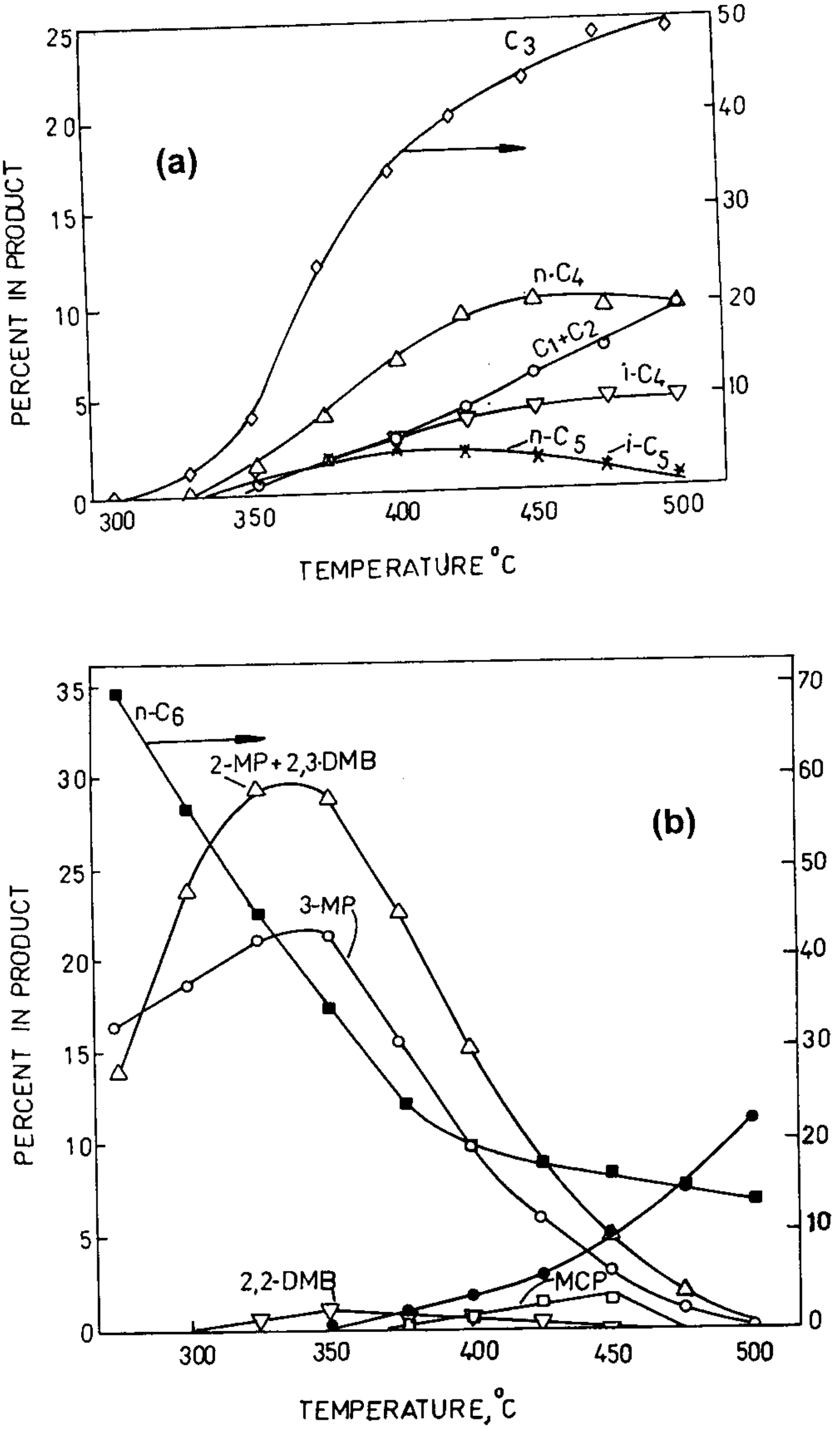

Fig. 37. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.30% Pt/F-DA-H-Z catalyst.

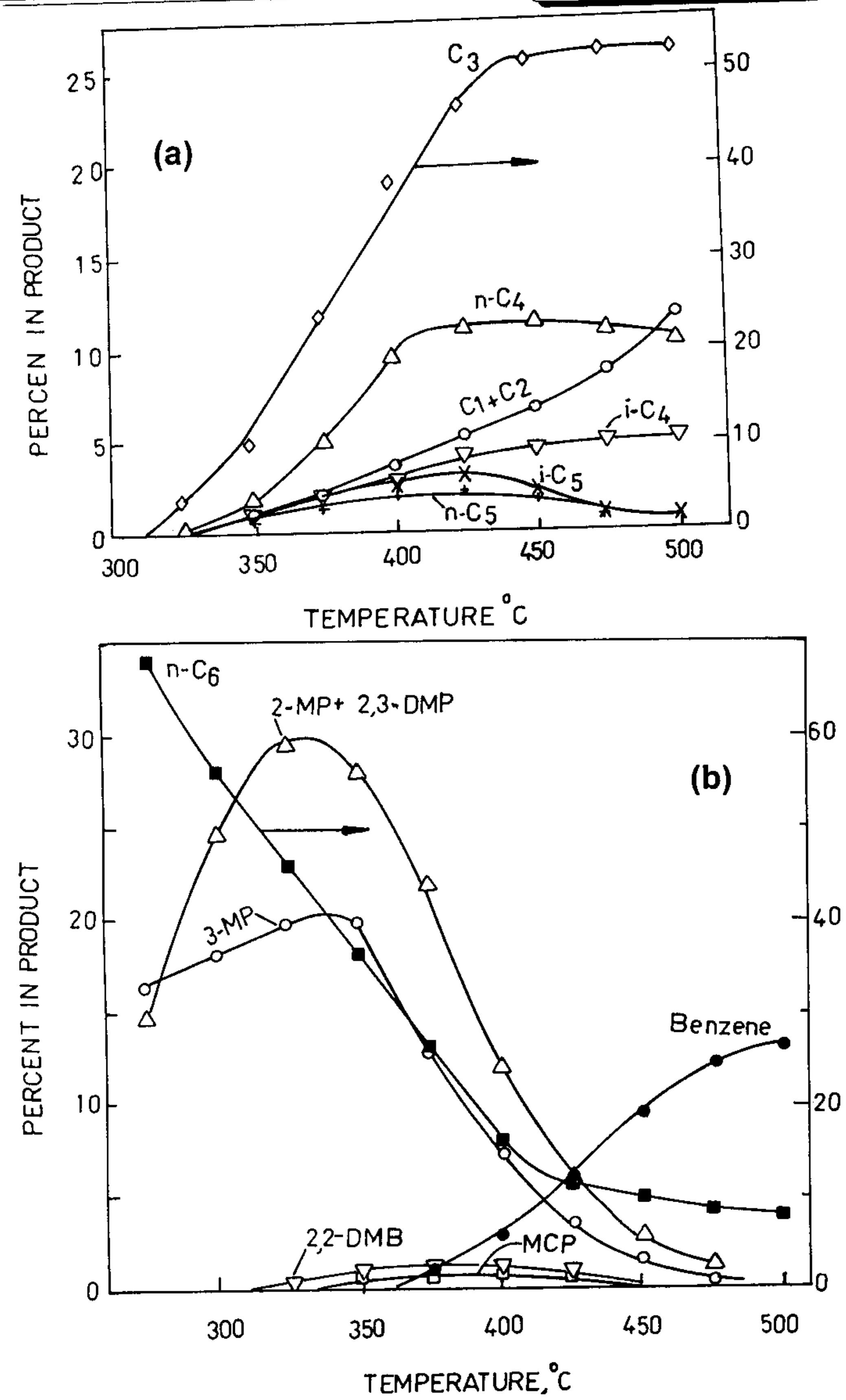

Fig. 38. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.60% Pt/F-DA-H-Z catalyst.

0.15% Pt/H-Z > 0.15% Pt/ DA-H-Z > 0.15% Pt/F-DA-H-Z
> 0.15% Pt/F-H-Z

This arrangement appears to be consistent with the order of hydrophilicity of the catalysts. The most hydrophilic catalyst contain the "as synthesized" H-Z zeolite, having a Si/Al ratio of 22%, which is the lowest Si/Al ratio among the catalysts containing 0.15%Pt. The DA-H-Z and F-H-Z catalysts have Si/Al ratios of 39.1 and 36.2, respectively, whereas the F-DA-H-Z catalyst has a Si/Al ratio of 52.5.

It has been assumed that Fluorination of alumina produces Al fluoride and Al hydroxyfluoride which acquire low surface area **[204-208]**. However, in the H-ZSM-5 zeolite, fluorination, on the contrary, significantly increases the hydroconversion activity (principally hydrocracking), which does not reveal the formation of deactivating fluoride and oxyfluoride phases. This indicates that a strong deactivation takes place when Pt is incorporated in the zeolite presence of F, which may indicate that the low-surface deactivating materials are catalyzed in presence of Pt.

The activities of these catalysts for benzene production can be arranged in the order:

0.15% Pt/H-Z > 0.15% Pt/DA-H-Z > 0.15% Pt/F-H-Z
> 0.15% Pt/F-DA-H-Z;

since benzene production amounts to 5.2-22.8%, 1.6-18.0%, 2.1-18.1% and 1.0-10.3%, respectively. Benzene is the most polar C_6 component in the products of n-hexane hydroconversion and its opportunity to be formed should increase with decreasing the hydrophobicity of the catalyst used, i.e., decreasing the Si/Al ratio.

On the other hand, a correlation of the hydrocracking activities at a temperature of 400°C shows that using the 0.15% Pt/H-Z, 0.15% Pt/DA-H-Z, 0.15% Pt/F-H-Z and 0.15% Pt/F-DA-H-Z catalysts, hydrocracked products amount to: 56.4, 68.5, 19.6 and 25.9%, respectively. This shows that the catalyst containing the zeolite dealuminated with EDTA is the most active for hydrocracking, whereas the F-treated catalysts are less active for this reaction.

Although fluorination of the zeolite (unloaded) has increased the acid sites strength than any other treatment and also this increase has been associated with a significant increase in the catalytic activity (Fig. 35), contra-wise, when Pt is incorporated in the F-H-Z zeolite (Pt/F-H-Z) (Tables 23-25), the catalytic activity for n-hexane hydrocracking has been significantly supressed, principally due to the enhancement of the competing isomerization reaction. At a temperature of 400°C, the hydrocracking selectivity is 25.5%, whereas the isomerization selectivity is as high as 66.0%. For comparison, using the 0.15% Pt/DA-H-Z catalyst, the hydrocracking selectivity is 76.2%, whereas the isomerization selectivity is only 19.4%. However, using the catalysts containing 0.15%Pt supported on the dually-treated zeolite (0.15% Pt/F-DA-H-Z) the selectivity for hydrocracking is 36.0%, whereas that for isomerization is 59.6%. Using the 0.15% Pt/H-Z catalyst at 400 °C, the hydrocracking selectivity amounts to 61.2%, whereas the isomerization selectivity amounts to 25.1%. This comparison of selectivities shows that at a relatively high reaction temperature of 400 °C, fluorine inclusion in the 0.15% Pt/H-Z catalysts, whether treated or untreated with EDTA for dealumination, the hydroisomerization selectivity is greatly enhanced.

The concentration of Pt in the Pt/F-DA-H-Z catalysts is effective for increasing the hydrocracking activity relative to the hydroisomerization activity. Hence, it is found that at a reaction temperature of 400 °C, the hydrocracked product comprises 25.9, 51.7 and 59.4% using the 0.15% Pt, 0.30% Pt and 0.60% Pt/F-DA-H-Z catalysts, respectively, whereas the hexane isomers comprise 42.9, 25.8 and 20.5%, respectively, although the number and strength of acid sites decreases as the Pt content increases from 0.15 up to 0.60%. The hydrocracked product/isomerized product increases indicating the effect of Pt for enhancing hydrocracking and/or hydrgenolysis on the account of hydroisomerization.

Fig. 39 shows that the C_1+C_2 percentage in the hydrocracked fraction decreases with temperature and Pt content in the Pt/F-DA-H-Z catalysts, i.e., effect of Pt on enhancing hydrogenolysis. Fig. 40 shows that at temperatures lower than 325 °C, the dibranched isomer 2,2-DMB is negligible, whereas the monobranched 3-MP is increased with temperature to reach the equilibrium values at 350-375 °C then decreases at higher temperatures.

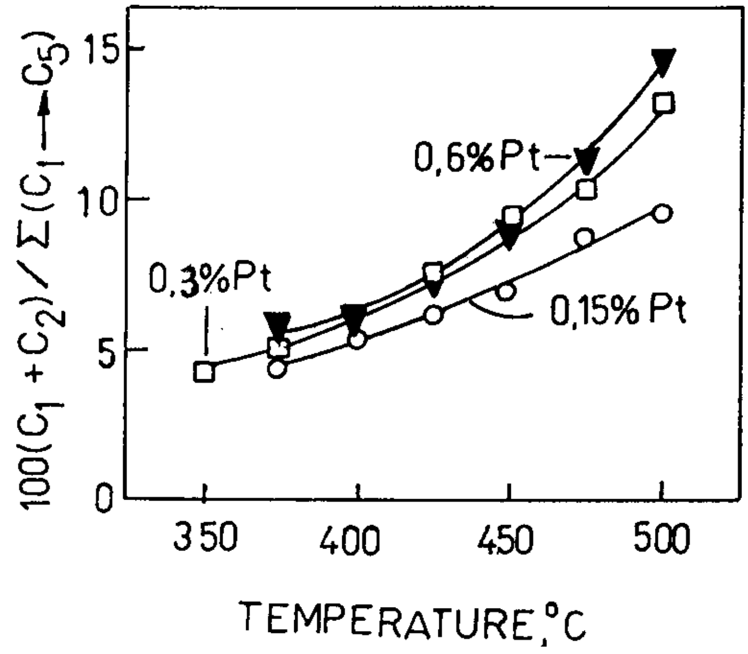

Fig. 39. C_1-C_2 in the hydrocracked product of n-hexane using the Pt/F-DA-H-Z catalysts.

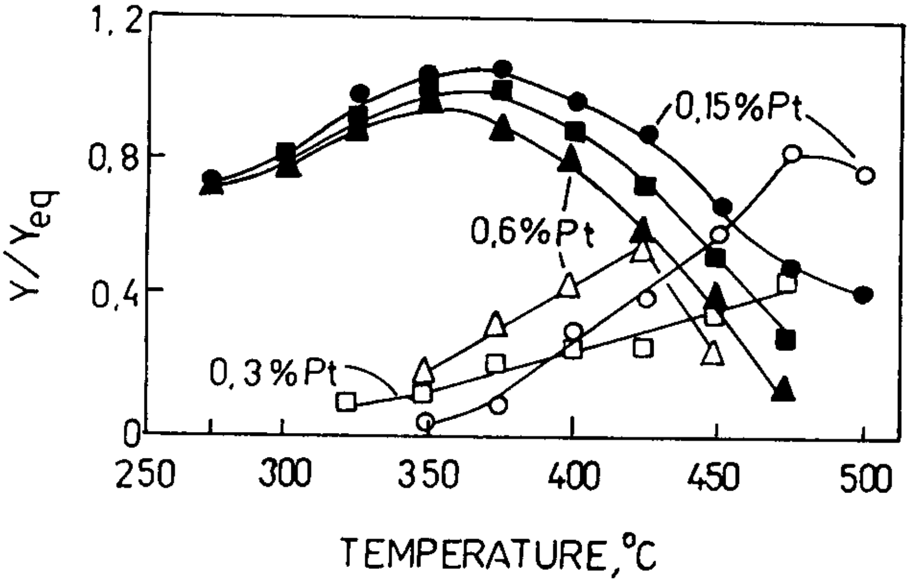

Fig. 40. 3-MP and 2,2-DMB in the hydroconversion product of n-hexane relative to their equilibrium concentrations (Y/Y_{eq}) at different reaction temperatures using the Pt/F-DA-H-Z catalyst

3.5.3. Acid Sites Strength Distribution via Temperature-Programmed Desorption (TPD) of NH_3 from the Unloaded Modified Zeolite Catalysts

From the NH_3-TPD data depicted in Fig. 7 and given in Table 6, it is evident that the unloaded modified zeolite catalysts give NH_3-desorption enthalpy values higher than their respective Pt-containing versions (Fig. 6 and Table 5). The highest acid sites number is exhibited by the unmodified H-Z catalyst (115.5 Jg^{-1}). All modified catalysts are considered dealuminated versions of H-Z, i.e., via EDTA-treatment (DA-H-Z), via fluorination (F-H-Z) (highest activity; Fig. 41), via steaming or hydrothermal dealumination (St H-Z), as well as via double-modification using EDTA-dealumination followed by fluorination (F-DA-H-Z) and steaming followed by fluorination (F-St H-Z) (lowest activity; Fig. 41). Those modified zeolite versions are thus more hydrophobic than the mother H-Z form. The highest loss of acid sites are found in the case of the double-modified catalysts namely F-DA-H-Z and F-St H-Z where loss of 52.1 and 36.7%, respectively, are performed. The lowest loss of acid sites is accomplished via fluorination (15.4%) and steaming (16.7%). In both treatments aluminium removed from the framework remains mostly in the zeolite.

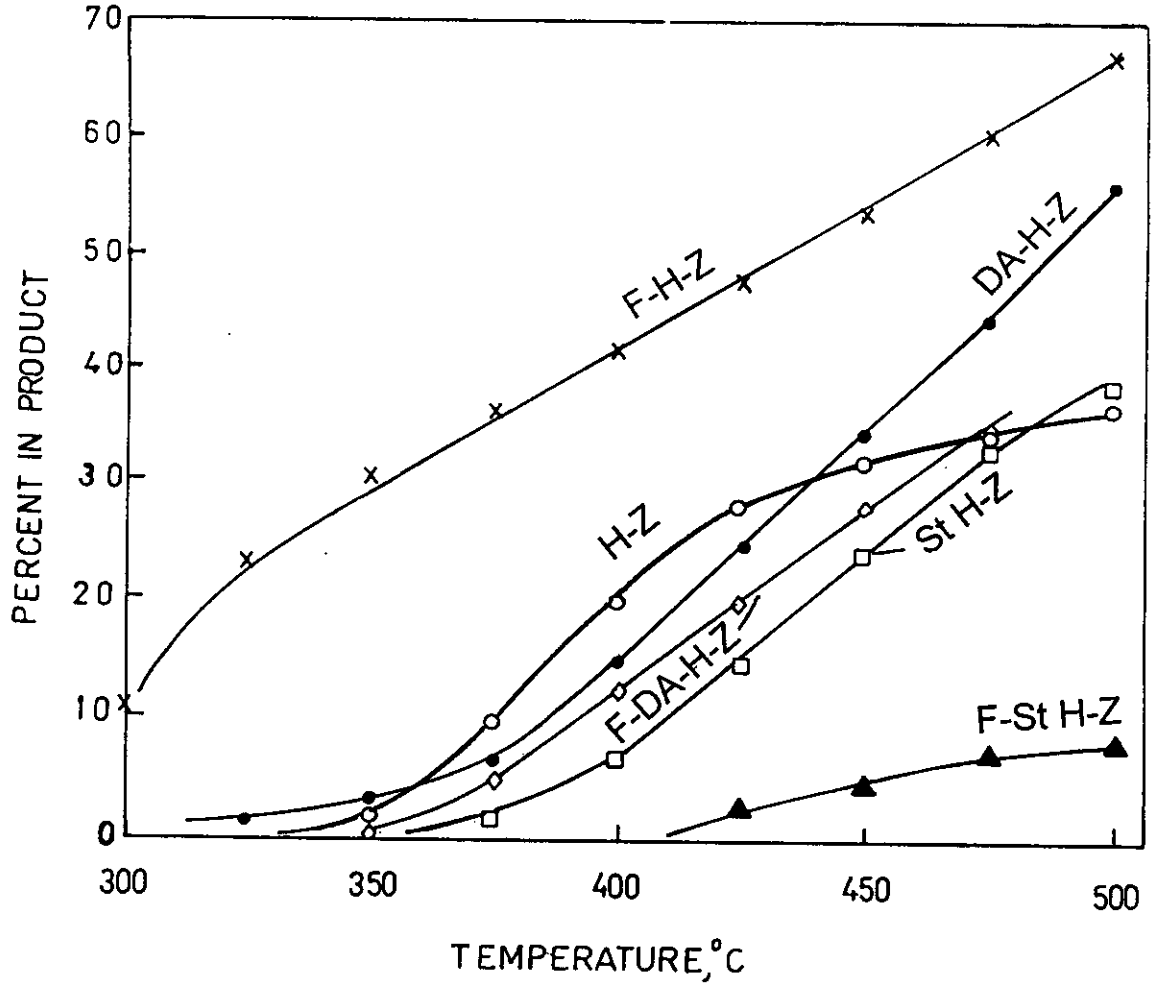

Fig. 41. Hydroconversion products of n-hexane using the unloaded modified H-Z Catalysts.

3.5.4. Acid Sites Strength Distribution via Temperature-Programmed Desorption (TPD) of NH_3 from Pt-Loaded Modified Catalysts

The TPD values obtained for the Pt-containing modified zeolite catalysts show, in general, that an unloaded zeolite version possesses a larger number and more strongly acidic sites than the corresponding Pt-containing versions, and that as Pt content increases, both acid sites number and strength are found to decrease. Nevertheless, data in Table 6 show that the F-H-Z catalyst acquires a large number of strong acid sites than the DA-H-Z zeolite, since NH_3-desorption ΔH from the former is 104.1 Jg^{-1} vs. 98.5 Jg^{-1} from the latter. Moreover, the desorption peak temperature for the former zeolite seems somewhat higher than that for the latter ,i.e., higher acid strength. This difference in acidity can be considered the major factor influencing the hydroisomerisation activities of these catalysts. Although these unloaded zeolites are inactive or very slightly active for isomerization, the values of hexane isomers obtained may be indicative of the intrinsic activities of these zeolites. Using the F-H-Z catalyst, the isomerization selectivity amounts to 9.2% at 325 °C and decreases with increasing temperature to reach 2.3% at 500 °C, whereas the DA-H-Z catalyst is completely inactive for isomerization of n-hexane at all temperatures.

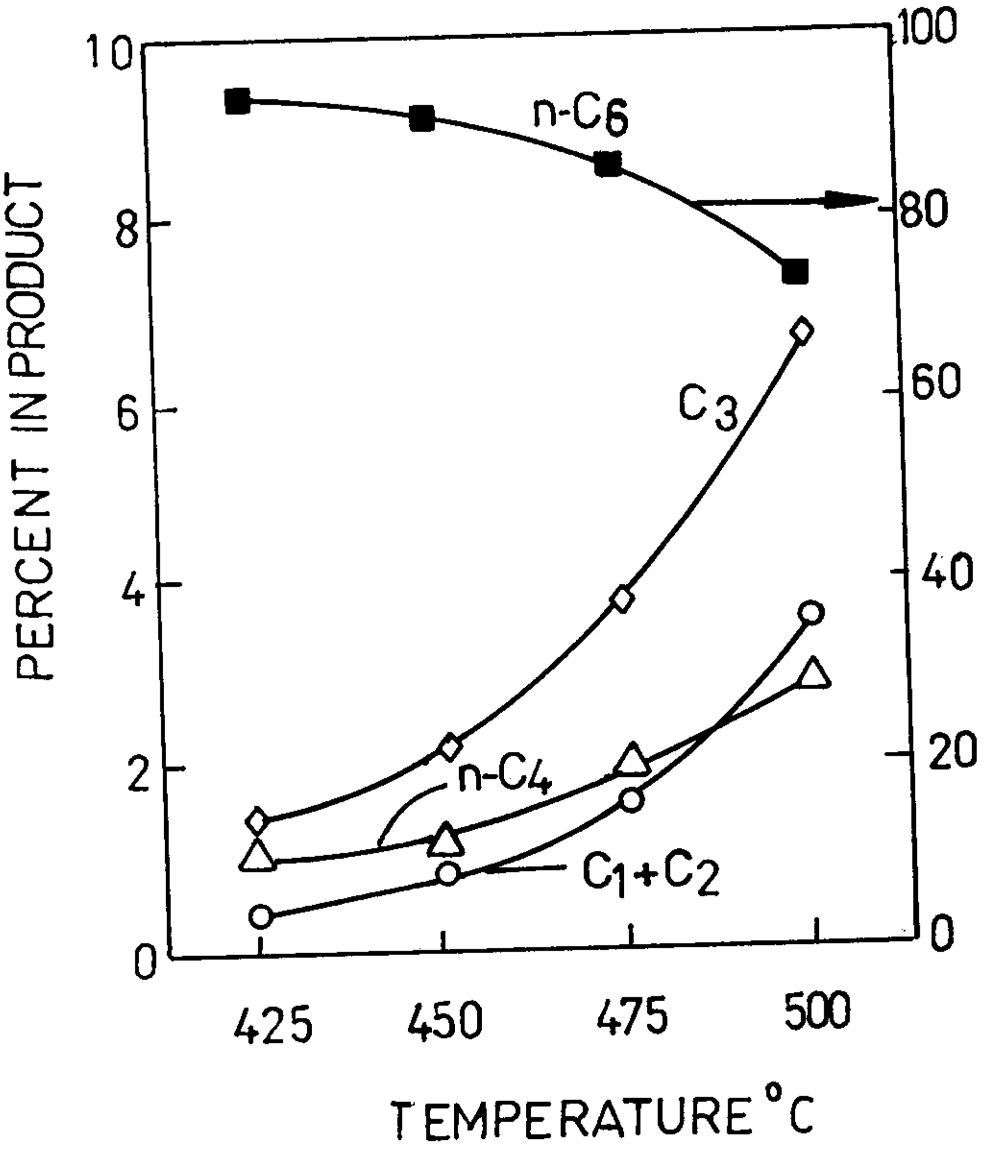

Fig. 42. Hydroconversion products of n-hexane using the F-St H-Z Catalyst.

Table 26 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using F St H-Z Catalyst.

Component in Product, %	Reaction , Temperature, C°			
	425	450	475	500
Methane + Ethane	0.5	0.9	1.6	3.5
Propane	1.5	2.3	3.8	6.7
Isobutane	0.0	0.0	0.0	0.0
n-Butane	0.9	1.2	1.9	2.8
Isopentane	0.0	0.0	0.0	0.0
n-Pentane	0.0	0.0	0.0	0.0
2,2-Dimethylbutane	0.0	0.0	0.0	0.0
2-Methylpentane + 2,3-Dimethylbutane	0.0	0.0	0.0	0.0
3-Methylpentane	0.0	0.0	0.0	0.0
n-Hexane	97.1	95.6	92.7	87.0
Methylcyclopentane	0.0	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0
Hydrocracking %	2.9	4.4	7.3	13.0
Hydroisomerization %	0.0	0.0	0.0	0.0
Hydrocyclization %	0.0	0.0	0.0	0.0
Total Conversion	2.9	4.4	7.3	13.0
Hydrocracking Selectivity	100	100	100	100
Hydroisomerization selectivity	0.0	0.0	0.0	0.0
Dehydrocyclization Selectivity	0.0	0.0	0.0	0.0
Isobutane / n-Butane	0.0	0.0	0.0	0.0
Isopentane / n-Pentane	0.0	0.0	0.0	0.0

HF-doping differs widely from HF-leaching of Al from the zeolite framework. In the doping technique the principal reaction is fluorination whereby a fluorine ion replaces a surface hydroxyl group, thus reducing the number of surface protons. However, this does not mean that framework Al is not removed. Actually, a small fraction of framework Al is removed as shown from the data in Table 21.

Nevertheless, the steaming technique (hydrothermal treatment) is specifically a dealumination method, but a Si/Al ratio of 28.0 is obtained for the St H-Z zeolite version. This figure seems low relative to a value of 27.7 for F-H-Z. In fact, the efficiency of steam-treatment for dealumination may be comparable to that of EDTA-dealumination technique via which the Si/Al ratio is 31.3 (Table 21). This considerable difference between the Si/Al values for St H-Z and DA-H-Z zeolites indicates that a significant fraction of the Al removed from the zeolitic framework is deposited in non-framework positions in the channels and cages of the zeolite.

3.6. n-Hexane Hydroconversion Using F-St H-Z Containing Catalysts

3.6.1. Using the F-St H-Z

Table 26 and Fig. 42 give the hydroconversion product distribution using the F-St H-Z catalyst. This catalyst exhibits the lowest activity among all catalysts investigated. This catalyst is inactive neither for hydroisomerization nor for cyclization reactions, whereas it is of only

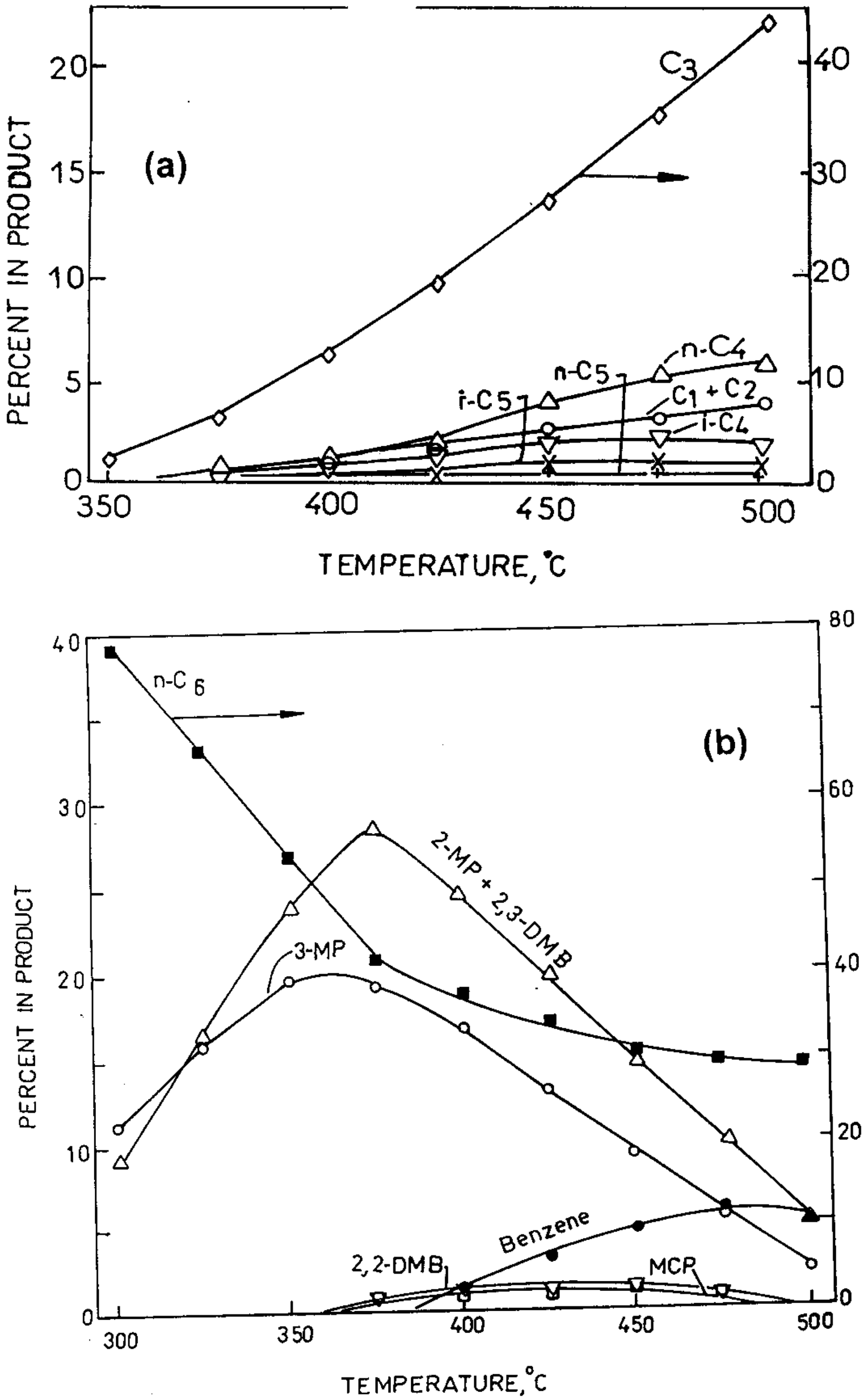

Fig. 43. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.15% Pt/F-St H-Z catalyst

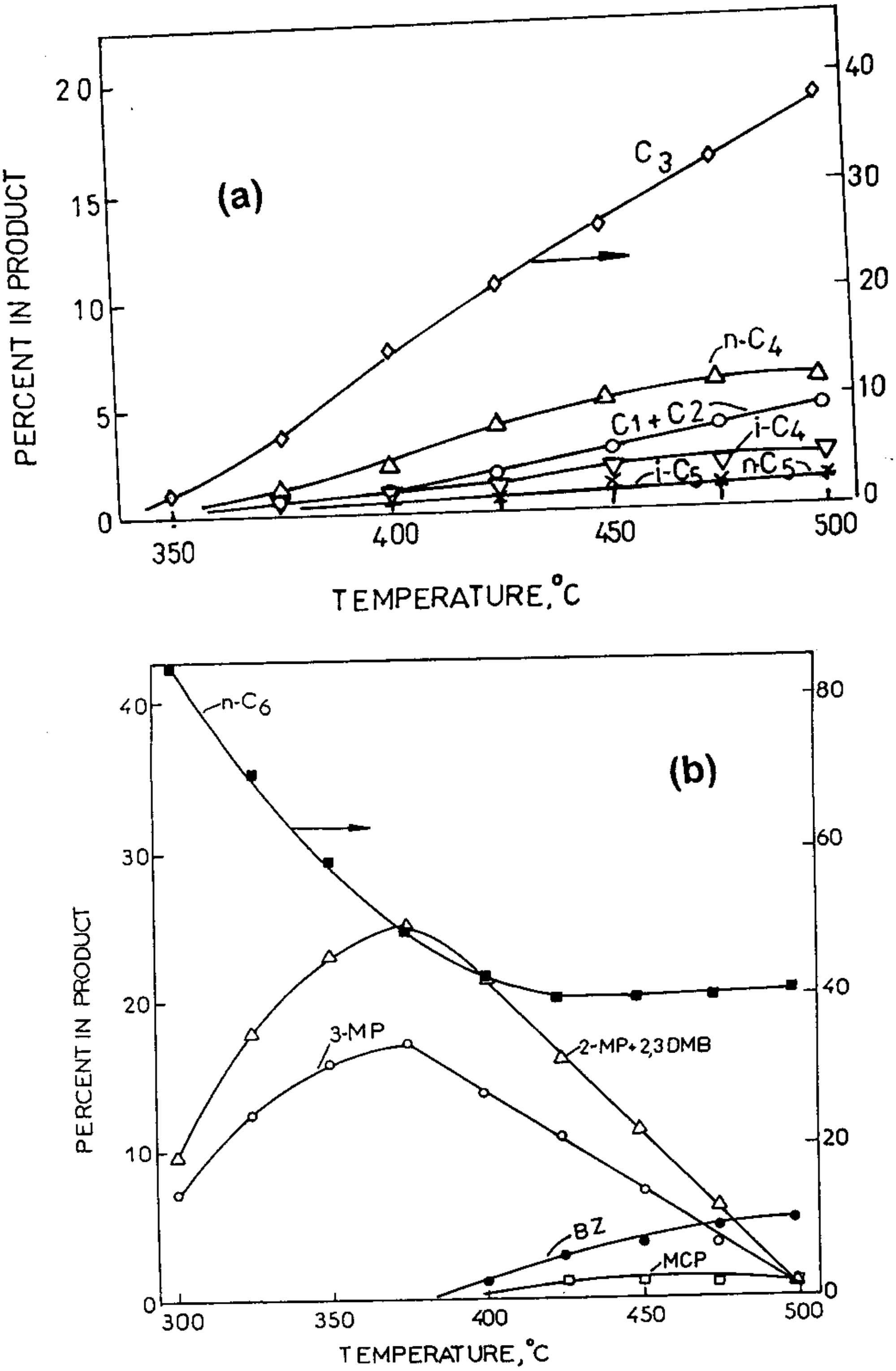

Fig. 44. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.30% Pt/F-St H-Z catalyst.

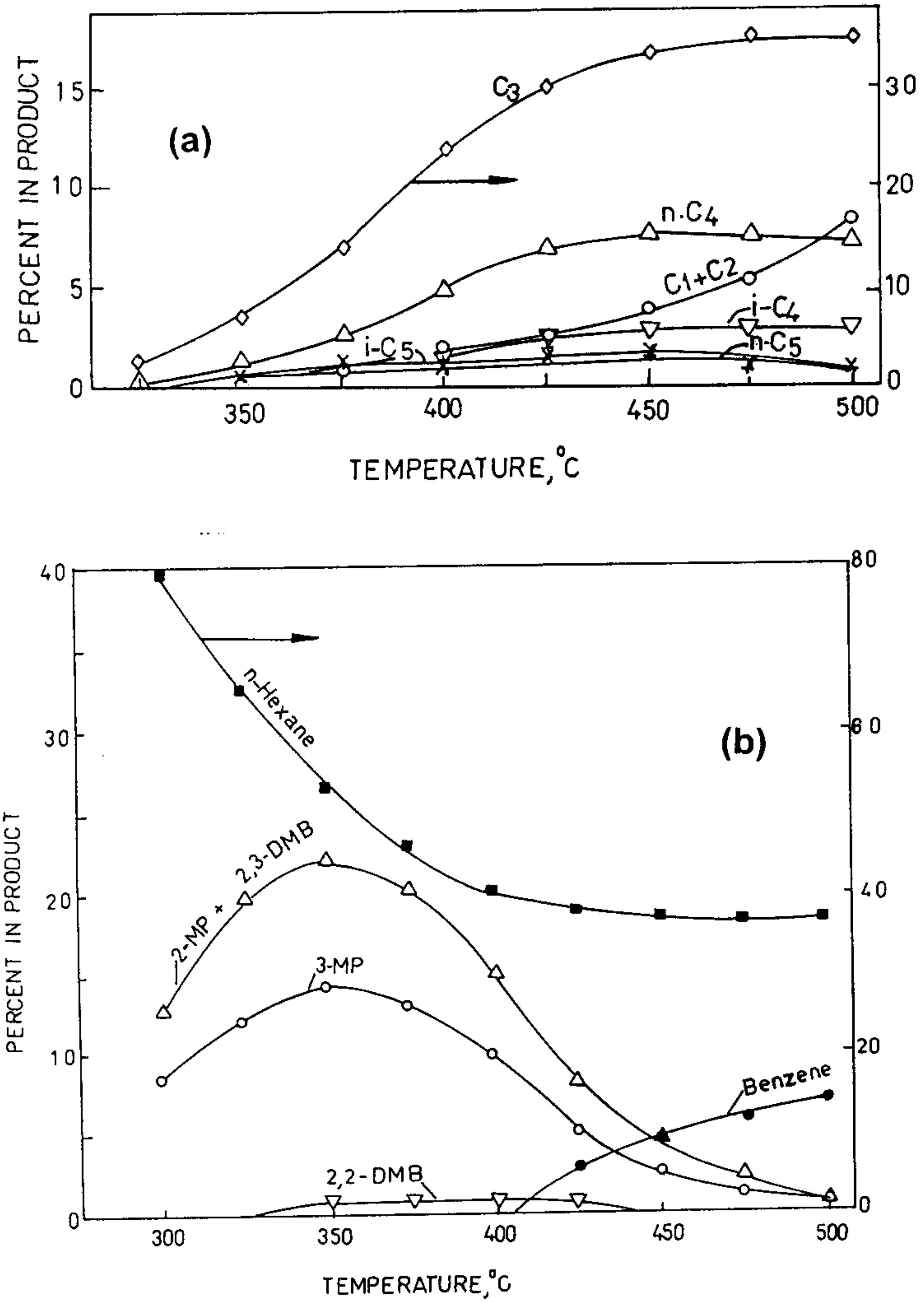

Fig. 45. Hydrocracked components (a); and C_6 components (b) in the hydroconversion product of n-hexane using the 0.60% Pt/F-St H-Z catalyst.

Table 27 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.15% Pt/ F-St H-Z Catalyst

Component In Product, %	Reaction , Temperature, C°								
	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.2	0.4	0.9	1.9	2.5	3.2	4.1
Propane	0.0	0.0	1.0	6.5	12.5	19.5	27.5	34.9	44.0
Isobutane	0.0	0.0	0.3	0.4	1.1	1.8	2.0	2.5	2.1
n-Butane	0.0	0.0	0.3	0.6	1.3	2.2	4.2	5.2	6.0
Isopentane	0.0	0.0	0.0	0.0	0.2	0.6	1.0	0.9	0.8
n-Pentane	0.0	0.0	0.0	0.0	0.1	0.3	0.6	0.6	0.6
2,2-Dimethylbutane	0.0	0.0	0.0	0.7	1.2	1.4	1.4	0.8	0.3
2-Methylpentane + 2,3-Dimethylbutane	9.4	16.7	24.2	28.6	24.8	19.8	14.4	9.8	5.3
3-Methylpentane	11.3	16.2	19.9	19.5	16.9	13.5	9.3	6.2	2.5
n-Hexane	79.3	67.1	54.1	42.5	38.4	34.5	30.8	29.6	29.0
Methylcyclopentane	0.0	0.0	0.0	0.8	1.0	1.0	1.4	0.7	0.0
Benzene	0.0	0.0	0.0	0.0	1.6	3.5	4.9	5.6	5.3
Hydrocracking %	0.0	0.0	1.8	7.9	16.1	26.3	37.8	47.3	57.6
Hydroisomerization %	20.7	32.9	44.1	48.8	42.9	34.7	25.1	16.8	8.1
Hydrocyclization %	0.0	0.0	0.0	0.8	2.6	4.5	6.3	6.3	5.3
Total Conversion	20.7	32.9	45.9	57.5	61.6	65.5	69.2	70.4	71.0
Hydrocracking Selectivity	0.0	0.0	3.9	13.7	26.1	40.2	54.6	67.2	81.1
Hydroisomerization selectivity	100	100	96.1	84.9	69.7	52.9	36.3	23.9	11.4
Dehydrocyclization Selectivity	0.0	0.0	0.0	1.4	4.2	6.9	9.1	8.9	7.5
Isobutane / n-Butane	0.0	0.0	1.0	1.5	0.85	0.82	0.48	0.48	0.35
Isopentane / n-Pentane	0.0	0.0	0.0	0.0	2.0	2.0	1.67	1.5	1.33

Table 28 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.30% Pt/F-St H-Z Catalyst

Component in Product, %	Reaction, Temperature, C°								
	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.0	0.0	0.4	1.0	1.5	2.6	3.5	4.5
Propane	0.0	0.0	2.3	6.6	14.7	20.3	26.0	32.1	37.5
Isobutane	0.0	0.0	0.5	0.5	0.9	1.4	1.7	1.9	2.1
n-Butane	0.0	0.0	0.6	1.1	2.3	4.1	5.0	5.7	5.8
Isopentane	0.0	0.0	0.0	0.0	0.5	1.2	1.1	1.0	0.9
n-Pentane	0.0	0.0	0.0	0.0	0.4	1.0	0.8	0.9	0.8
2,2-Dimethylbutane	0.0	0.0	0.0	0.5	0.9	1.2	0.7	0.0	0.0
2-Methylpentane + 2,3- Dimethylbutane	9.5	17.5	22.7	25.2	21.3	15.5	10.8	5.6	1.0
3-Methylpentane	7.1	12.4	15.6	16.9	13.6	10.4	7.0	3.5	0.5
n-Hexane	83.4	70.1	58.3	48.8	43.4	40.0	39.9	40.4	41.0
Methylcyclopentane	0.0	0.0	0.0	0.0	0.0	1.0	0.9	0.9	0.8
Benzene	0.0	0.0	0.0	0.0	1.0	2.4	3.5	4.5	5.1
Hydrocracking %	0.0	0.0	3.4	8.6	19.8	29.5	37.2	45.1	51.6
Hydroisomerization %	16.6	29.9	38.3	42.6	35.8	27.1	18.5	9.1	1.5
Hydrocyclization %	0.0	0.0	0.0	0.0	1.0	3.4	4.4	5.4	5.9
Total Conversion	16.6	29.9	41.7	51.2	56.6	60.0	60.1	59.6	59.0
Hydrocracking Selectivity	0.0	0.0	8.1	16.8	35.0	49.1	61.9	75.7	87.5
Hydroisomerization selectivity	100	100	91.9	83.2	63.2	45.2	30.8	15.3	2.5
Dehydrocyclization Selectivity	0.0	0.0	0.0	0.0	1.8	5.7	7.3	9.0	10.0
Isobutane / n-Butane	0.0	0.0	0.83	0.45	0.39	0.34	0.34	0.33	0.36
Isopentane / n-Pentane	0.0	0.0	0.0	0.0	1.25	1.2	1.38	1.11	1.12

Table 29 : Distribution of Reaction Products Through Hydroconversion of n-Hexane at Different Temperatures Using 0.60% Pt/ F-St H-Z Catalyst

Component in Product, %	Reaction , Temperature, C°								
	300	325	350	375	400	425	450	475	500
Methane + Ethane	0.0	0.2	0.5	1.0	2.0	2.8	4.0	5.8	8.4
Propane	0.0	2.2	6.5	13.3	24.0	30.0	33.4	35.0	35.0
Isobutane	0.0	0.0	0.7	0.9	1.5	2.6	3.1	2.8	2.8
n-Butane	0.0	0.6	1.3	2.6	4.8	6.7	7.4	7.5	7.1
Isopentane	0.0	0.0	0.3	0.8	1.1	1.6	1.6	1.0	0.7
n-Pentane	0.0	0.0	0.4	0.7	0.8	1.4	1.4	0.7	0.6
2,2-Dimethylbutane	0.0	0.0	0.9	0.9	0.8	0.9	0.0	0.0	0.0
2-Methylpentane + 2,3-Dimethylbutane	12.6	19.9	22.0	20.4	14.9	8.1	4.4	2.5	1.1
3-Methylpentane	8.4	12.3	14.5	13.3	9.9	5.0	2.8	1.5	0.5
n-Hexane	79.0	64.8	52.9	46.1	40.2	38.2	37.5	37.0	36.8
Methylcyclopentane	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Benzene	0.0	0.0	0.0	0.0	0.0	2.7	4.4	6.2	7.0
Hydrocracking %	0.0	3.0	9.7	19.3	34.2	45.1	50.9	52.8	54.6
Hydroisomerization %	21.0	32.2	37.4	34.6	25.6	14.0	7.2	4.0	1.6
Hydrocyclization %	0.0	0.0	0.0	0.0	0.0	2.7	4.4	6.2	7.0
Total Conversion	21.0	35.2	47.1	53.9	59.8	61.8	62.5	63.0	63.2
Hydrocracking Selectivity	0.0	8.5	20.6	35.8	57.2	73.0	81.4	83.8	86.4
Hydroisomerization selectivity	100	91.5	79.4	64.2	42.8	22.7	11.5	6.4	2.5
Dehydrocyclization Selectivity	0.0	0.0	0.0	0.0	0.0	4.3	7.1	9.8	11.1
Isobutane / n-Butane	0.0	0.0	0.54	0.35	0.31	0.39	0.42	0.37	0.39
Isopentane / n-Pentane	0.0	0.0	0.75	1.14	1.38	1.14	1.14	1.43	1.17

modest activity towards hydrocracking, which ranges between 2.9% at 425 °C and a maximum of 13.0% at 500 °C.

Table 26 shows that even the hydrocracked iso-components, namely; isobutane and isopentane are absent in the product, and only C_1+C_2, propane and n-butane are the reaction products. The major cracked product is propane.

3.6.2. Pt-Loaded Fluorinated-Steamed H-ZSM-5 Catalysts (Pt/F-St H-Z Catalysts)

A great enhancement of the activity of the unloaded F-St H-Z zeolite is observed via promotion with Pt. The total hydroconversion using the 0.15% Pt, 0.30% Pt and 0.60% Pt/F-St H-Z catalysts amounts to 20.7-71.0%, 16.6-59.0% and 21.0-63.2%, respectively, at reaction temperatures of 300-500 °C, respectively (Figs. 43-45 and Tables 27-29). The hydroisomerization maxima amount to 48.8% at 375 °C over the 0.15% Pt catalyst, 42.6% at also 375 °C over the 0.30% Pt catalyst, and 37.4% at 350°C using the 0.60% Pt catalyst. Maximum benzene production on these catalysts amounts to 5.3, 5.9 and 7.0%, respectively, at 500 °C. The catalysts support (F St-H-Z) is one of the most hydrophobic zeolites in this study; hence, benzene which is a highly polar hydrocarbon is not favoured as a product of n-hexane hydroconversion.

Propane is the major hydrocracked product, it comprises 44.0, 37.5 and 35.0% using the 0.15, 0.30 and 0.60% Pt/F-St H-Z catalysts, respectively, at 500 °C. The other hydrocracked components are relatively

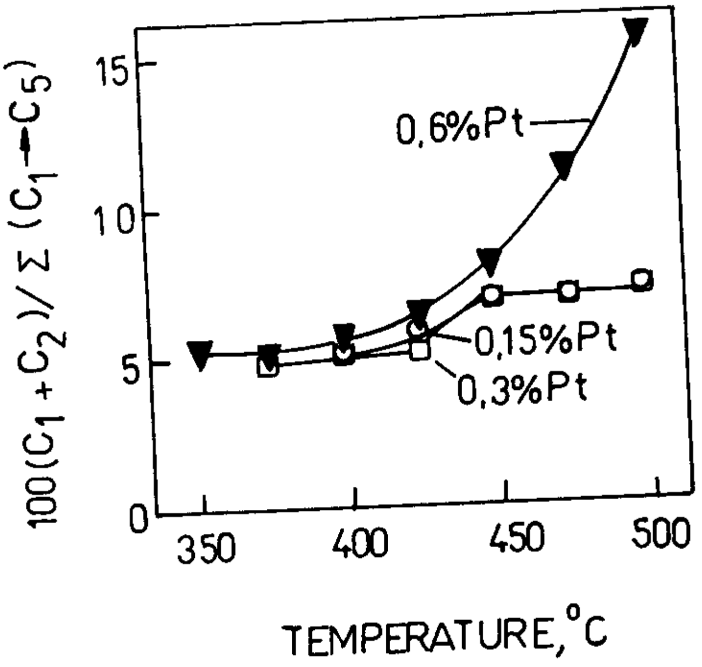

Fig. 46. C_1-C_2 in the hydrocracked product of n-hexane using the Pt/F-St H-Z catalysts.

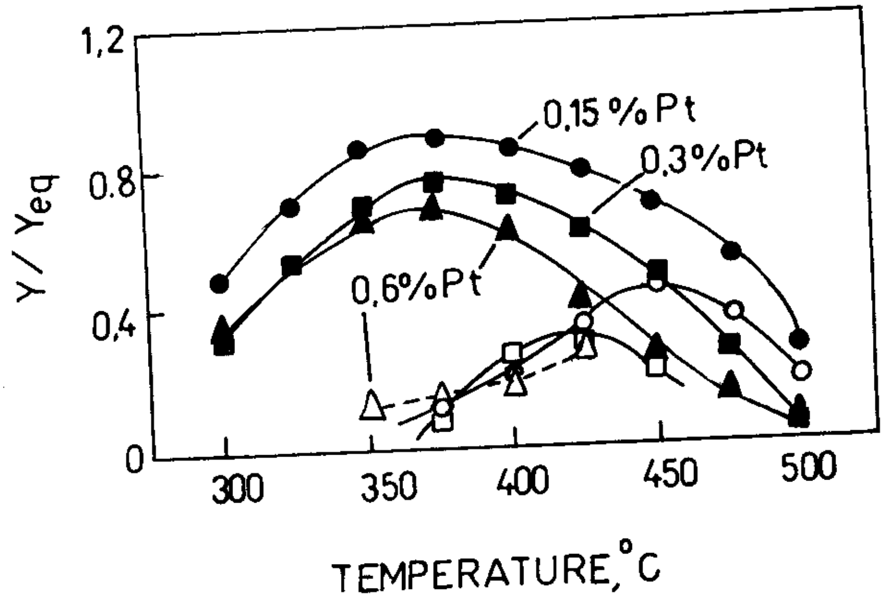

Fig. 47. 3-MP and 2,2-DMB in the hydroconversion product of n-hexane relative to their equilibrium concentrations (Y/Y_{eq}) at different reaction temperatures using the Pt/F-St H-Z catalyst

lower (Tables 27-29; and Figs. 43-45). The 0.15 and 0.30% Pt/F-St H-Z catalysts can be considered as selective catalysts for centric hydrocracking.

The C_1+C_2 in the hydrocracked product are low on the 0.15 and 0.30% Pt/F-St H-Z catalysts, but significantly higher on the 0.60% Pt-containing catalyst at higher temperatures (Fig. 46). At the high Pt-content (0.60%), hydrogenolysis is favoured.

A correlation of the 3-MP and 2,2-DMB components in the isomers mixture relative to their equilibrium concentrations at different reaction temperatures using the Pt/F-St H-Z catalysts are shown in Fig. 47. It is evident that the dimethyalated isomer is of low significance whereas 3-MP is much higher; it increases with temperature up to 325°C then slows down with a further increase of temperature. Nevertheless, the Y/Y_{eq} values do not reach unity at any conditions.

Using this series of Pt-loaded catalysts, the isobutane/n-butane ratio amount to 1.5-0.35, 0.83-0.36, and 0.54-0.39 using the 0.15%, 0.30% and 0.60% Pt/ F-St H-Z catalysts, respectively, whereas the iso-pentane/ n-pentane ratio amount to 2.0-1.33, 1.25-1.12, and 0.75-0.17, respectively, at temperatures up to 500°C. However, higher values are obtained in the middle of this range of temperature.

Table 30: Apparent Reaction Rate Constant, kK (mol atm^{-1} g^{-1} s^{-1}), For n-Hexane Hydroconversion at Different Temperatures Using the Unloaded Zeolite Catalysts.

Catalyst	Temperature, °C								
	300	325	350	375	400	425	450	475	500
Pt/H-Z	0.0	0.0	7.85×10^{-4}	4.344×10^{-3}	0.0101	0.0155	0.0181	0.0195	0.0206
St H-Z	0.0	0.0	2.2055×10^{-4}	7.9922×10^{-4}	3.0043×10^{-3}	6.687×10^{-3}	0.0119	0.0174	0.0214
F- H-Z	6.077×10^{-3}	0.0133	0.0177	0.02196	0.0261	0.0313	0.0368	0.0439	0.0521
F-St H-Z	0.0	0.0	0.0	0.0	0.0	1.2949×10^{-3}	1.9799×10^{-3}	3.3353×10^{-3}	6.1275×10^{-3}
DA-H-Z	0.0	6.650×10^{-4}	1.3402×10^{-3}	3.0514×10^{-3}	7.2026×10^{-3}	0.0127	0.0185	0.0254	0.12199
F-DA-H-Z	0.0	0.0	4.8668×10^{-4}	2.3496×10^{-3}	5.8754×10^{-3}	9.6536×10^{-3}	0.0144	0.0187	0.0202

Table 31: Apparent Reaction Rate Constant, kK(mol atm^{-1} g^{-1} s^{-1}), For n-Hexane Hydroconversion at Different Temperatures Using Pt/H-Z Catalysts.

Catalyst	Temperature, °C										
	250	275	300	325	350	375	400	425	450	475	500
Pt/H-ZSM-5											
0.15% Pt/H-Z	0.0251	0.0402	0.0504	0.0578	0.0680	0.082	0.1123	0.1529	0.1984	∞	∞
0.30% Pt/H-Z	0.0	0.0	0.0421	0.0589	0.0793	0.1013	0.1641	0.1911	∞	∞	∞
0.60% Pt/H-Z	0.0	0.0	0.0434	0.05196	0.06505	0.0837	0.1224	0.1744	0.1820	∞	∞

Table 32: Apparent Reaction Rate Constant, kK(mol atm^{-1} g^{-1} s^{-1}), For n-Hexane Hydroconversion at Different Temperatures Using Pt/DA-H-Z Catalysts

Catalyst	Temperature, °C									
	275	300	325	350	375	400	425	450	475	500
0.15%Pt/ DA-H-Z	0.0423	0.0481	0.0568	0.0647	0.0798	0.1009	0.1210	0.1318	0.1475	0.1573
0.30% Pt/ DA-H-Z	0.0403	0.0527	0.0610	0.0710	0.0835	0.1027	0.1134	0.1276	0.1364	0.1623
0.60% Pt/ DA-H-Z	0.0305	0.0485	0.0621	0.0780	0.0952	0.1238	0.1679	0.1744	0.1848	0.1946

Table 33: Apparent Reaction Rate Constant, kK(mol atm^{-1} g^{-1} s^{-1}), For n-Hexane Hydroconversio at Different Temperatures Using Pt/F-H-Z Catalysts

Catalyst	Temperature, °C								
	300	325	350	375	400	425	450	475	500
0.15%Pt/ F-H-Z	0.0207	0.0348	0.0430	0.0540	0.0643	0.0820	0.1004	0.1203	0.1451
0.30% Pt/F-H-Z	0.0334	0.0451	0.0520	0.0598	0.0672	0.0826	0.0992	0.1245	0.1606
0.60% Pt/F-H-Z	0.0200	0.0289	0.0404	0.0608	0.0881	0.1183	0.1345	0.1558	0.1463

Table 34: Apparent Reaction Rate Constant, kK(mol atm^{-1} g^{-1} s^{-1}), For n-Hexane Hydroconversion at Different Temperatures Using Pt/St H-Z Catalysts

Catalyst	Temperature, °C										
	250	275	300	325	350	375	400	425	450	475	500
0.15% Pt/St H-Z	$4.8319x10^{-3}$	0.0107	0.0197	0.0302	0.0399	0.0496	0.0598	0.0702	0.0750	0.0767	0.0767
0.30% Pt/ St H-Z	$2.7694x10^{-3}$	$9.1632x10^{-3}$	0.01815	0.0294	0.0440	0.0624	0.0755	0.0881	0.1004	0.1060	0.1036
0.60% Pt/ St H-Z	$7.9342x10^{-3}$	0.0161	0.0244	0.0335	0.0489	0.0621	0.0775	0.0865	0.1040	0.1176	0.1245

Table 35: Apparent Reaction Rate Constant, kK(mol atm^{-1} g^{-1} s^{-1}), For n-Hexane Hydroconversion at Different Temperatures Using Pt/F-DA-H-Z Catalysts

Catalyst	Temperature, °C									
	275	300	325	350	375	400	425	450	475	500
0.15%Pt/ F-DA-H-Z	0.0	0.0184	0.0285	0.03734	0.0463	0.0560	0.0637	0.0670	0.0704	0.0715
0.30% Pt/ F-DA-H-Z	0.0160	0.0245	0.0348	0.0450	0.0617	0.0708	0.0767	0.0787	0.0835	0.0847
0.60% Pt/ F-DA-H-Z	0.0166	0.0254	0.0341	0.0441	0.0594	0.0785	0.0905	0.1013	0.1064	0.1128

Table 36: Apparent Reaction Rate Constant, kK(mol atm^{-1} g^{-1} s^{-1}), For n-Hexane Hydroconversion at Different Temperatures Using Pt/F-St H-Z Catalysts

Catalyst	Temperature, °C								
	300	325	350	375	400	425	450	475	500
0.15%Pt/ F-St H-Z	0.0102	0.0172	0.0270	0.0376	0.0421	0.0468	0.0518	0.0536	0.0545
0.30% Pt/F-St H-Z	7.987×10^{-3}	0.0156	0.0237	0.0316	0.0367	0.0403	0.0404	0.0399	0.0392
0.60% Pt/F-St H-Z	0.0104	0.0191	0.0280	0.0341	0.0401	0.0423	0.0432	0.0437	0.0440

Kinetics of n-Hexane Hydroconversion; Rate Constants and Arrhenius Plots

The data obtained for the hydroconversion of n-hexane using the unloaded catalysts under study are given in Fig.41. The F-H-Z catalyst is evidently the most active, indicating that F has a powerful promoting effect on the H-ZSM-5 zeolite for n-paraffins hydroconversion. The H-Z catalyst occupies a second position of reactivity up to a reaction temperature of 425 °C, beyond which the rate of hydroconversion slows down with the increase of temperature.

The apparent reaction rate constant for first order pulsed reactions, kK, is calculated according to ***Bassett and Habgood*** **[209]** applying the equation: $\mathbf{kK = F^o/273\ RW\ (Ln\ 1/1\text{-}x)}$

where; k is the intrinsic first order reaction rate constant, K is the adsorption equilibrium constant, F^o is the carrier gas flow rate (cm^3s^{-1}), R is the ideal gas constant, W is the weight of the catalyst, and x is the weight percent converted divided by 100. The kK values obtained are given In Tables 30-36.

To calculate the apparent activation energy, Ea, the Arrhenius equation and plots of ln kK vs. I/T are used

$$\mathbf{kK = A\ exp\ (-Ea/RT)}$$

$$\mathbf{ln\ kK = ln\ A - Ea/RT}$$

Table 37: Apparent Activation Energy, J mol^{-1}, for n-Hexane Hydroconversion using the unloaded Catalysts.

Catalyst	LT	HT
H-Z	93,745	10,005
DA-H-Z	108,810	
F-H-Z	31,250	
St H-Z	161,540	
F-DA-H-Z	171,585	77,840
F-St H-Z	96,255	

Table 38: Apparent Activation Energy ,J mol^{-1}, for n-Hexane Hydroconversion Using the Pt-Loaded Modified Zeolite Catalysts

Catalyst	LT	Whole range	HT
0.15% Pt/H-Z	17,575		43,524
0.30% Pt/H-Z		39,340	
0.60% Pt/H-Z	23,435		49,383
0.15% Pt/DA-H-Z		22,880	
0.30% Pt/DA-H-Z		19,810	
0.60% Pt/DA-H-Z		32,645	
0.15% Pt/F-H-Z		30,130	
0.30% Pt/F-H-Z		25,110	
0.60% Pt/F-H-Z		48,545	
St 0.15% Pt/ H-Z	56.915		31.805
St 0.30% Pt/ H-Z	61.940		46.035
St 0.60% Pt/ H-Z		41.850	
0.15% Pt/F-DA-H-Z		28.460	
0.30% Pt/F-DA-H-Z		35.155	
0.60% Pt/F-DA-H-Z		35.155	
0.15% Pt/F-St-H-Z	51,055		16,740
0.30% Pt/F-St-H-Z	66,125		26,785
0.60% Pt/F-St-H-Z		32,645	

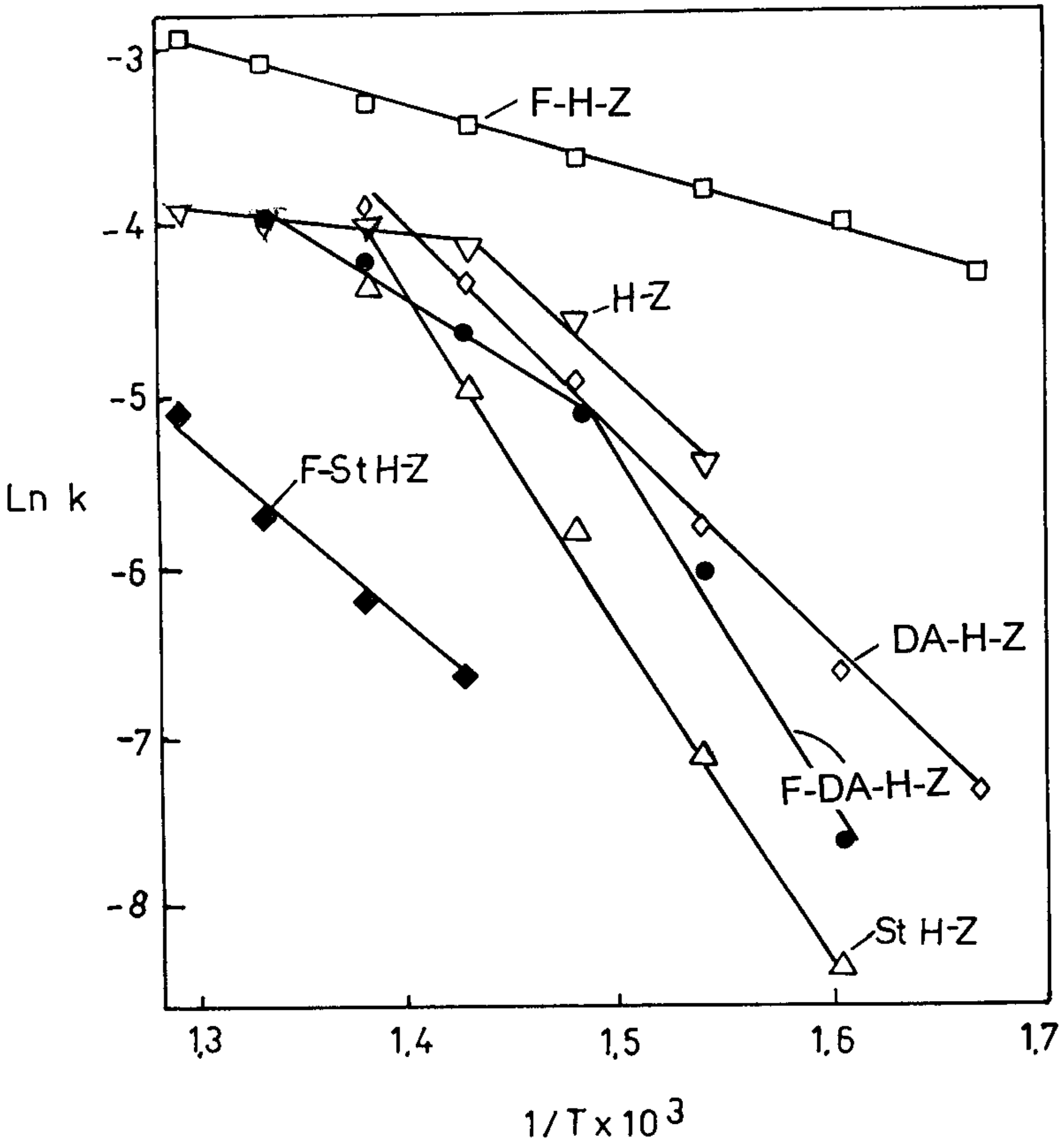

Fig. 48. Arrhenius plots for n-hexane hydroconversion using the unloaded modified H-Z catalysts.

where A; is the pre-exponential factor, Ea; is the apparent activation energy, R is the ideal gas constant and T is the absolute reaction temperature. Hence, the slope of an Arrhenius plot is equal to Ea/R.

The unloaded zeolite catalysts, can be arranged in their activity order as follows:

F-H-Z > H-Z > DA-H-Z > F-DA-Z > St H-Z > F-St-H-Z

Figs. 48-54 gives the Arrhenius plots and Tables 37 and 38 give the values of Ea for the hydroconversion of n-hexane using the unloaded and Pt-loaded catalysts.

The Arrhenius plots for the hydroconversion of n-hexane (Fig. 48) using the H-Z and F-DA-H-Z catalysts give two slopes with lower values at the higher temperature range (HT) and higher values at the lower temperature range (LT). The H-Z catalyst plot shows that the diffusion controlling-higher-temperature-region appears to be of very low activation energy (10,000 $Jmol^{-1}$). However, the LT region Ea value using this catalyst amounts to 93,745 $Jmol^{-1}$. This appears obvious from Fig. 41 where the reaction rate can hardly change beyond 425°C. Diffusion limitation is very significant in the channels of the H-Z catalyst, obviously due to their small diameter. The F-DA-H-Z catalyst possesses the largest Si/Al ratio (36.5) which means that the mother H-Z zeolite (Si/Al= 24.0) has suffered from the largest dealumination among the unloaded zeolites, under study, whereby the Si/Al ratio increases by 52.1%.

Nevertheless, the reaction using the F-DA-H-Z catalyst gives a measurable activation energy during the high temperature region (77.840 $Jmol^{-1}$)which indicates that diffusion limitation in the channels of this catalyst is much less significant than in the case of the H-Z catalyst. In case of the reaction using the F-DA-H-Z catalyst, diffusion limitation may result through the production of different forms of non-framework Al species **[127, 204-208]** inside the channels and cages of the zeolite. Since this catalyst has encountered two dealuminating treatments: **a)** EDTA-dealumination, and **b)** HF doping, both treatments remove Al from the framework but some of this aluminium species remains in non-framework positions inside the channels, thus, causing diffusion limitation of reactants and/or products along these channels. Some Al-F species are formed and left in the catalytic pores, in contradistinction to the procedure of HF-leaching which is carried out in excess solution, where these Al-species are washed outside of the channels **[96]**.

It is to be pointed out that although both treatments using EDTA and HF cause widening of the channels, yet, an over-compensating effect caused by deposition of Al-species debris appears to take place. During the LT range, the reaction activation energy using the F-DA-H-Z catalyst amounts to 171,585 $Jmol^{-1}$, whereas during the HT region a value of 77,840 $Jmol^{-1}$ is obtained.

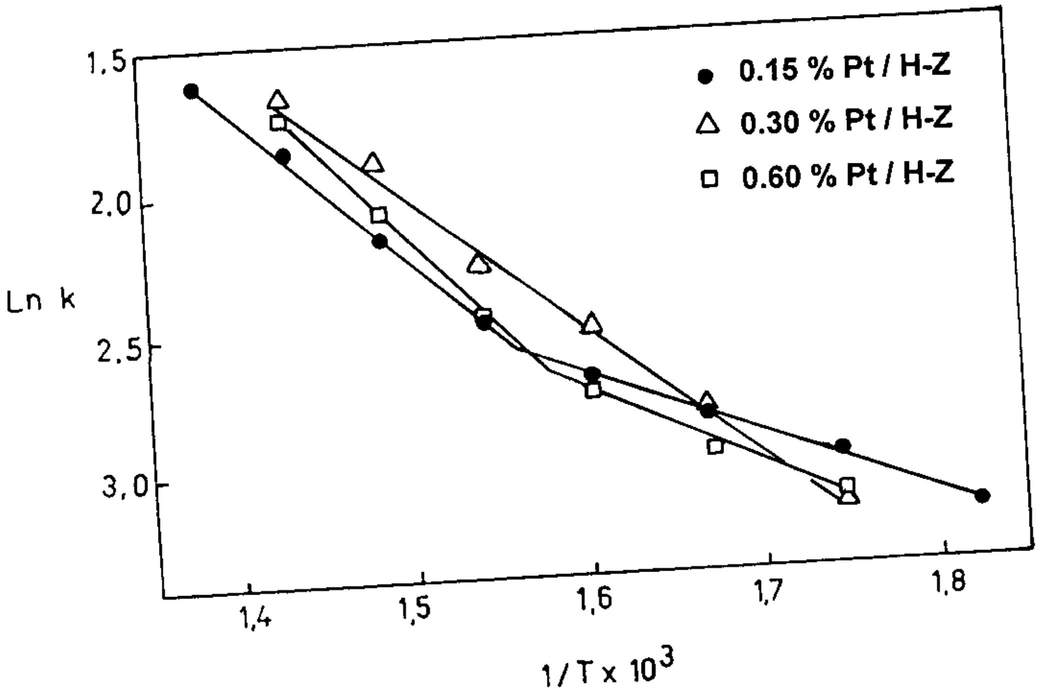

Fig. 49. Arrhenius plots for n-hexane hydroconversion using the Pt/H-Z catalysts.

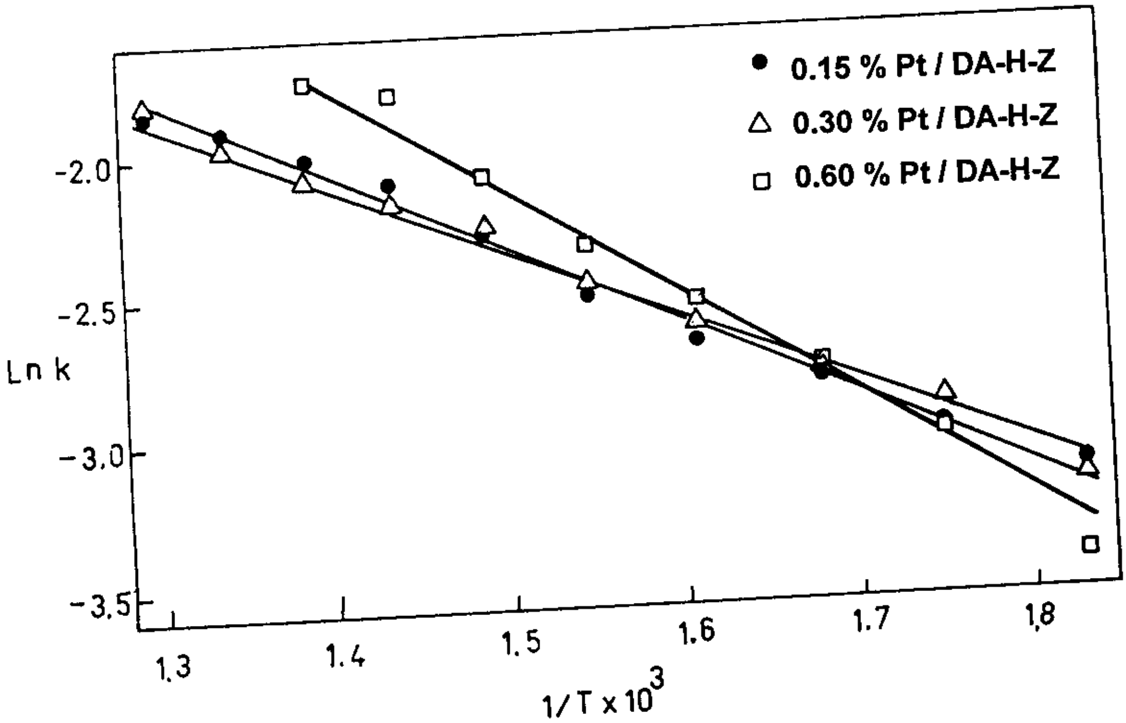

Fig. 50. Arrhenius plots for n-hexane hydroconversion using the Pt/DA-H-Z catalysts.

3.7.1. Pt/H-ZSM-5 Catalysts

Incorporation of Pt in the H-Z zeolite results in a large activation of the catalytic activities of these catalysts, whereby different behaviours of the Arrhenius plots are observed (Fig. 49). The kK values for n-hexane hydroconversion over these catalysts are given in Table 31. The 0.15% Pt and 0.60% Pt/ H-Z catalysts are more activated at the higher temperature range than during the lower temperature range, thus , exhibiting a behaviour that excludes the occurrence of diffusion limitation in the catalytic pores (Fig. 49). However, the catalyst containing 0.30% Pt shows a normal linear Arrhenius relationship. A reason for excluding pore diffusion limitation in the Pt/H-Z series of catalysts may be the decrease of acid sites number and strength as a result of Pt incorporation. Hence, Diffusion along the pores becomes easier than in the case of the unloaded H-Z zeolite catalyst.

3.7.2. Pt/DA-H-ZSM-5 Catalysts

The kK values obtained for n-hexane hydroconversion using the catalysts of this series are given in Table 32. All Arrhenius relationships obtained for the hydroconversion of n-hexane over the catalysts which are members of this group (Pt/DA-H-Z) show simple straight lines (no inflections observed) (Fig. 50). The highest Ea value (32,645 $Jmol^{-1}$) is obtained using the catalyst containing 0.60% Pt, which may be attributed to: a) higher hydrocracking activity producing smaller molecules which diffuse easily, as well as, b) a lower acid sites strength and number,

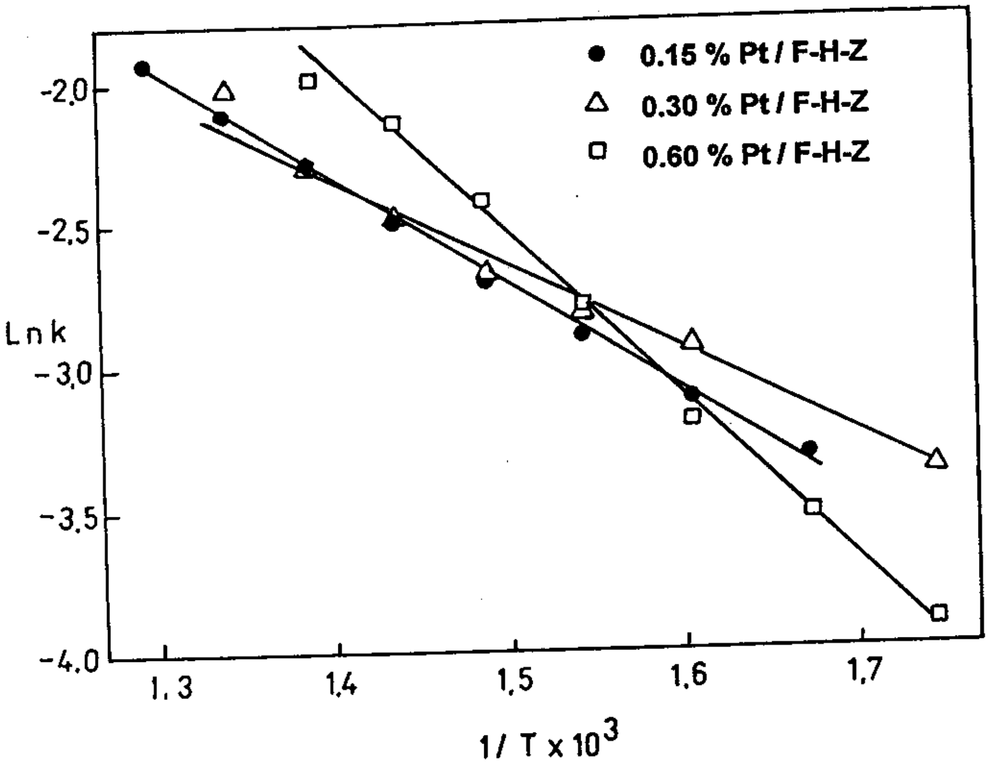

Fig. 51. Arrhenius plots for n-hexane hydroconversion using the Pt/F-H-Z catalysts.

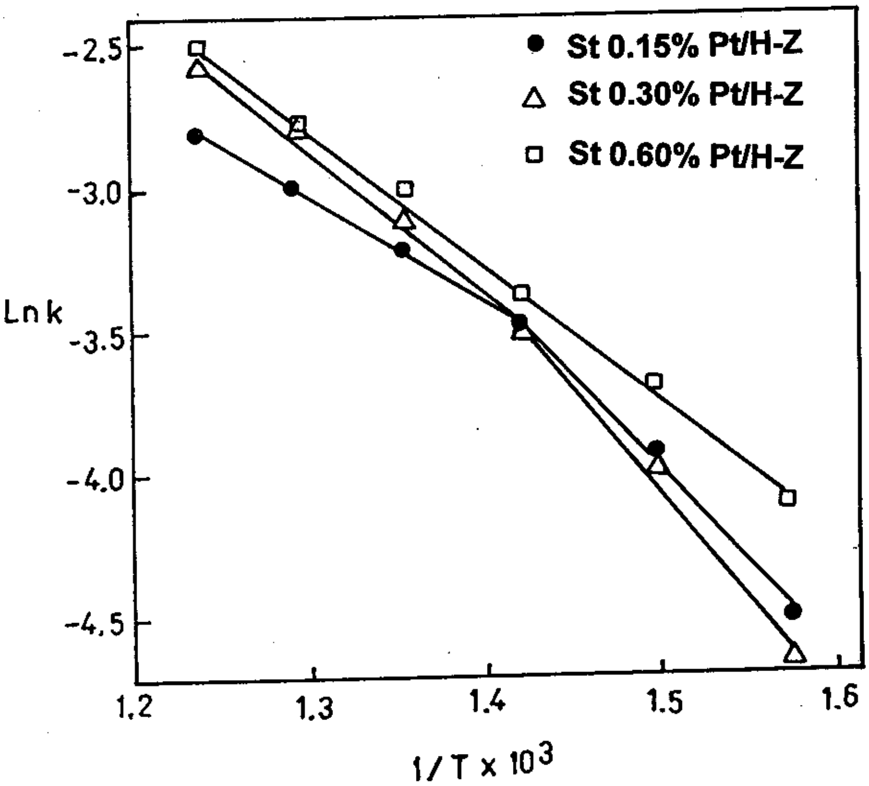

Fig. 52. Arrhenius plots for n-hexane hydroconversion using the **St Pt/H-Z** catalysts.

compared to the catalysts containing lower metal contents. Hence, the desorptivity and diffusion restriction of the reacting species drops via increasing the Pt content. The 0.15%Pt- and 0.30% Pt-containing catalysts show lower Ea values which are not markedly different, i.e., 22,880 and 19,810 J mol^{-1}, respectively.

3.7.3. Pt/F-H-ZSM-5 Catalysts

The kK values obtained for the reaction using the Pt/F-H-Z catalysts are given in Table 33. Correlation of the Arrhenius plots obtained using the catalysts of the Pt/DA-H-Z series (Fig. 50) and those of this series (Pt/F-H-Z) (Fig. 51) shows that the 0.60% Pt-containg catalysts in both series give the highest Ea values (32,645 and 48,545 Jmol^{-1}, respectively.), Although the difference in the Ea values obtained using the 0.15% Pt- and the 0.30% Pt-containing catalysts is still of a limited extent (30,130 and 25,110 J mol^{-1}, respectively), yet, the difference is significantly larger in case of the Pt/F-H-Z series than in the case of the Pt/DA-H-Z series. Hence, the activation energy for the reaction, under study, using the catalysts of the Pt/F-H-Z and Pt/DA-H-Z series can be arranged, based on Pt-contents, in the following order:

0.60% Pt > 0.15% Pt > 0.30 Pt

The low values of Ea obtained for the catalysts containing 0.30% Pt in both series, can be assumed to be the result of a compromise between the acid sites number and strength (adsorption effect) and the Pt-crystallites nature, i.e., bifunctionality.

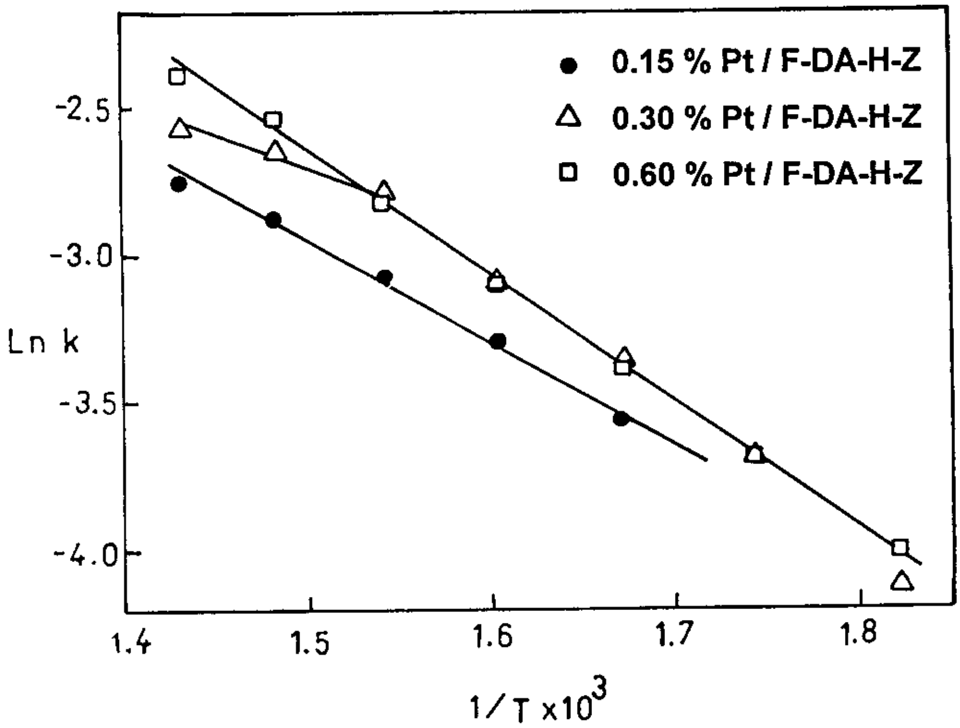

Fig. 53. Arrhenius plots for n-hexane hydroconversion using the Pt/F-DA-H-Z catalysts.

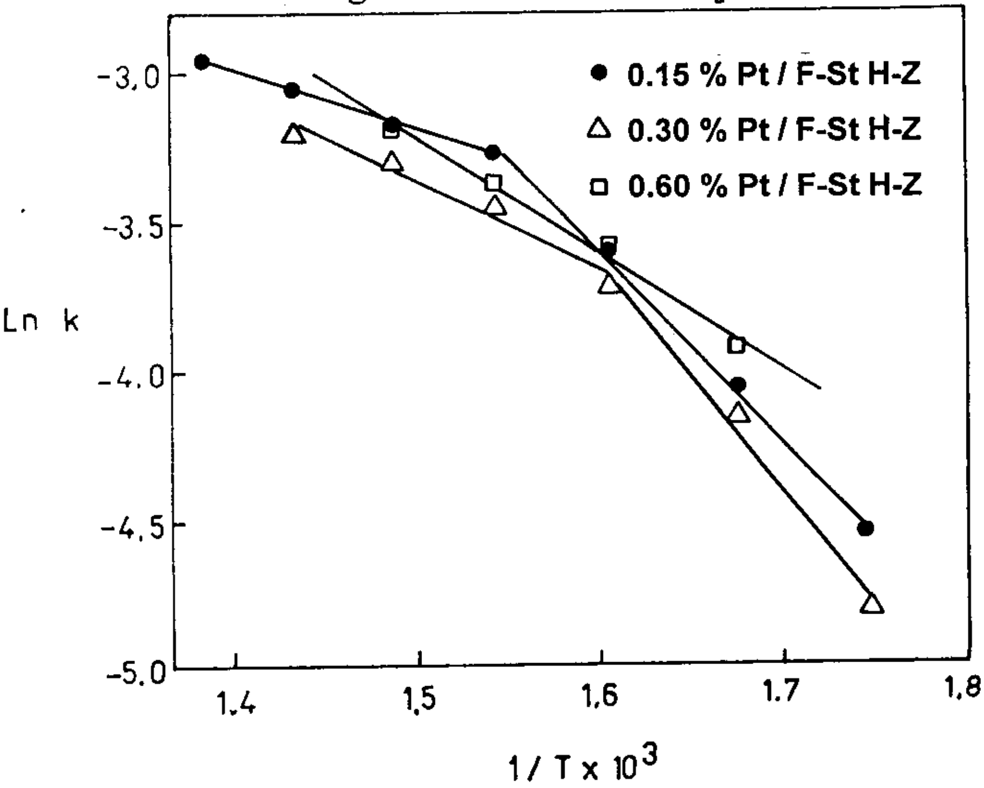

Fig. 54. Arrhenius plots for n-hexane hydroconversion using the Pt/F-St H-Z catalysts.

Both Pt/DA-H-Z and Pt/F-H-Z catalysts have been prepared via dealumination procedures. The insignificant difference in the behaviours of the Arrhenius plots (Figs. 50 and 51) may substantiate the occurrence of insignificant changes in the physical natures of these series of catalysts.

St Pt/ H-Z catalyst

The kK values obtained for the reaction using the St Pt/H-Z catalysts are given in Table 34. A single-slope straight line is obtained only for the hydroconversion reaction using the St 0.60% Pt/ H-Z catalyst and higher ln kK values also appear in the Arrhenius plot than using the St 0.15% and 0.30% Pt/H-Z catalysts (Fig.52). Using the two latter catalysts, inflected lines are obtained, whereby two activation energies can be obtained for each catalyst. The 0.30% Pt-containing catalyst shows an evidently larger slope (higher Ea value = 61,940 $Jmole^{-1}$) at the lower temperature region and a lower slope (Ea value = 46,035 $Jmole^{-1}$) at the higher temperature region as compared to the reaction on the 0.15% Pt-containing catalyst. The rate constants obtained using the 0.15% and 0.30% Pt-containing catalysts of these series are considerably lower than those obtained using the 0.60% Pt-containing catalyst during the lower temperature region.

Pt/F-DA-H-Z Catalysts

The apparent reaction rate constants for n-hexane hydroconversion using the Pt/F-DA-H-Z Catalysts are given in Table 35. This series contains catalysts which have been doubly-treated via dealumination with EDTA, followed by treatment with HF. The 0.30% and 0.60% Pt-containing catalysts have equal Ea values (~ 35,155 Jmol^{-1}) due to equal ln kK values throughout a temperature range of 300-450°C, beyond which the 0.6% Pt-containing catalyst continues with its linearity during the higher temperature region (Fig. 53). However, the 0.15% Pt/F-DA-H-Z catalyst shows somewhat lower Ea value (28,460 Jmol^{-1}) . The relative effectiveness of these dually-dealuminated zeolites containing 0.30% and 0.60% Pt, may be attributed to their larger Pt contents. Nevertheless, it can be assumed that a significant part of Pt in the catalyst containing 0.60% Pt has been masked by the Al-species removed from the zeolite framework and deposited in the non-framework positions in this zeolite. The widening of the pores due to the double-treatment may play a role for retaining non-inflected straight lines.

3.7.6. Pt/F-St H-ZSM-5 Catalysts

The kK values obtained for the reaction using the Pt/F-St H-Z catalysts are given in Table 36. A similar behaviour is observed on correlating the Arrhenius plots (Figs. 52 and 54) for hydroconverting n-hexane using the Pt/St H-Z and Pt/F-St H-Z catalysts, respectively. The 0.60% Pt-containing catalysts in both series give single straight-line Arrhenius relationships, whereas the 0.15% and 0.30% Pt-containing catalysts in the two series show inflected relationships with lower Ea values at the higher temperature region. The highest deposition of the Al-species during the different dealumination procedure takes place in the steaming step, since a significant fraction or even all the Al species removed are kept inside the channels and cages **[208]**. Fluorination also results in a significant non-framework Al species in the channels and cages, hence, the Pt/F-St H-Z catalysts are considered to encounter the most significant diffusion limitation encountered during treatments. This may explain why hydroconversion using the unloaded F-St H-Z catalyst is largely inhibited (Fig.41), whereby maximum hydroconversion comprises only 13.0% at 500°C. The presence of non-framework Al debris together with the enhanced widening of the pores via the double dealumination procedure, appear to reflect their deteriorative effect on the hydroconversion reaction using the unloaded zeolite catalyst. A somewhat increase of activity is observed via Pt incorporation which may indicate that a large part of the Pt content is deposited on the external surface of the zeolite.

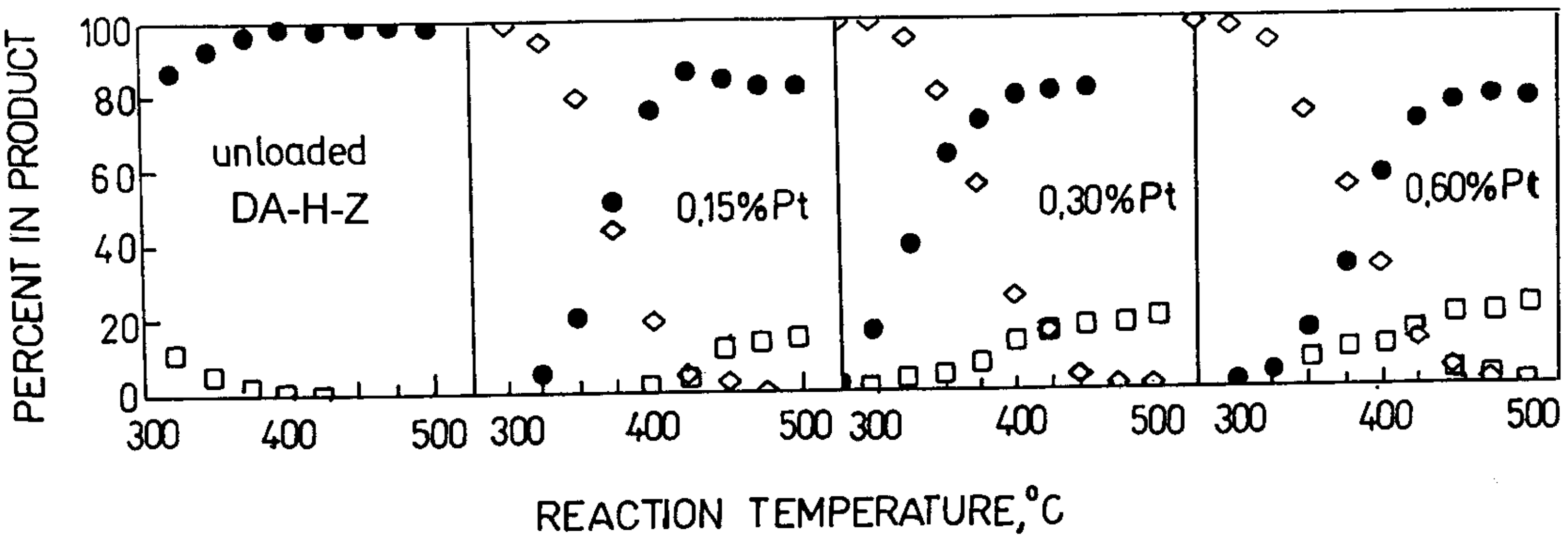

Fig. 56. Selectivities of n-Hexane hydroconversion reactions: ◇ hydroisomerization, ● hydrocracking, □ dehydrocyclization using unloaded and Pt-loaded DA-H-Z catalysts.

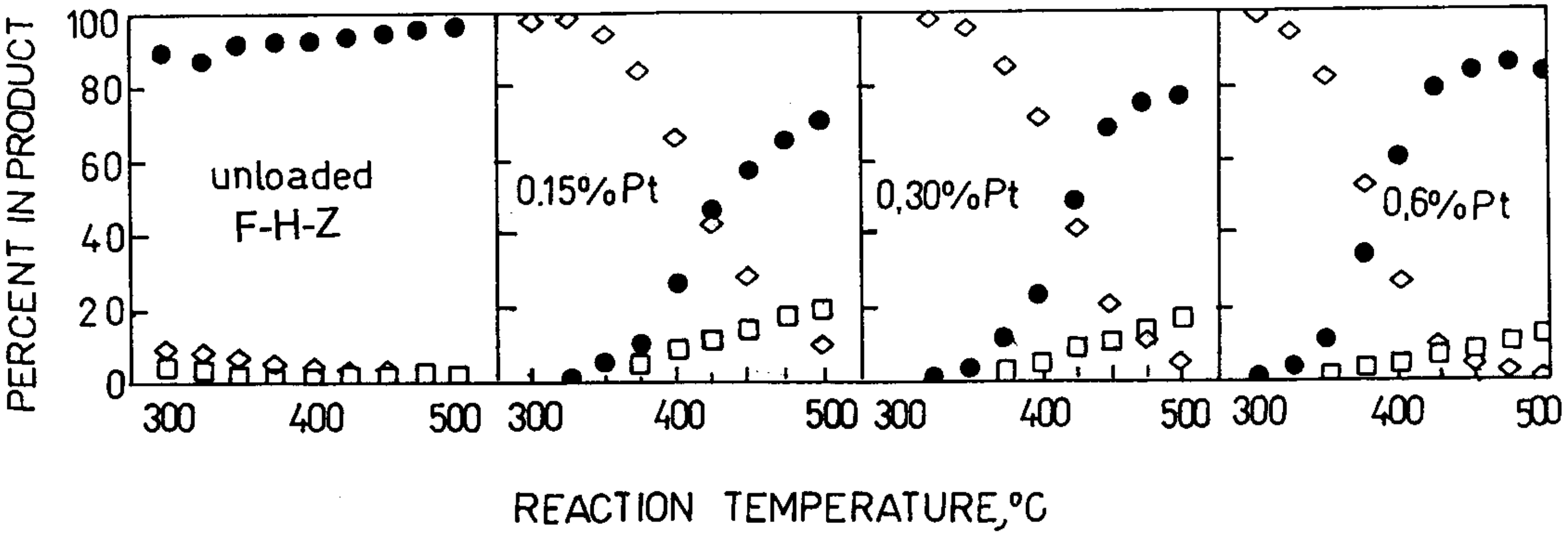

Fig. 57. Selectivities of n-Hexane hydroconversion reactions: ◇ hydroisomerization, ● hydrocracking, □ dehydrocyclization using unloaded and Pt-loaded F-H-Z catalysts.

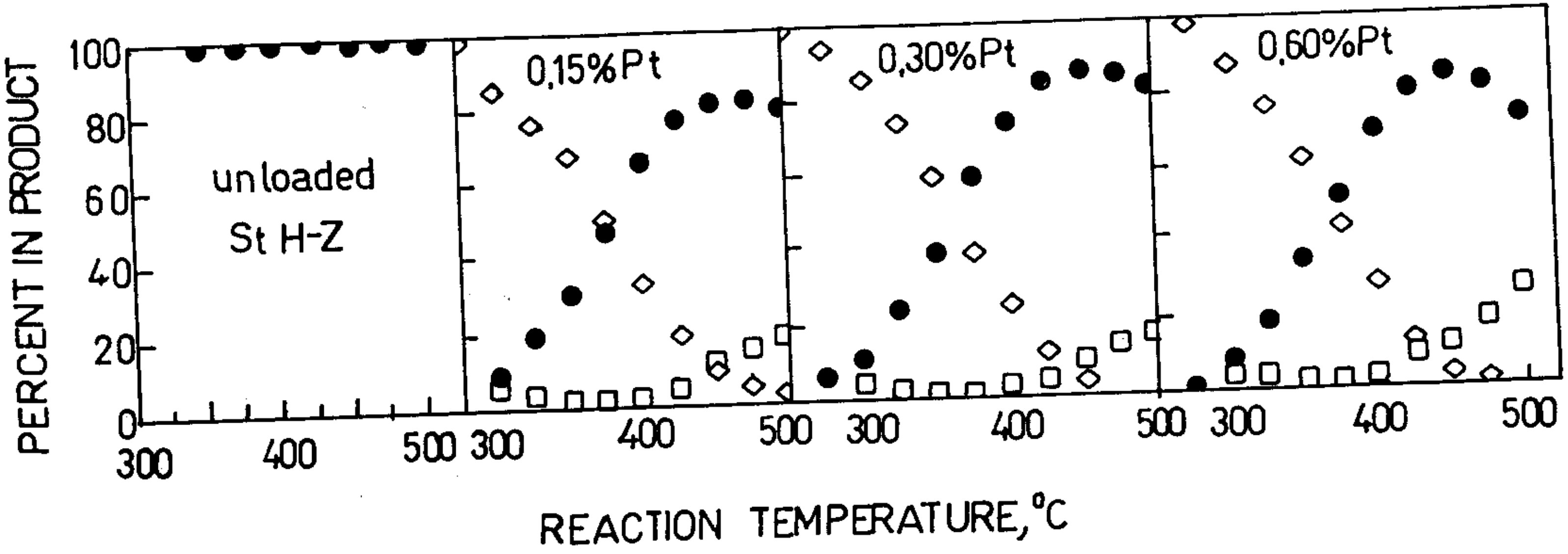

Fig. 58. Selectivities of n-Hexane hydroconversion reactions: ◇ hydroisomerization, ● hydrocracking, □ dehydrocyclization using unloaded and Pt-loaded St H-Z catalysts.

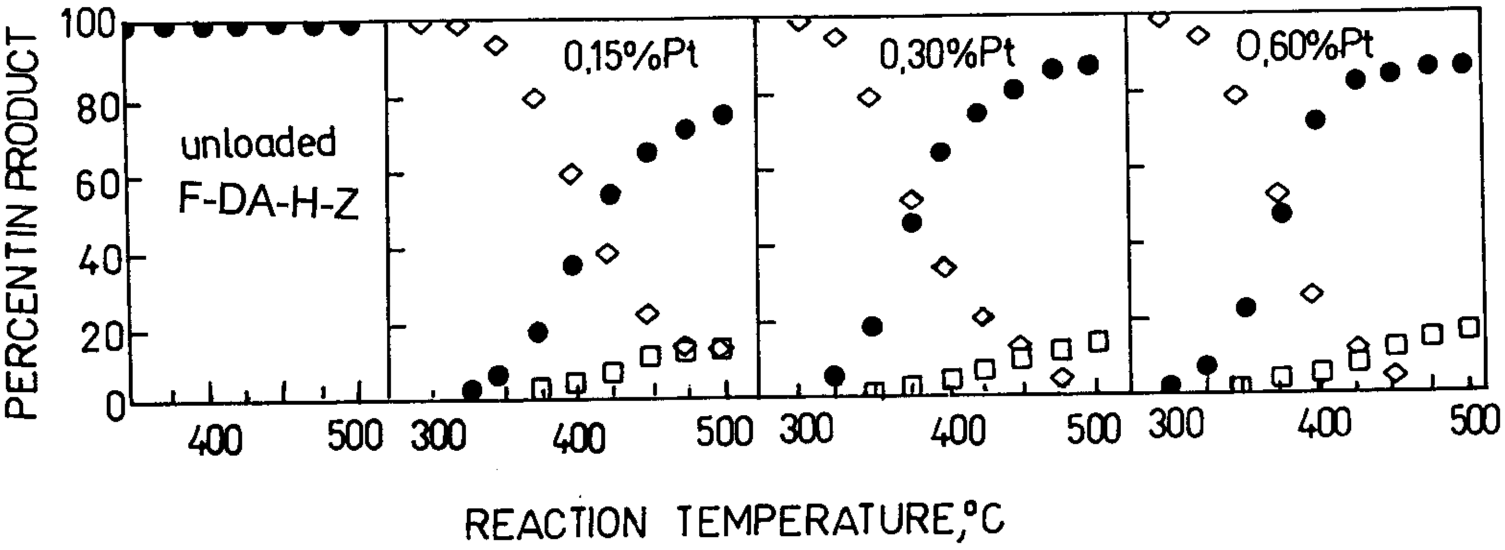

Fig. 59. Selectivities of n-Hexane hydroconversion reactions: ◇ hydroisomerization, ● hydrocracking, □ dehydrocyclization using unloaded and Pt-loaded F-DA-H-Z catalysts.

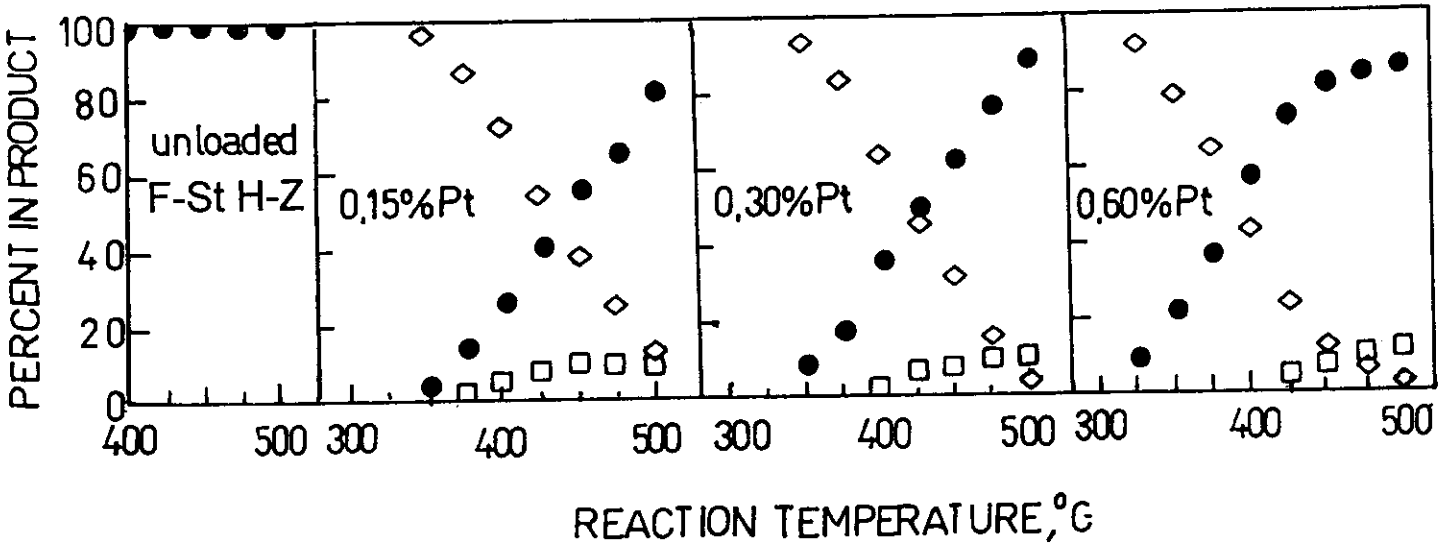

Fig. 60. Selectivities of n-Hexane hydroconversion reactions: ◇ hydroisomerization, ● hydrocracking, □ dehydrocyclization using unloaded and Pt-loaded F-St H-Z catalysts.

3.8. Selectivities of Unloaded and Pt Loaded Zeolite Catalysts

The use of unloaded H-ZSM-5 zeolite (H-Z catalyst; Fig. 55),either unmodified or after being modified via EDTA-dealumination (DA-H-Z catalyst; Fig. 56), treatment with HF (F-H-Z catalyst; Fig. 57), steaming at 500°C (St H-Z; Fig. 58), dual-treatment via EDTA-dealumination followed by HF doping (F-DA-H-Z catalyst; Fig. 59) dual-treatment via steaming followed by HF doping (F-St H-Z; Fig. 60) as catalysts for the hydroconversion of n-hexane produces principally hydrocracked products. Each Figure contains four plots; the first represents the selectivities for the three hydroconversion reactions using the unloaded zeolite catalyst, whereas the three other plots give selectivities of the reactions using 0.15% Pt, 0.30% Pt and 0.60% Pt-loaded versions.

Fig. 55(a) shows a major hydrocracking selectivity using the H-Z catalyst and very low selectivities for isomers formation and benzene production. In Fig. 56(a), the DA-H-Z catalyst shows modest cyclization at low temperatures but a major hydrocracking selectivity. Fig. 57(a) also shows a modest selectivity for isomerisation with a lower cyclisation selectivity; beside a high selectivity for hydrocracking. On the other hand, Figs. 58-60 show that using the St H-Z, F-DA-H-Z and F-St H-Z catalysts, respectively, the hydrocracking selectivities are always 100% , irrespective of the hydroconversion values.

The 0.15% and 0.30% Pt/DA-H-Z can be considered the catalysts of choice for n-hexane Hydroisomer-ization in the present study.