

# AROMATIZATION OF C<sub>6</sub> HYDROCARBONS ON ZN /H-ZSM-5 CATALYST

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**abstract:** The distribution of reaction products in the aromatization of C<sub>6</sub> hydrocarbons depends on the molecular structure of the hydrocarbon and, as a consequence, on the reaction temperature. If for the C<sub>6</sub> alkanes cracking is prevalent, and begins at low temperatures, for the cycles cracking diminishes, the temperature for the break of the cycles shifts to higher values and the aromatic content of the reaction products increases; in the special case of cyclohexene, aromatization appears at low temperatures and this evolution was confirmed by the IR spectra of adsorbed cyclohexene.

**keywords:** Aromatization, H-ZSM-5, modified ZSM-5 zeolites.

## Introduction

The formation of aromatics from light alkanes represents one way for better utilization of these hydrocarbons, which have fewer uses in petrochemistry [1]. On the other hand, aromatics are valuable intermediates in many syntheses, so obtaining them in another process than catalytic reforming is of great interest. There are many data in the literature concerning the aromatization process of C<sub>3</sub>-C<sub>4</sub> alkanes, using as catalysts ZSM-5 zeolites, in the protonic form or modified with zinc or gallium [2÷5]. ZSM-5 zeolites are used for their strong acidity and for their shape selectivity [6] that lead to a convenient distribution of mononuclear aromatics, with a high concentration for the BTX (benzene-toluene-xylenes) fraction. Modifiers (zinc or gallium) lead to a higher selectivity of the catalyst towards aromatics, due to their involvement mainly in the dehydrogenating steps of the process [3]. Although the literature is so rich in experimental data, the reaction pathways for this process are far from being elucidated [7÷11]. It is known that alkenes are intermediates in the transformation, but it is not clear the way the aromatic ring is formed from alkenes oligomers. It is supposed that these oligomers dehydrogenate through a transfer of protons and hydride ions to other alkenes from the reaction mixture, and then cycles are formed and further dehydrogenated to aromatics [12]. In addition, another problem is that although most of the studies are made on C<sub>3</sub> hydrocarbons, the aromatics that predominate in the reaction products are toluene and xylenes.

In this paper we report our results concerning the dependence of catalytic performances of a ZSM-5 sample on the reaction temperature, for several C<sub>6</sub> hydrocarbons, in order to study

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the way these hydrocarbons convert to aromatics. The C<sub>6</sub> hydrocarbons were chosen because they can react in one of two ways: either direct dehydrogenation to benzene, or a cracking reaction, which produces C<sub>2</sub>–C<sub>4</sub> alkenes, and these transform into aromatics.

## Experimental

The catalyst sample, 0.57% Zn/H-ZSM-5, was obtained from the parent zeolite (Si/Al = 92) by impregnation with a zinc nitrate solution, drying and calcination. The sample was characterized for crystallinity, surface area, porosity, and Brønsted and Lewis acidity. Cyclohexene adsorption measurements were carried out on 5 mg.cm<sup>-2</sup> wafers, previously degassed in a quartz in situ cell equipped with two KBr windows, at 400°C and 10<sup>-3</sup> Pa overnight, followed by evacuation for 5 h at the same temperature.

The catalytic tests were performed in a fixed bed reactor, as previously reported [13], at atmospheric pressure and temperatures between 200° and 500°C. Before the catalytic tests, the catalyst was heated at 550°C in airflow, and then the temperature was lowered to the reaction temperature. After reaction, the catalyst was regenerated at 550°C in airflow for 1 h. After the reactor, the reaction products were cooled and the liquid and gaseous fractions separately collected and analyzed by gas chromatography. n-Hexane (Merck, 99%), 2-methylpentane (Fluka AG, 97%), cyclohexane (Merck, 99.7%) and cyclohexene (Jensen Chimica, 99%) were used as starting materials. Catalytic tests were performed with 2.0 h<sup>-1</sup> VHSV (volume hourly space velocity) for the hydrocarbon feed. Total conversion (C<sub>T</sub>) was calculated as the amount of the feed transformed into products divided by the amount of feed introduced in the reactor. The conversion to liquid fraction was calculated as the amount of feed transformed into liquid products divided by the amount of feed introduced in the reactor. The quantity of aromatics (A) was calculated as the amount of aromatics in the liquid fraction multiplied by the conversion to liquid fraction.

## Results and discussion

In order to study the influence of temperature on the distribution of reaction products, each C<sub>6</sub> feed will be discussed separately.

### **a) n-Hexane**

The results obtained for the conversion of n-hexane on 0.57% Zn/H-ZSM-5, between 200° and 500°C, are summarized in Table 1 and Fig. 1.

As expected for endothermic reactions, the total conversion values increase with temperature, reaching almost complete conversion at 500°C. At low temperatures (200°C) the transformation is limited to the formation of small quantities of cracked products and isomers (2- and 3-methylpentane). Although the cracked products are in small quantities, butane concentration is higher than that for propane. This fact suggests that cracking proceeds at this temperature mainly through monomolecular mechanism for n-hexane according to Narbeshuber and co. [14]. As the temperature increases, the conversion values also increase, and the quantities of isomers in reaction products are decreasing.

**Table 1. Distribution of main reaction products (wt.%) and variation of the catalyst performances (%) in n-hexane conversion on 0.57% Zn/H-ZSM-5 at different temperatures (VHSV = 2 h<sup>-1</sup>).**

	200°C	300°C	350°C	400°C	450°C	500°C
i-Hexane	3.3	7.1	3.3	2.1	1.4	0.1
Benzene	-	-	0.2	0.8	0.3	3.4
Toluene	-	-	3.1	3.4	2.2	13.1
Ethylbenzene + xylenes	-	-	9.0	4.5	2.1	8.4
C <sub>T</sub>	10.6	30.6	40.9	74.7	78.9	98.7
A	0	0	3.2	3.1	2.6	25.4

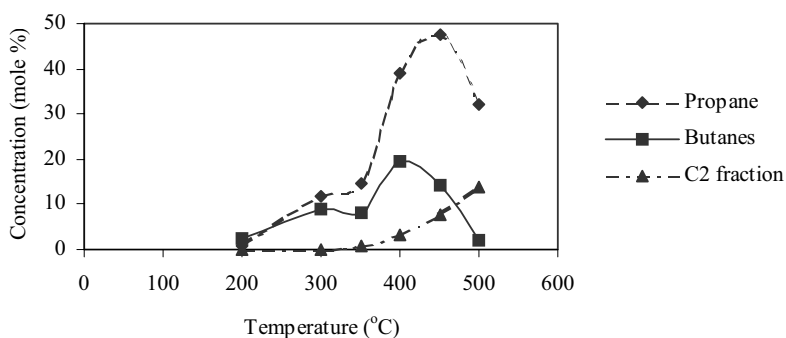


Fig. 1: Variation of main gaseous products concentration with increasing temperature, in n-hexane conversion on 0.57% Zn/H-ZSM-5 (VHSV = 2h<sup>-1</sup>).

Above 300°C, propane concentration has a larger increase than butane. As the conversion values grow, larger quantities of adsorbed carbocations will exist on the surface, so n-hexane cracking takes place in larger extent through bimolecular mechanism, leading to the formation of propane and propene [14]. On its turn, propene can be transformed into aromatics, or it can extract a hydride ion from another alkane. This way the large propane quantity in reaction products can be explained. Propane and butane concentrations pass each trough a maximum, but at different temperatures. The temperatures corresponding to these values (400°C for butane and 450°C for propane) are the temperatures at which  $DG_r$  for the conversion of alkanes in aromatics become negative, according to Seddon [2], so they are the minimum temperatures above which propane and butanes are converted in aromatics. This explains the increase of the quantity of aromatics formed at high temperatures and the decrease of the propane and butane concentrations at these temperatures. When temperature becomes higher, the concentration of C<sub>1</sub>-C<sub>2</sub> fraction increases, probably due to the intensification of the cracking reactions.

Aromatics appear in the reaction products at 350°C, because  $DG_r$  for their formation from hexane becomes negative above 320°C [2]. Their distribution is modified with increasing temperature: up to 400°C xylenes are predominant among aromatics, and above 400°C toluene becomes prevalent. It is possible that dealkylation and disproportionation reactions have a certain influence, but it is less probable that these reactions modify so significantly the distribution of aromatics. Although the concentration of benzene rises with temperature, it is at all temperatures smaller than those of toluene and xylenes. In the literature [10] this

behavior was explained by the rapid disproportionation and isomerization reactions for toluene and xylenes, based on the observation that the distribution of aromatics is similar (at high temperatures – 500°C) with the one from the disproportionation of toluene. We consider that, although these secondary reactions of aromatics cannot be ignored, the main reason for such a distribution is the formation of reaction intermediates from the alkenes that resulted from cracking, the first reaction step. The way alkenes react between them, the nature of these alkenes and the succession of reactions that lead to the formation of aromatics are the main factors that influence the nature of the aromatics that are formed.

The presence of large quantities of alkanes in the reaction products (and the presence of isobutane and hexane isomers) reflects the large extent that the hydride transfer mechanism has in the formation of aromatics on 0.57% Zn/H-ZSM-5. In this reaction the main function is the acidic one, the dehydrogenating function (zinc) having a less important role, which becomes evident only at 500°C. This fact suggests that the transformation of hexane takes place on this catalyst mainly on the acid sites of the zeolite.

### **b) 2-Methylpentane**

The results obtained for the conversion of 2-methylpentane on 0.57% Zn/H-ZSM-5, between 200° and 500°C, are summarized in Table 2. As for n-hexane, the total conversion and the quantity of aromatics increase with temperature. At low temperature (200°C), small quantities of isomers (3-methylpentane and n-hexane) and cracked products (mainly propane) are formed. As the temperature rises, the cracking reaction intensifies, and above 350°C aromatics appear in the products, their concentration slowly growing with temperature.

**Table 2. Distribution of main reaction products (wt.%) and variation of the catalyst performances (%) in 2-methylpentane conversion on 0.57% Zn/H-ZSM-5 at different temperatures (VHSV = 2 h<sup>-1</sup>).**

	200°C	300°C	350°C	400°C	450°C	500°C
Propane	0.6	0.5	1.8	7.5	14.1	16.8
Butanes	0.1	1.0	2.1	5.4	11.4	7.0
Benzene	-	0.1	0.4	0.7	0.9	2.5
Toluene	-	0.5	0.7	4.0	6.3	9.8
Ethylbenzene + xylenes	-	-	1.4	6.5	6.2	9.1
C <sub>T</sub>	3.8	10.3	23.2	46.8	50.2	67.9
A	0	0	0.4	4.3	4.4	12.8

The share of gaseous hydrocarbons in the products is small, and among them propane and butanes are the most important, but without exceeding 25% even at 500°C. Methane and ethane have low concentrations, as do the C<sub>2</sub>-C<sub>4</sub> alkenes and butadiene. This behavior can be explained by the lower cracking rate of 2-methylpentane (approx. half) compared to n-hexane [15]. Because this reaction is the first step in the transformation of the alkane, it is obvious that lower values for the total conversion will be obtained. Also, because the cracking of 2-methylpentane is slow, the concentration of the alkenes on the catalyst surface will be low and, as a consequence, the quantity of resulted aromatics will be low.

Among aromatics, at 350° and 400°C xylenes have the highest concentration, but it decreases with temperature. The concentration of toluene rises constantly with temperature, while benzene practically remains constant.

The distribution and variation of the reaction products with temperature suggest that the transformation of 2-methylpentane takes place through a first, cracking step, that is probably performed mainly on the acid function of the catalyst. Because the cracking rate is relatively small, the conversion values are also small, the concentrations of alkenes and aromatics being, as a consequence, low. The main aromatics are, again, toluene and xylenes. The dehydrogenating function has a relatively small role in the conversion, and this fact was also observed from the low hydrogen concentration in reaction products.

### c) Cyclohexane

The results that were obtained in the conversion of cyclohexane on 0.57% Zn/H-ZSM-5, between 200° and 500°C, are summarized in Table 3 and Fig. 2. The total conversion has a large increase with temperature above 350°C, reaching about 85% at 500°C. The high stability of the saturated cycle can be the explanation for the smaller conversion values compared to the ones obtained for *n*-hexane, and also for the fact that up to 350°C the conversion values are around 10%. The quantity of aromatics has a similar evolution, reaching 30% at 500°C, with values slightly higher than those for *n*-hexane.

The distribution of the reaction products shows that at low temperatures cracking is the main reaction. Because the C<sub>3</sub> fraction has the highest concentration among gaseous hydrocarbons, we can assume that the cracking of cyclohexane molecule takes place mainly in a symmetrical way, leading to two propene molecules. In a lower extent butanes are formed. Lighter hydrocarbons (C<sub>1</sub>, C<sub>2</sub>) have a very low concentration (traces) up to 350°C, and increasing only above 400°C.

Starting from 350°C aromatics are formed and, as for the other feeds, up to 400°C xylenes are the main aromatics, only above 450°C toluene having a higher concentration. The variation of distribution is similar with the ones observed for *n*-hexane and 2-methylpentane, indicating a common way of formation from different feeds, through common intermediaries.

**Table 3. Distribution of main reaction products (wt.%) and variation of the catalyst performances (%) in cyclohexane conversion on 0.57% Zn/H-ZSM-5 at different temperatures (VHSV = 2 h<sup>-1</sup>).**

	200°C	300°C	350°C	400°C	450°C	500°C
Propane	5.4	3.8	1.9	7.3	23.2	24.3
Propene	0.7	0.7	0.2	0.2	0.7	2.6
Butanes	3.4	1.3	1.1	2.3	6.0	7.3
C <sub>T</sub>	10.8	8.5	12.2	38.9	73.2	84.3
A	0	0	0	6.0	21.0	28.0

The transformation of cyclohexane is influenced by temperature in a similar way with *n*-hexane and 2-methylpentane, the performances being different only in their values.

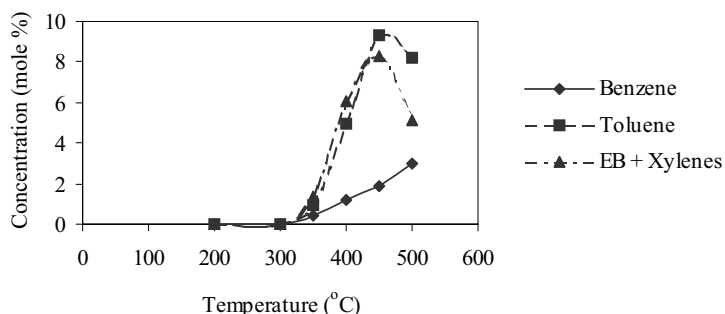


Fig. 2: Distribution of BTX in aromatics fraction with increasing temperature, in cyclohexane conversion on 0.57% Zn/H-ZSM-5 ( $VHSV = 2h^{-1}$ )

#### d) Cyclohexene

The results that were obtained in the conversion of cyclohexene on 0.57% Zn/H-ZSM-5, between 200° and 500°C, are summarized in Table 4.

**Table 4. Distribution of main reaction products (wt.%) and variation of the catalyst performances (%) in cyclohexene conversion on 0.57% Zn/H-ZSM-5 at different temperatures ( $VHSV = 2 h^{-1}$ ).**

	200°C	300°C	350°C	400°C	450°C	500°C
Ethene	-	-	0.3	1.1	1.7	4.6
Propane	-	0.1	2.4	6.7	5.8	7.7
Propene	-	-	1.3	2.0	3.1	5.4
Butanes	-	-	4.2	6.9	6.9	4.5
Butadiene	-	-	0.3	0.4	0.3	0.2
Benzene	-	0.4	2.8	4.1	4.6	11.0
Toluene	0.2	1.3	10.7	20.6	25.7	20.8
Ethylbenzene + xylenes	0.5	5.6	34.2	27.5	29.2	19.2
$C_T$	28.4	53.1	92.9	94.5	97.1	94.9
A	0.2	20.1	44.4	45.2	61.5	55.0

Cyclohexene has a high reactivity, which is reflected in the high values of conversion even at low temperatures. The quantity of aromatics that is formed is high, reaching 60% at 450°C. At 500°C a slight decrease is observed, that can be explained by the intense cracking reactions leading to methane and  $C_2$  fraction. The formation of aromatics (even in small quantities) begins at low temperatures (200°C).

Up to 350°C, reaction products contain only traces of gaseous hydrocarbons, indicating that, for this feed, cracking is less important at low temperatures. The formation of cyclohexane and n-hexane was observed, suggesting the presence of hydrogenation and disproportionation reactions. Dehydrogenation to benzene is also possible. However, we consider that none of these paths has a large importance, because cyclohexane and benzene concentrations are small, and at all temperatures benzene has a low concentration (it is the least important aromatic hydrocarbon).

As the temperature increases, cracking reactions intensify, leading to unsaturated compounds. The highest probability in such a cracking reaction is for ethene and butadiene to be formed, and they were indeed observed in reaction products. Alkynes were never observed, and we never found in the literature any indication concerning alkynes formation in the cracking step, so we consider this path to have a low probability. Another argument for butadiene formation in cracking reaction is the high concentration of butanes and butenes in reaction products, and also the high concentration of xylenes – the main aromatic hydrocarbon up to 450°C. The lower concentration of C<sub>3</sub> fraction in products suggests that the probability of a symmetrical cracking of cyclohexene, is less important.

It is obvious that at this Zn concentration (0.57%), the dehydrogenation of cyclohexene is less important, the reactions by hydride transfer mechanism on the acidic function being predominant.

The dependence of cyclohexene conversion on temperature was also studied by *in situ* IR spectroscopy [16] on a sample of the same zeolite, but with 2% Zn. Although the zinc concentration is different, the effect is similar. Even at 210°C the presence in the IR spectrum of some bands characteristic to the aromatic ring was observed (1485 cm<sup>-1</sup>, 3000÷3100 cm<sup>-1</sup>), simultaneously with the attenuation of the absorption bands for cyclohexene (1420÷1440 cm<sup>-1</sup>, 2800÷3000 cm<sup>-1</sup>). This fact demonstrates that the conversion to aromatics takes place even at low temperatures. The simultaneous attenuation of the band characteristic to Brønsted acid sites at 3610 cm<sup>-1</sup> suggests the cyclohexene interacts with this type of sites. Increasing the temperature up to 450°C indicates a substantial modification of the IR spectrum, with lower intensity of the cyclohexene bands and intensification of the bands due to aromatic ring.

## Conclusions

For all C<sub>6</sub> hydrocarbons used as feed, increasing temperatures lead to higher conversion values, due to the fact that all the reactions are endothermic. At low temperatures the transformation involves mainly cracking reactions (except for cyclohexene), leading to C<sub>3</sub>-C<sub>4</sub> hydrocarbons. At high temperatures important quantities of C<sub>2</sub> fraction and methane are formed. Aromatics appear above 300°C (except for cyclohexene, that leads to aromatics even at 200°C), and the quantity of aromatics rises with temperature up to 450°C. At 500°C a decrease was observed for some of the feed hydrocarbons, probably due to more advanced cracking of reaction intermediates. For all feeds, xylenes are the main aromatic up to 400°C, above this temperature toluene becoming predominant. Benzene has low concentrations, only slightly increasing with temperature. Because of this behaviour, we concluded that direct dehydrogenation is not an important pathway for the C<sub>6</sub> hydrocarbons conversion to aromatics on 0.57% Zn/H-ZSM-5 catalyst.

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