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Catalytic Conversion of *n*-Heptane in Vapour Phase

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The catalytic conversion of *n*-heptane in vapour phase was carried out over Zn-Y zeolite and an Egyptian natural aluminosilicate catalysts. The Zn-Y zeolite catalyst was prepared using the sodium form of SK-40 molecular sieve as starting material, by exchanging the sodium ion for Zn by using continuous flow exchange method. The clay catalyst was activated with $ZnCl_2$ solution. The catalytic reactions were conducted using a conventional fixed bed reactor under atmospheric pressure at space velocity 0.5 hr^{-1}. The reaction temperature was varied between 300–550°C. The activities and selectivities of the catalysts in *n*-heptane conversion were calculated at different reaction temperatures.

INTRODUCTION

The catalytic conversion of *n*-heptane is considered as the most important demand in the petroleum industry because of increasing need for raising the octane number of motor and aviation gasoline, lowering the freezing point of jet fuels and lowering the pour points of diesel fuels and lubricating oils.

Normal alkane conversion throug alkylation, isomerization, cracking and dehydrocyclization have commonly many features. In particular they are catalyzed by acids. Both, mechanisms and process engineering aspects of normal alkane conversion has been studied over different catalysts[1–8].

The catalysts used in normal alkane conversion are either electronic acidic or electronic-acidic. The activity of electronic catalysts[9,10] is attributed to their unfilled *d*-orbitals, whereas acidic catalysts promote the reactions proceeding via carbonium ions mechanism. The activity of acidic and electronic catalysts increases, normally, with rising their acidity[11]. Many catalysts have found limited commercial applications and at present the synthetic silica-alumina and natural clay catalysts dominate the field.

In the present work we studied the conversion of *n*-heptane catalyzed by natural aluminosilicate clay and synthetic Zn-Y type zeolite. The activity and selectivity of both catalysts were determined. The catalysts were activated by treating with 10% $ZnCl_2$ solution.

EXPERIMENTAL

Catalyst Composition

Two solid catalysts were employed. The first one is a kaolinite type

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Egyptian natural aluminosilicate having the following composition wt %); $SiO_2 = 42.42$, $Al_2O_3 = 42.47$, $TiO_2 = 1.08$, $F_2O_3 = 13.75$ and ignition loss 13.73. The solid was activated by washing with dilute HCl (10 %) then with water, dried and roasted at 350–400°C for 4 hrs. The second catalyst is SK–40 molecular sieve of type Na–Y zeolite having the following composition (wt %): $SiO_2 = 63.5$, $Al_2O_3 = 25.5$, $NaO = 13.0$, $Cl^- = 0.05$, $F^- = 0.05$. The two catalysts were soaked over night in 10% $ZnCl_2$ solution and finally dried at 100°C till constant weight.

Apparatus and procedure

The catalytic reaction was carried out in continuous flow fixed bed reactor. The reactor system and procedure were described elsewhere[12]. The operating conditions employed are reaction temperatures between 300–550°C, space velocity 0.5 hr^{-1}; at atmospheric pressure.

The gaseous and liquid products were determined by gas liquid chromatography (GLC) using a column 30 feet length and 0.5 cm diameter packed with 20% squalane on chromosorb w for liquid. While that used for gases, two columns were used in parallel 8 and 20 feet length, 0.5 cm diameter packed with 10% diisodecylphthalate and 20 % dimethylsulfolane respectively, on chromosorb P. Hydrogen was detected using a column 120 cm length, 0.5 cm diameter packed with charcoal activated by heating at 300°C in presence of pure hydrogen carrier.

RESULTS AND DISCUSSION

The complete analysis of products of *n*-heptane conversion over synthetic Zn-Y zeolite and natural aluminosilicate catalysts are represented in Tables 1 and 2. These Tables indicate the different products, solid, liquid and gases obtained on each catalyst. Tables 1 and 2 show that the total conversion is much higher in case of Zn–Y zeolite than in contact with the other catalyst. More than 90% yield was obtained when the reaction was catalyzed by synthetic zeolite at 500°C and about 45% yield was only obtained in the case of natural aluminosilicate catalyst at the same reaction temperature. In both cases the percentage reaction increases by increasing the reaction temperature from 300–525°C. The essential constituents of this particular catalytic reaction are the liquid phases which constitutes more than 50% of the reaction products. The gaseous products represent about 50% of the liquid especially at temperature varied between 300–425°C. The solid products, which are coke deposits, represent in both catalyst a negligible fraction, especially, at temperature between 450°C.

The effect of reaction temperature on each of solid, liquid and gaseous products is also indicated in Tables 1 & 2. The chromatographic analysis of liquid products revealed the presence of benzene, toluene, ethylbenzene, xylenes and $C_3 + C_4$ alkylaromatics hydrocarbons as well as different isomers of *n*-heptane together with heptenes. The presence of heptenes indicate the dehydrogenation of *n*-heptane. In fact hydrogen gas was chromatographically detected in the gaseous reaction products (*cf.* Tables 1 & 2). The presence of aromatic hydrocarbons indicate dehydrocyclization and disproportionation reactions. While the presence of iso C_7 hydrocarbons point out the occurrence of skeletal isomerization reactions. Cracking reactions occured also in contact with two employed catalysts. The selectivity of natural aluminosilicate and synthetic Zn–Y zeolite towards the above mentioned reactions were calculated, the data obtained are given in Table 3. The selectivities towards cracking reactions increase by increasing the reaction temperature over synthetic aluminosilicate. In contrast, this selectivity was found to decrease by increasing the reaction temperature in case of the other catalyst in temperature varies between 325–475°C. The selectivity of synthetic aluminosilicate for aromatization reaction increases monotonically by increasing reaction temperature from 300–475°C and decreases by further increase in temperature. In contact with natural aluminosilicate the selectivity for aromatization reaction which is relatively small as compared with that of Zn–Y zeolite, remains unchanged in the temperature range 300–350°C, then increases regularly by increasing the reaction temperature up to 500°C. The selectivity of both catalysts for isomerization reaction decreases by increasing the reaction temperature and became negligibly small at temperature $\geqslant$ 475°C. Finally, the selectivity for dehydrogenation reactions, as indicated by the formation of heptenes is much greater in case of natural aluminosilicate than in the Zn–Y zeolite.

It is worthy to mention, here, that the extent of heptenes formed in contact of natural aluminosilicate is much higher under all the reaction temperatures studied as compared to that produced on Zn–Y zeolite. So it is recomended to employ such cheap catalyst (natural aluminosilicate clay) in the conversion of *n*-heptane in order to obtain a remarkable yield of heptenes.

The relative high activity of Zn–Y zeolite catalyst in conversion reaction of *n*-heptane can be attributed to its open structure (high surface area above 500 m^2/g)[13] and also to a high concentration of acid centers which catalyzed the reaction proceeding via carbonium ion mechanism (i.e. all the above mention reactions with the exception of dehydrogenation reactions.)

The effect of reaction temperature on chemical composition of liquid products was studied and the results obtained are given in Tables 1 & 2, which show that, the yield of benzene was found to increase continuously by increasing the reaction temperature. While that of ethylbenzene was found to increase by increasing the reaction temperature reaching a

TABLE 1

PRODUCTS OF CATALYTIC CONVERSION OF *n*-HEPTANE OVER Zn–Y ZEOLITE AT DIFFERENT TEMPERATURES

Reaction Temperature °C	300	325	350	375	400	425	450	475	500	525
Total conversion wt. % feed	16.76	29.73	39.11	50.90	57.01	65.50	77.47	87.19	92.77	97.65
Products distribution (wt. % on feed)										
TOTAL LIQUIDS	10.52	20.00	24.52	32.49	34.21	37.25	41.53	46.48	43.79	40.40
Total Aromatics	1.84	5.91	6.13	9.30	18.24	30.96	37.02	42.16	40.75	37.90
benzene		0.10	0.12	0.30	1.00	2.37	4.50	6.20	7.90	10.26
toluene		1.07	1.10	2.30	5.32	14.73	21.00	25.40	22.40	19.21
ethylbenzene	0.67	1.00	0.98	1.31	2.01	5.20	2.07	0.56	0.22	0.13
xylene			0.02	0.35	1.01	3.50	6.50	8.50	9.30	7.84
C_3 & C_4 alkyl aromatics	1.17	3.80	3.91	5.10	8.90	5.16	2.95	1.50	0.90	0.46
Total iso C_7	8.40	13.68	17.84	22.40	15.14	5.00	1.95	1.50	1.00	0.60
2,3 & 3,4 DMP	0.37	0.60	1.25	2.28	1.07	0.40	0.06	0.04	0.03	0.02
3 MH & 3,3 DMP		0.01	0.01	0.32	0.06	0.02	0.02	0.01		
2,8 DMP	3.91	6.37	7.02	8.59	6.56	1.96	0.79	0.61	0.41	0.25
3 MH	3.93	6.40	8.98	10.95	6.42	2.47	1.05	0.81	0.53	0.32
3 EP	0.19	0.31	0.58	0.61	0.77	0.11	0.03	0.02	0.02	0.01
Heptenes	0.28	0.35	0.55	0.79	0.83	1.29	2.55	2.82	2.01	1.90
TOTAL GASES	5.91	9.58	14.37	17.87	21.75	26.55	33.50	37.21	44.36	51.30
Hydrogen	0.03	0.08	0.15	0.20	0.38	0.59	0.82	0.99	1.15	1.20

Total cracked gases	5.88	9.50	14.22	17.67	21.37	25.96	32.68	36.22	43.21	50.10
Methane	0.06	0.10	0.15	0.22	0.32	0.40	0.95	1.91	2.22	6.58
Ethane	0.07	0.11	0.27	0.30	0.40	0.50	0.65	0.79	0.88	3.04
Ethylene	0.03	0.04	0.07	0.13	0.12	0.10	0.20	0.20	0.23	0.30
Total C_1 & C_2	0.16	0.25	0.49	0.65	0.84	1.00	1.85	2.90	3.33	9.92
Propane	0.67	1.09	1.63	2.30	2.45	2.86	4.33	5.39	6.48	4.18
Propene	0.21	0.35	0.52	0.60	0.81	1.39	1.87	2.90	3.25	2.11
Total C_3	0.88	1.44	2.15	2.9	3.26	4.25	6.00	8.29	9.73	6.29
Iso butane	1.25	2.02	3.02	3.80	5.50	6.29	8.42	9.75	10.96	11.32
n-butane	1.20	1.95	2.81	2.96	3.20	5.22	6.55	7.15	8.37	8.64
isobutylene	0.02	0.03	0.04	0.06	0.05	0.08	0.10	0.12	0.18	0.18
butene-1	0.27	0.41	0.79	0.90	1.10	1.40	0.99	1.50	1.83	1.79
butene-2-trans	0.15	0.19	0.51	0.60	0.72	0.81	0.85	0.92	1.01	0.89
butene-2-cis	0.16	0.35	0.25	0.40	0.45	0.49	0.52	0.60	0.78	0.89
1,3 butadiene	0.01	0.02	0.02	0.05	0.03	0.05	0.10	0.14	0.28	0.29
Total C_4	3.06	4.97	7.44	8.77	11.05	14.34	17.53	20.18	23.41	24.00
iso pentane	1.21	1.96	2.86	3.30	3.41	3.26	3.51	2.35	2.73	4.27
n-pentane	0.15	0.25	0.40	0.55	1.01	1.07	1.80	1.81	1.85	3.18
pentene-1	0.02	0.05	0.02	0.25	0.30	0.17	0.11	0.09	0.07	0.18
pentene-2-trans	0.01	0.02	0.03	0.08	0.09	0.07	0.07	0.06	0.06	0.08
pentene-2 cis	0.01	0.01	0.02	0.05	0.06	0.03	0.05	0.05	0.05	0.05
Total C_5	1.4	2.29	3.39	4.93	4.87	4.60	5.54	4.36	4.76	7.76
Total iso C_6	0.19	0.16	0.35	0.52	0.65	0.73	0.46	0.29	0.50	0.53
3 Methyl pentane	0.08	0.01	0.15	0.23	0.29	0.16	0.20	0.08	0.07	0.18
2 methyl pentane	0.06	0.07	0.11	0.16	0.21	0.11	0.15	0.06	0.23	0.13
Methycyclopentane	0.05	0.08	0.09	0.13	0.15	0.46	0.11	0.15	0.20	0.22
n-hexene	0.19	0.39	0.40	0.60	0.70	1.04	1.30	0.30	1.48	1.60
Total C_6	0.38	0.55	0.75	1.12	1.35	1.79	1.76	0.59	1.98	2.13
Coke deposits	0.05	0.15	0.22	0.54	1.05	1.70	2.44	3.50	4.62	5.95

TABLE 2

PRODUCTS OF CATALYTIC CONVERSION OF *n*-HEPTANE OVER NATURAL ALUMINOSILICATE AT DIFFERENT TEMPERATURES

Reaction temperature °C	325	350	375	400	425	450	475	500	525	550
Total conversion wt. % on feed	4.08	6.65	12.58	16.93	23.22	30.30	36.54	43.05	55.45	59.70
Products distribution (wt. % on feed)										
TOTAL LIQUIDS										
Total liquids	2.39	4.10	8.01	11.08	15.21	20.13	23.92	27.92	31.55	26.43
Total aromatics	0.25	0.40	0.59	2.30	6.00	0.13	11.15	16.36	21.37	16.79
benzene				0.05	0.17	0.54	0.95	1.40	2.77	3.31
toluene			0.05	0.29	0.90	2.03	5.83	11.14	14.38	8.13
ethylbenzene	0.05	0.12	0.15	0.90	1.29	4.52	1.51	0.46	0.10	0.06
xylenes					0.17	0.67	2.21	3.25	3.98	5.18
C_3 & C_4 alkyl aromatic	0.20	0.28	0.39	1.06	3.47	1.36	0.56	0.11	0.14	0.11
Total iso C_7	1.84	3.00	6.46	7.20	5.00	3·04	2.11	1.54	0.33	0.21
2–3 & 3–4 DMP	0.08	0.13	0.45	0.73	0.35	0.24	0.07	0.04	0.01	0.01
2 MH & 3.3 DMP					0.10	0.04	0.02	0.02	0.01	
2.3 DMP	0.86	1.40	2.54	2.76	2.17	1.19	0.85	0.63	0.14	0.09
3 MH	0.86	1.40	3.25	3.51	2.12	1.50	1.14	0.83	0.16	0.11
3 EP	0.04	0.07	0.22	0.20	0.26	0.07	0.03	0.02	0.01	
Heptenes	0.30	0.70	0.96	1.58	4.21	7.96	10.66	10.02	9.85	9.34
TOTAL GASES	1.59	2.31	4.12	5.15	6.98	7.67	8.92	12.08	17.40	25.35
Hydrogen	0.01	0.03	0.08	0.15	0.22	0.43	0.52	0.61	0.70	0.78

Total cracked gases	1.58	2.28	4.04	5.00	6.76	7.24	8.40	11.47	16.70	24.57
methane	0.01	0.01	0.06	0.08	0.07	0.02	0.10	0.10	0.20	0.69
ethane	0.01	0.01	0.02	0.03	0.05	0.02	0.05	0.09	0.10	0.20
ethylene	0.02	0.02	0.04	0.02	0.13	0.13	0.10	0.12	0.20	0.43
Total $C_1 + C_2$	0.04	0.04	0.12	0.13	0.25	0.17	0.25	0.31	0.50	1.32
Propane	0.04	0.07	0.13	0.17	0.23	0.23	0.25	0.31	1.04	1.24
Propene	0.21	0.31	0.0	0.85	0.98	1.10	1.11	2.02	2.20	3.25
Total $C_3 + C_3$	0.25	0.38	0.83	1.02	1.21	1.33	1.63	2.33	3.24	4.49
isobutane	0.05	0.06	0.12	0.15	0.23	0.25	0.15	0.08	0.50	0.60
n-butane	0.04	0.06	0.09	0.11	0.10	0.14	0.55	0.23	1.10	1.29
isobutylene	0.03	0.03	0.04	0.05	0.03	0.03	0.10	0.05	0.20	0.75
butene–1	0.46	0.62	1.18	1.35	1.60	1.56	1.87	3.12	3.62	4.51
butene–2–trans	0.26	0.29	0.76	0.90	1.05	1.30	1.07	1.92	1.99	2.25
butene–2–cis	0.27	0.52	0.37	0.61	0.65	0.85	0.66	1.25	1.55	2.24
1,3 butadiene	0.02	0.05	0.06	0.08	0.08	0.09	0.15	0.06	0.10	0.86
Total C_4 + iso C_4 + C_4	1.13	1.63	2.62	3.25	3.77	4.22	4.55	6.71	9.06	12.50
isopentane	0.02	0.02	0.05	0.66	0.09	0.10	0.08	0.04	0.15	0.23
n-pentane	0.05	0.06	0.07	0.09	0.19	0.10	0.15	0.25	0.30	0.60
pentene–1	0.04	0.05	0.06	0.08	0.50	0.49	0.59	0.59	1.19	2.81
pentene–2–trans	0.01	0.01	0.02	0.03	0.15	0.20	0.38	0.40	1.02	1.29
pentene–2–cis	0.01	0.01	0.02	0.01	0.16	0.09	0.27	0.33	0.85	0.86
Total C_5 + iso C_5 + C_5 iso hexane	0.13	0.15	0.22	0.27	1.09	0.98	1.47	1.61	3.51	5.79
3 Methyl pentane	0.01	0.01	0.02	0.03	0.02	0.02	0.05	0.04	0.10	0.09
2 Methyl pentane		0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.04	0.05
Methylcyclopentane	0.01	0.05	0.12	0.18	0.26	0.34	0.33	0.31	0.05	0.03
n-hexane	0.01	0.01	0.10	0.11	0.15	0.17	0.10	0.15	0.20	0.30
Total C_6 + iso C_6	0.03	0.08	0.25	0.33	0.44	0.54	0.50	0.51	0.39	0.47
Coke deposits	0.1	0.24	0.45	0.70	1.03	2.5	3.70	5.05	6.50	8.00

TABLE 3

SELECTIVITY OF Zn-Y ZEOLITE AND NATURAL ALUMINOSILICATE CATALYSTS IN *n*-HEPTANE CONVERSION

Reaction temp. °C	Selectivity (wt. %) for Zn-Y					Selectivity (wt. %) for natural clay				
	Total Gases	Total Liquid	Total aromatic	Total iso C_7	heptenes	Total Gases	Total Liquid	Total Aromatic	Total iso C_7	heptenes
300	35.65	63.83	11.17	50.97	1.69					
325	31.95	67.27	19.87	47.56	1.19	38.72	58.58	6.12	45.1	7.35
350	36.38	62.72	15.69	45.63	1.40	32.02	57.58	5.62	42.13	9.83
375	34.72	63.83	18.27	44.01	1.55	32.11	63.67	4.68	51.35	7.63
400	37.48	60.01	31.99	26.56	1.46	29.53	65.44	13.59	42.52	9.33
425	39.63	55.87	47.27	7.63	1.97	29.11	65.50	25.84	21.53	18.13
450	42.18	53.61	47.78	2.52	3.29	23.90	66.45	30.13	10.04	26.27
475	41.56	53.30	48.35	1.72	3.23	22.99	65.46	30.51	5.77	29.17
500	46.57	47.2	43.92	1.08	2.17	25.66	61.98	36.32	3.42	22.24
525	51.28	41.35	38.79	0.61	1.95	29.96	56.59	38.51	0.59	17.76
550						41.1	44.21	28.09	0.35	15.77

maximum value at 425° and 450°C in case of Zn-Y zeolite and activated clay respectively. In case of toluene and xylenes their amounts increase regularly by increasing the reaction temperature to a maximum attained at 475° and 525°C in case of toluene and 500° and 525°C in case of xylenes in contact with the Zn-Y and activated clay respectively. Finally the percentage yield to heavy C_3 and C_4 alkylaromatic hydrocarbons was influenced by reaction temperature and catalyst type, in a similar manner, as the yield of ethylbenzene, toluene and xylenes, but attaining its maximum value at 400° and 425°C in the presence of Zn-Y and activated clay. The formation of heavy C_3 and C_4 alkylaromatic hydrocarbons at lower reaction temperature may be attributed to the alkylation of the produced aromatics especially toluene with the formed paraffins and olefins in the reaction medium reaching its maximum value at temperatures 400° and 425°C above which it begins to decrease. This decrease may be due to the reverse reaction (dealkylation) or disproportionation to give toluene and ethylbenzene. Ethylbenzene will also suffer a decomposition but a relatively higher reaction temperatures than those in the case of C_3 and C_4 alkylaromatics to give benzene, toluene and/or xylenes.

This was confirmed from the detection of benzene, toluene and xylenes at relatively high temperature just or above those at which alkyl-aromatics and ethylbenzene begin to decompose, and the continuous increase of their yield by reaction temperature. Also toluene may be undergo cracking or disproportionation to yield benzene and xylenes, which was confirmed by the increase of their yields on expense of toluene (*cf.* Tables 1 & 2).

On the other hand, the formation of toluene and benzene may be due to aromatization (dehydrocyclization) of the reactant or the cracked products. In this case toluene is produced from dehydrocyclization of *n*-heptane, this was confirmed by the increase of its yield by the increase of reaction temperature to a maximum value and then decreases due to the increase of the rate of backward reaction. If benzene was produced from aromatization of C_6 hydrocarbons, formed from cracking of *n*-heptane, a maximum value would be attained as in the case of toluene thus, the continuous increase in benzene yield, with reaction temperature without attaining a maximum value in addition to the presence of small quantities of C_6 cracked hydrocarbon, stand as other evidence confirming the formation of benzene by decomposition of toluene. This speculation was also confirmed by the observed increase in C_1 cracked hydrocarbon (Tables 1 & 2).

Tables (1 & 2) also show that the yield of each of the five isomers of *n*-heptane behave in a parallel manner as the total iso C_7 hydrocarbons with respect to the reaction temperature. The extent of these isomers increases by increasing the reaction temperature reaching a maximum value then decreases. This decrease, which is noticable, at higher reaction temperatures ($\geqslant$ 450°C) may be attributed to the cracking effect[14], where most of these isomers are cracked to isobutanes, which increase as a function of reaction temperature (Table 1 & 2).

Also the higher isomers are cracked to lower ones. From the isomer distribution (Tables 1 and 2), it is clear that 2, 3 dimethyl-pentane and 3 methylhexane form the majority of heptane isomers (82–90%) which have higher octane number ranging between (65–82).

It can be concluded from the above mentioned results that the optimum conditions for isomerization of *n*-heptane is to carry out the reaction in our case at temperature not exceeding 375°C.

Table 4, represent the distribution of total saturate, unsaturate and isoparaffins having carbon number from C_1 to C_6. These Table indicate that, over Zn–Y zeolite catalyst, both saturate and isoparaffins hydrocarbons, while that, the unsaturate represent the smallest constituent. In case of natural aluminosilicate catalyst the unsaturate represents the main constituent of cracked hydrocarbons and its amount (150–83%) is generally, greater than these of saturate and isoparaffin hydrocarbons at all studied temperature this, clearly indicate that the natural catalyst has an excellent dehydrogenation activity.

From the product distribution of individual cracked hydrocarbon (Tables 1 and 2), it is shown that, the major constituent of these products are C_3 and C_4 hydrocarbons. This indicate that, the process is mainly catalytic and the cracking occurs preferentially at the middle of the molecule rather than at its end[15]. Increasing the raction temperature up to 450°C causes a negligiable change in dry gases ($C_1 + C_2$) and remarkable increase in l.b.g. constituents ($C_3 + C_4$) and this increase is more intense at higher temperatures (above 400°C), at 500°C an abrupt increase in the quantity of the dry gas is noticed with decrease in quantity of C_3 content and a slight increase in total C_4 content. This may be due to the effect to thermal cracking, where cracking occurs preferentially at terminal of the molecule rather than in its center by the free-radical mechanism[16–18]. This is confirmed also by the noticeable increase in the contents of both C_5 and C_6 hydrocarbons.

TABLE 4

EFFECT OF REACTION TEMPERATURE AND CATALYSTS TYPE ON DISTRIBUTION OF SATURATE, UNSATURATE AND ISOPARAFFINS OF *n*-HEPTANE CONVERSION

Catalyst type	Zn–Y zeolite				natural aluminosilicate			
R. temp. °C	Total gases	Total saturate	Total unsaturate	Total isomers	Total gases	Total saturate	Total unsaturate	Total isomers
300	5.88	2.33	0.90	2.65				
325	9.50	3.80	1.47	4.23	1.58	0.16	1.34	0.08
350	14.22	5.70	2.29	6.23	2.29	0.22	1.91	0.16
375	17.67	6.92	3.12	7.63	4.04	0.47	3.25	0.32
400	21.37	8.08	3.73	9.56	5.00	0.59	3.96	0.45
425	25.96	11.09	4.59	10.28	6.76	0.82	5.23	0.71
450	32.68	15.13	5.16	12.39	7.24	0.68	5.14	0.72
475	36.22	17.25	6.68	12.39	8.40	1.47	6.30	0.63
500	43.21	21.22	7.80	14.19	11.47	1.13	9.86	0.48
525	50.10	24.52	8.55	17.45	16.70	2.94	13.12	0.64
550					25.67	4.42	19.75	0.40

The decrease in total C_3 content may be also due to the disproportionation of propylene under our experimental conditions especially at high temperature to give $C_1 + C_2$ and $C_2 + C_4$ gaseous hydrocarbons. The disproportionation of propylene was observed in the oligomerization of propylene over different cation exchanged zeolite[19]. Accordingly, the yield of individual gaseous hydrocarbons depend differently on the reaction temperature.

CONCLUSIONS

The results obtained in the present investigation permitted us to propose the following conclusions:

(1) A naturally occurring aluminosilicate clay, present in huge amounts in Egypt, could be successively employed as active and selective catalyst in *n*-heptane conversion in producing heptene and unsaturated hydrocarbons having carbon number from C_2 to C_6.

(2) A synthetic Zn–Y zeolite catalyst exhibited an excellent catalytic activity in *n*-heptane conversion, however, its selectivity towards heptene formation and cracked olefins is much lower than that observed for natural aluminosilicate clay.

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