

Dehydrocyclization of *n*-heptane over a PtBa/KI catalyst: reaction mechanism

Adolfo Arcoya*, Xosé L. Seoane, Javier M. Grau¹

Department of Applied Catalysis, Instituto de Catálisis y Petroleoquímica, CSIC, C/Marie Curie No. 2, Cantoblanco, 28049-Madrid, Spain

Received 13 September 2004; received in revised form 13 January 2005; accepted 13 January 2005

Available online 10 February 2005

Abstract

The dehydrocyclization of *n*-heptane to toluene over a 1 wt.% PtBa/KL catalyst was studied in a fixed bed tubular reactor, at 723 K, 100 kPa and space-time in the range of 1.8–117.0 g h mol⁻¹. The catalyst was prepared by incipient wetness impregnation of a KL zeolite, previously alkalinized with BaO, using an aqueous solution of tetraammineplatinum(II) hydroxide as platinum precursor. The solid was successively calcined in an oxygen stream and reduced in flowing hydrogen, at 773 K. Reaction is highly selective towards toluene (>60%) at conversion levels even close to 100%, with benzene, heptenes, methylcyclohexane and ethylcyclopentane as major byproducts. From the product distribution and the dehydrocyclization results of the reaction products performed in separate experiments, a macroscopic mechanism is proposed. Essentially, *n*-heptane is adsorbed and transformed on the catalyst surface through an alkene-like intermediate (σC_7^-), following five possible parallel interconnected paths, involving hydrogenolysis, isomerization, dehydrogenation and cyclization reactions. Formation of toluene as a primary product is explained by a “rake scheme” in which the σC_7^- intermediate is successively transformed, following two possible routes: (a) C₁–C₆ ring closure and subsequent further dehydrogenation; (b) successive dehydrogenation to heptatriene and then cyclization to toluene. These transformations occur in the adsorbed phase and on the same active site, in such a way that only a small fraction of the total adsorbed intermediates formed appear in the gas phase. The rest are not desorbed due to their high reactivity.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Pt/KL catalysts; *n*-Heptane dehydrocyclization mechanism; Toluene; Methylcyclohexane; Ethylcyclopentane

1. Introduction

Ever since Bernard [1] reported the high selectivity of the non-acid Pt/KL catalysts to transform *n*-hexane into benzene, several geometric and electronic hypothesis have been proposed to explain the improved aromatization selectivity of these catalysts. Several authors [2–4] have attributed this singular property to electron rich Pt particles, formed by interaction of the metal with the basic framework of the zeolite. Iglesia and Baumgartner [5], however, claimed that

the aromatizing activity is actually an intrinsic property of a clean platinum surface, whatever the support is. The role of the KL zeolite would be, for these authors, to prevent carbon fouling of the Pt particles, because the channels structure inhibits bimolecular reactions leading to coke formation. Jacobs et al. [6] among others confirmed these finding comparing KL with non-microporous basic and non-acidic supported metal oxides. These authors also confirmed the rapid deactivation by coke deposits of the unprotected Pt clusters on the catalysts. McVicker et al. [7] on the other hand claimed that the KL-zeolite hinders the agglomeration of platinum particles. According to the geometric explanation proposed by Tauster and Steger [8], the structure of the KL zeolite orients the alkane molecule in the linear channels, in such a way that it favors the terminal C-adsorption and the C₁–C₆ ring closure on Pt sites. For Derouane and Vanderveken [9]

* Corresponding author. Tel.: +34 91 5854804; fax: +34 91 5854760.

E-mail address: aarcoya@icp.csic.es (A. Arcoya).

¹ Present address: Instituto de Investigaciones en Catálisis y Petroquímica, INCAPE (UNL, FIQ-CO), Santiago del Estero 2654, 3000 Santa Fe, Argentina.

the cavities of the zeolite would lead to preorganization of the hydrocarbon chain adsorbed on C_1 to adopt a structure resembling the transition state for the C_1 – C_6 cyclization from the *n*-alkane (confinement model). Triantafyllou et al. [10] considered, on the other hand, that the high aromatizing selectivity of Pt/KL could be attributed to some combination of effects such as, size of the Pt clusters, basicity of the zeolite and constrictions imposed by the support channels. These hypotheses are basically derived from studies of the catalyst and essentially oriented to explain the formation of the C_1 – C_6 cycle, but dehydrocyclization is a very complex process involving multiple individual reactions, such as cyclization, dehydrogenation, skeletal isomerization and hydrogenolysis, with formation of numerous intermediates and final products. To our knowledge, papers dealing with the paths or chemical routes that follow the reactants through the intermediates to arrive to the final products on Pt/KL zeolite catalysts are rather scarce and mainly devoted to *n*-hexane [11–13]. Lafyatis et al. [14] using a TAP reactor evidenced that partially dehydrogenated linear C_6 molecules are intermediates between *n*-hexane and benzene in a monofunctional reaction pathway. In this mechanism dehydrogenation steps occur rapidly while the 1,6 ring closure is the slow step.

In synthesis, it seems that the more shared opinion about the principal path leading to benzene involves the successive dehydrogenation of *n*-hexane to more and more deeply unsaturated lineal C_6 -hydrocarbons followed by C_1 – C_6 ring closure. For isoalkanes it is generally accepted that they are preferentially formed via hydrogenolysis of the cyclopentane ring formed upon C_1 – C_5 cyclization, rather than by bond-shift reaction from *n*-hexane.

Regarding *n*-heptane, to our knowledge, there is not any paper describing an overall path-model for the dehydrocyclization on Pt/KL catalysts. In an early work dealing with the aromatization of *n*-heptane on “non-acid” Pt/ Al_2O_3 catalysts, Pines and Nogueira [15] found that direct cyclization C_1 – C_6 occurs via ring closure of heptatrienes to methylcyclohexadiene. Skeletal isomerization takes place by hydrogenolysis of ethylcyclopentane and to a smaller extent by a bond-shift process. Iglesia et al. [16] studied the dehydrocyclization mechanism on a tellurium-based catalyst using *n*-heptane-1- ^{13}C and found that toluene is formed by the successive heptane dehydrogenation and thermal cyclization of an equilibrated mixture of conjugated and nonconjugated heptatrienes. Heptane isomers would be formed predominantly by methyl and ethyl shift-reaction of heptenes, probably on Te/NaX weak acid, and not by hydrogenolysis of C_5 -ring species. The authors found that this catalyst only exhibits dehydrogenation activity but not cyclization function. Davis [17] in an extensive and well documented review of the alkanes dehydrocyclization mechanisms for monofunctional catalysts, pointed out that, at all pressures, aromatics are primary products, which are formed by a mechanism involving direct six-carbon ring formation.

In previous works, we studied the effect of Ba and La on the properties and performance of Pt/KL catalysts in the

dehydrocyclization of *n*-heptane. We found that the partial exchange of K^+ by Ba^{2+} does not substantially modify the *n*-heptane aromatization activity of Pt/KL, while the exchange by La^{3+} significantly decreases the dehydrocyclization activity and promotes the acid activity of the catalyst [18]. In contrast, when KL zeolite was impregnated with barium nitrate followed by calcination at 873 K, the barium oxide species formed improve the dehydrocyclization activity of Pt/KL [19]. XPS and TEM-XEDS measurements evidenced that, in these catalysts, barium and platinum are reasonably well distributed in such a way that platinum is always in the close vicinity of barium. Additionally, from the characterization results and the coke amounts measured in the spent samples we concluded that, at atmospheric pressure, the PtBa/KL catalysts are more aromatizing than Pt/KL, because BaO produces two effects, namely, inhibition of coke formation and electronic promotion of platinum inside the channels. Both effects positively cooperate in the dehydrocyclization of *n*-heptane.

In order to derive a reaction mechanism, dehydrocyclization of *n*-heptane was studied at 723 K, 100 kPa and contact time between 1.8 and 117.0 g h mol $^{-1}$, and the reactivity of some of the reaction products evaluated under comparable experimental conditions.

2. Experimental

2.1. Catalyst preparation

A portion of KL zeolite (Union Carbide, SK-45, $K_9Al_9Si_{27}O_{72}$, in atoms per unit cell) calcined in air at 873 K for 3 h, pelleted and crushed to 0.6–1.0 mm particle size, was impregnated by incipient wetness technique with a barium nitrate aqueous solution in the required concentration to obtain 3 wt.% Ba. The solid was successively dried at 393 K, calcined at 873 K for 3 h and then loaded with 1 wt.% of Pt by incipient wetness impregnation, using an aqueous solution of tetraammineplatinum(II) hydroxide (>99%). After calcining at 573 K in an oxygen stream, the solid was successively reduced in flowing hydrogen at 773 K for 3 h and evacuated under flow of helium at room temperature. The catalyst, labeled as PtBa/KL, was stored in a desiccator.

2.2. Dehydrocyclization activity measurements

The catalytic activity measurements were carried out in a fixed bed tubular reactor at 723 K and atmospheric pressure, with a molar ratio hydrogen/*n*-heptane = 7.3 and space-time (W/F), referred to the liquid fed, between 1.8 and 117.0 g h mol $^{-1}$. A bed of carborundum above the catalyst bed in the reactor was employed as preheater. High purity hydrogen was successively passed through a Deoxo purifier and a 5 Å molecular sieve filter. The catalyst was prereduced at 773 K for 1 h under the hydrogen flow used in the reaction

and then cooled down to 723 K. Once the system was stabilized, *n*-heptane was fed and the first sample of the reactor effluent collected 5 min later. Most of the reaction products were condensed at 273 K and later analyzed by gas chromatography in a 1,2,3-tris(2-cyanoethoxy)propane 10 wt.%/Chromosorb P column. Exit gas was also analyzed in the same column and in another of powdered activated charcoal, this last to determine methane. In order to know the effect of the time on stream on the product distribution, samples of the reactor effluent were taken each 15 min for 5 h. From the flow of *n*-heptane fed, the amount of liquid collected, the exit gas flow and the chromatographic results, the carbon mass balance was made. The mass balance error in all experiments performed in this work was estimated to be about $\pm 3\%$.

In order to prevent both external and internal diffusional limitations two sets of experiments were previously performed, namely, (a) working with catalyst weight between 2.4 and 8.0 g, but maintaining constant the space–time ($W/F = 30 \text{ g h mol}^{-1}$), the conversion remained constant; (b) using catalyst particle sizes in the ranges of 2.38–1.41, 1.41–1.0, 1.0–0.6 and 0.6–0.47 mm, the conversion increased, going from 2.38–1.41 to 1.41–1.0 mm, and then remained constant. These results indicate that under the experimental conditions used in this work, the process is essentially controlled by the kinetics of the reaction and verify that either internal or external diffusional limitations are negligible.

In order to determine the reproducibility of the measurements, some experiments were repeated several times and the standard deviations for *n*-heptane conversion and yields of the main products calculated. From the values obtained, the average standard deviation was estimated to be $\pm 2.5\%$. Reactivity of some reaction products, probable intermediates in the reaction of toluene formation (1- and 2-heptene, methylcyclohexane, 2- and 3-methylhexane, ethylcyclopentane, ethylpentane, benzene and toluene) was evaluated at 8 and 30 g h mol^{-1} at 723 K, following a similar procedure as was used in the case of *n*-heptane.

3. Results and discussion

Extensive characterization of the catalyst by ICP, $\text{H}_2\text{-O}_2$ titration, TPR, CO/FT-IR, TEM-XEDS and XPS was reported in Ref. [17] (sample CBaPt3). Briefly, some results are: platinum loaded 0.97 wt.%, barium content 2.87 wt.%, platinum dispersion 34% and average platinum crystal size 2.64 nm. This last value is larger than the dimensions of the cavities ($0.48 \text{ nm} \times 1.24 \text{ nm} \times 1.07 \text{ nm}$) and windows (0.71 nm) of the zeolite, but it does not imply that platinum is only located on the external surface of the support. Our TEM-XEDS results, discussed in Ref. [19] rather indicate that there is a bimodal distribution of metal particles, with small clusters located inside the channels and larger particles on the external surface. On the other hand, the ICP results of

the used catalyst samples indicated that no loss of either platinum or barium occurs during the reaction.

3.1. Effect of the space–time on the dehydrocyclization of *n*-heptane

To establish the path model of dehydrocyclization of *n*-heptane it is necessary to discriminate between primary and secondary products of reaction, as well as between intermediate and final products. With this purpose we have studied the product distribution as a function of the space–time between 1.8 and 117.0 g h mol^{-1} , at 723 K. In all cases, the major products were toluene and benzene, with heptane and heptene isomers, methylcyclohexane, ethylcyclopentane and hydrogenolysis products as byproducts. The catalytic performance has been characterized by *n*-heptane conversion (X), defined as the percentage of reactant fed to the reactor transformed into products and yield to a product i (Y_i) as the number of *n*-heptane molecules transformed into i per 100 molecules of *n*-heptane fed. Selectivity toward a product i (S_i) is the number of *n*-heptane molecules transformed into i per 100 molecules of *n*-heptane transformed. The initial rate of transformation of *n*-heptane into a product i ($\text{mol } n\text{-heptane g}_{\text{cat}}^{-1} \text{ h}^{-1}$) is calculated from the slope of the curve $Y_i = f(W/F)$ at the origin.

Plots in Fig. 1 show the *n*-heptane conversion versus space–time for the fresh and stabilized catalyst. For the fresh catalyst (5 min on stream) the rate of reaction is constant up to 70% conversion and then progressively decreases until reaching 100% conversion. In all the runs it was observed that conversion decreases during the initial stage of operation (5–60 min) and then it reaches a pseudo steady state, which remains practically stable for several hours (stabilized catalyst). Since no loss of platinum was detected during the runs, deactivation is attributed to coke deposition. It is highly probable that the coke deposition occurs on part of the larger metal particles located on the external surface of the zeolite, which are unprotected from the bimolecular collisions, as it was found by Resasco and coworkers for *n*-hexane dehydrocyclization [6].

To illustrate the effect of the deactivation on the catalytic performance, the product selectivities obtained after 5 and 120 min on stream for a representative experiment have been summarized in Table 1. It can be seen that while conversion decreases from 69 to 50%, selectivities are not significantly modified, indicating that the effect of coke is merely to block the platinum clusters located outside the zeolite and, consequently, decrease the effective metal surface. Thus, in order to establish the reaction mechanism we have used the results obtained at 120 min on stream, when the catalyst performance is well stabilized.

Yield to products is plotted as a function of the space–time in Figs. 2–6. From the shapes of the curves and values of their slopes at the origin (r_i , initial formation rates summarized in Table 2) one can identify primary products ($r_i > 0$), secondary products ($r_i = 0$), intermediates (a

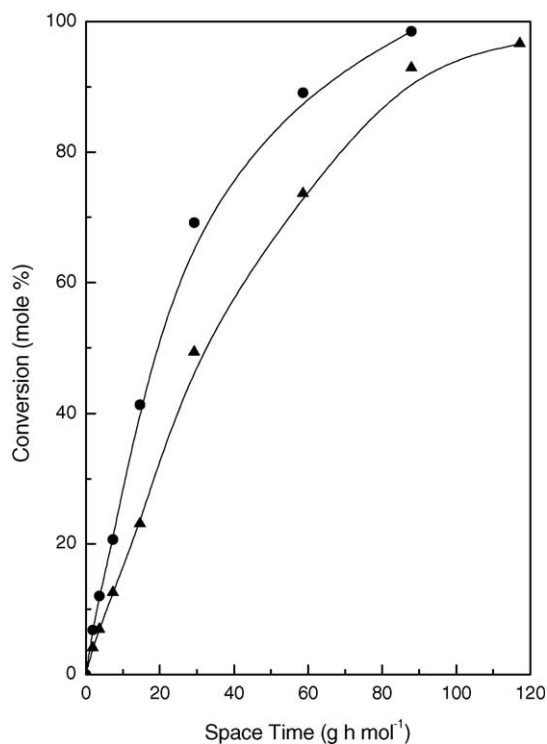


Fig. 1. Effect of space-time on conversion of *n*-heptane at 723 K, 100 kPa and H_2/n -heptane = 7.3 mol/mol on the Pt/BaKL catalyst after 5 (●) and 120 min (▲) on stream.

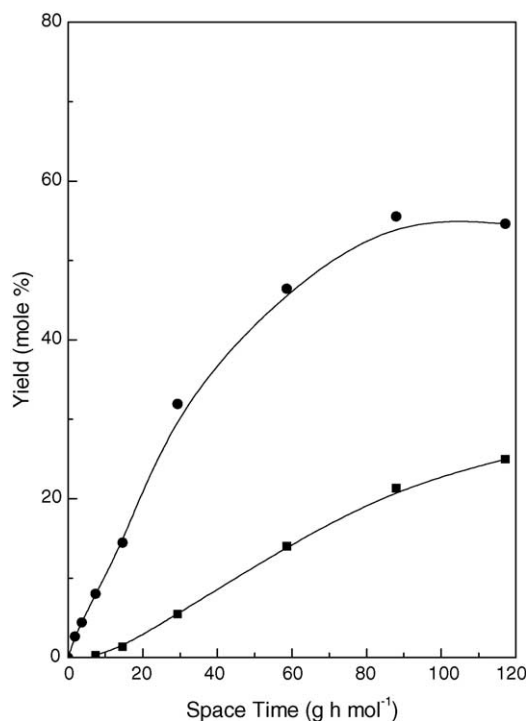


Fig. 2. Dehydrocyclization of *n*-heptane over Pt/BaKL catalyst at 723 K, 100 kPa and H_2/n -heptane = 7.3 mol/mol. Yield to toluene (●) and benzene (■) vs. space-time.

maximum) and final products (positive slope in the entire curve).

3.1.1. Formation of aromatics

Fig. 2 shows that toluene is formed from the beginning of reaction ($r_T = 9.61 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$) i.e., it is a primary product. Its yield trends upward with space-time to a maximum for $W/F = 90 \text{ g h mol}^{-1}$ ($Y_{\text{max}} = 96\%$) and then decreases indicating that it is converted into other products. The appearance of toluene as a primary product suggests that it is formed directly from *n*-heptane, probably through a

Table 1

Dehydrocyclization of *n*-heptane over PtBa/KL after 5 and 120 min on stream

	Time on stream (min)	
	5	120
Conversion (mol%)	68.6	50.0
Selectivity (mol%) to:		
Toluene	61.6	62.1
Benzene	11.3	11.0
Methane	3.2	3.2
Alkanes C ₂ –C ₆	12.0	11.8
<i>i</i> -Heptanes	3.3	1.7
Heptenes	2.9	3.1
Cycloalkanes C ₇	3.5	5.5
Cycloalkanes C ₅ –C ₆	2.2	1.6

H_2/n -C₇H₁₆ = 7.3 mol/mol, $W/F = 30 \text{ g h mol}^{-1}$, $T = 723 \text{ K}$ and $P = 100 \text{ kPa}$.

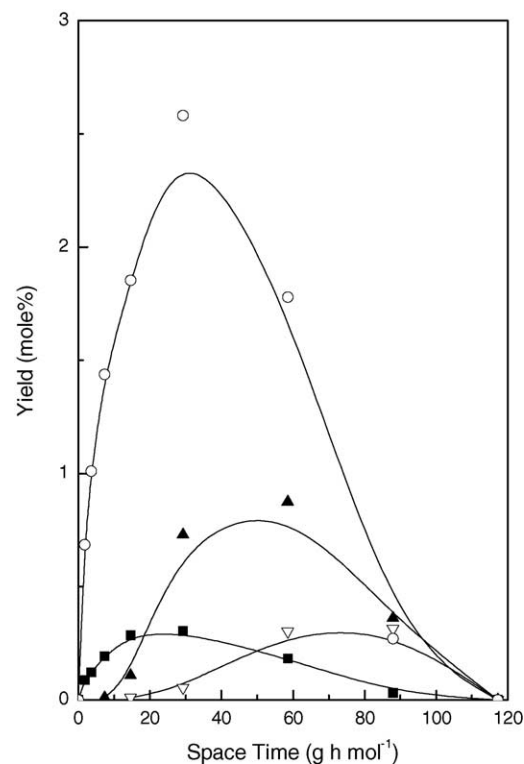


Fig. 3. Dehydrocyclization of *n*-heptane over Pt/BaKL catalyst at 723 K, 100 kPa and H_2/n -heptane = 7.3 mol/mol. Yield vs. space-time for methylcyclohexane (■), ethylcyclopentane (○), methylcyclopentane (▲) and cyclopentane (▽) at 723 K, 100 kPa and H_2/n -heptane = 7.3 mol/mol.

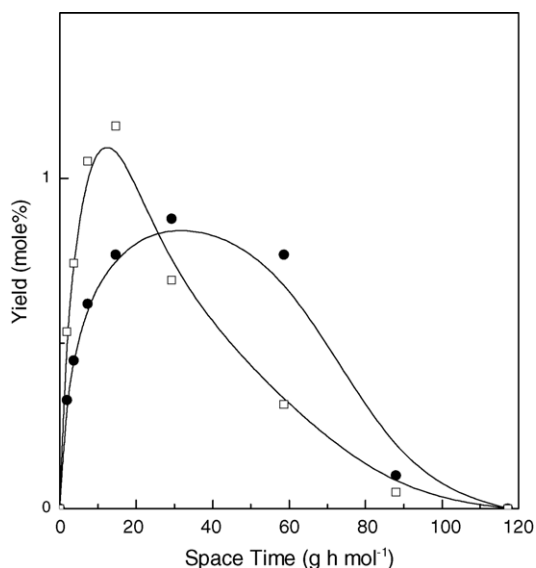


Fig. 4. Dehydrocyclization of *n*-heptane over Pt/BaKL catalyst at 723 K, 100 kPa and H_2/n -heptane = 7.3 mol/mol. Yield vs. space-time for 1-heptene (●) and 2-heptene (□) at 723 K, 100 kPa and H_2/n -heptane = 7.3 mol/mol.

consecutive process in which the intermediates are adsorbed species that quickly transform on the same active site of the catalyst surface from heptane to toluene. Benzene appears after an induction period ($r_B = 0$) and then its yield continuously grows up, indicating that it is a secondary and final product. This is a logical result because benzene, in our case, is not formed directly from *n*-heptane, but from toluene, by hydrogenolysis of its lateral chain, and from the dehydrocyclization of hexane byproduct.

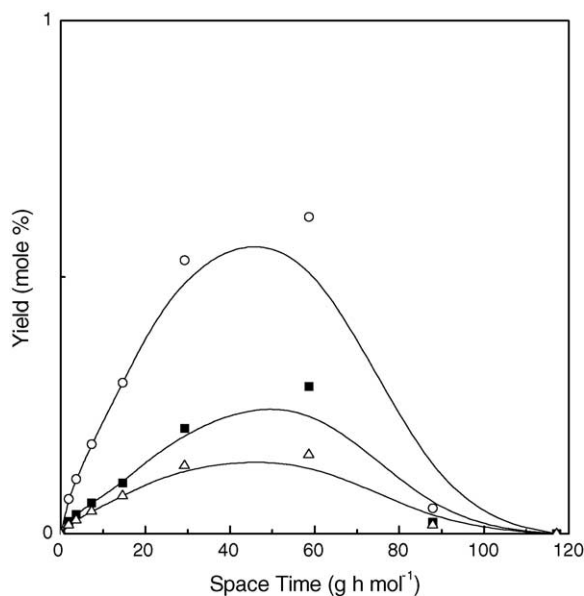


Fig. 5. Dehydrocyclization of *n*-heptane over Pt/BaKL catalyst at 723 K, 100 kPa and H_2/n -heptane = 7.3 mol/mol. Yields to heptane isomers as a function of the space-time: 2-methylhexane (■), 3-methylhexane (○) and ethylpentane (△), at 723 K, 100 kPa and H_2/n -heptane = 7.3 mol/mol.

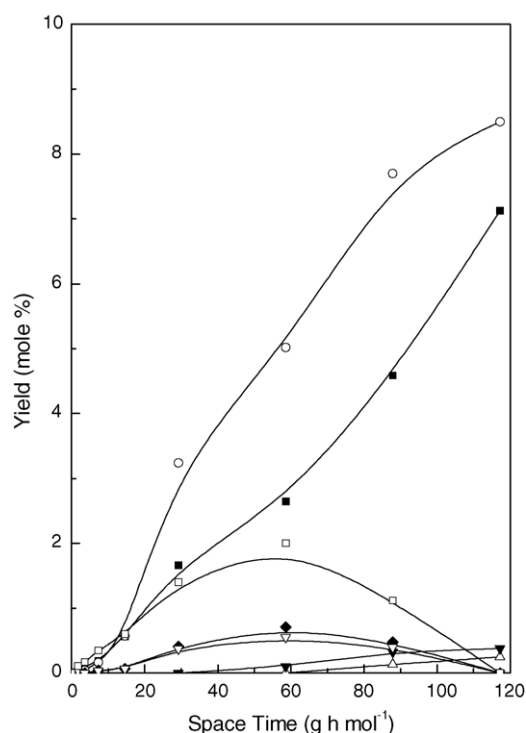


Fig. 6. Influence of the space-time on the yield to *iso*- and *n*-(C₆-C₁) alkanes in the dehydrocyclization of *n*-heptane at 723 K, 100 kPa and H_2/n -heptane = 7.3 mol/mol over Pt/BaKL catalyst: methane (■), C₂-C₃ alkanes (○), *n*-hexane (□), 2-methylpentane (◆), 3-methylpentane (▽), *i*-butane (△) and *i*-pentane (▼).

Table 2
Initial product formation rates after 120 min on stream

Product	r_i (mmol g _{cat} ⁻¹ h ⁻¹)
Aromatics	
Toluene	9.61
Benzene	0.00
Cycloalkanes	
Ethylcyclopentane	3.10
Methylcyclohexane	0.28
Methylcyclopentane	0.00
Cyclopentane	0.00
Alkenes	
1-Heptene	1.56
2-Heptene	2.27
Heptane isomers	
2-Methylhexane	0.07
3-Methylhexane	0.21
Ethylpentane	0.04
Alkanes C₆-C₁	
<i>n</i> -Hexane	0.56
2-Methylpentane	0.00
3-Methylpentane	0.00
<i>n</i> -(C ₅ -C ₂)	–
<i>i</i> -Pentane	0.00
<i>i</i> -Butane	0.00
Methane	0.47

H_2/n -C₇H₁₆ = 7.3 mol/mol, W/F = 30 g h mol⁻¹, T = 723 K and P = 100 kPa.

The few papers devoted to the dehydrocyclization of *n*-heptane over KL-supported catalysts do not report conclusions regarding to its primary or non-primary character. For benzene from *n*-hexane, Jacobs et al. [6] noticed that it is a secondary product, while Miller et al. [13] suggested that it is a primary product. Paál and coworkers [20] on the other hand, found that the primary or secondary character of benzene depends on the catalyst preparation method. However, due to their different molecular structure, extrapolation of the benzene conclusions to toluene cannot be accurate, because the relative values of the surface reaction rate constants of the intermediates and their adsorption–desorption equilibrium constants can be very different for both molecules.

3.1.2. Formation of cycloalkanes

The initial slopes of the curves in Fig. 3 indicate that methylcyclohexane (MCC6) and ethylcyclopentane (ECC5) are primary products ($r_{\text{MCC6}} = 0.28$ and $r_{\text{ECC5}} = 3.13 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$). The fact that these curves quickly reach a maximum and then fall to zero suggests that both cycloalkanes are very reactive intermediates. Methylcyclopentane (MCC5) and cyclopentane (CC5) are secondary products ($r_i = 0$) and, as deduced from Fig. 3, they are formed from ethylcyclopentane in a sequential hydrogenolysis process in the lateral chain.

Methylcyclohexane and ethylcyclopentane are formed by direct cyclization of *n*-heptane through two parallel reactions: C₁–C₆ and C₁–C₅ ring closure, respectively. Both reactions are claimed in the literature, although the 1,6-cyclization is more favored, at least over platinum on non-acid supports at the temperature used in the present work [21].

3.1.3. Formation of heptene and heptane isomers

Profiles in Fig. 4 show that 1-heptene (1-C₇[−]) and 2-heptene (2-C₇[−]) are primary products ($r_{1\text{-C}_7} = 2.27 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ and $r_{2\text{-C}_7} = 1.56 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$) and very reactive because they reach a maximum for relatively low values of space–time (<30 g h mol^{−1}) and then go to zero. In a similar way, the positive initial slopes of the yield curves for 3-methylhexane (3MC6), 2-methylhexane (2MC6) and ethylpentane (EC5) in Fig. 5 (see r_i values in Table 2) indicate that these three compounds are primary products. Furthermore, the fact that the yields pass through a maximum provides evidence that they are, as well, precursors of other products.

According to several authors [15] most of the skeletal isomerization of *n*-heptane on monofunctional Pt catalysts occurs via hydrogenolysis of the ethylcyclopentane ring, giving 3-methylhexane and ethylpentane. On the other hand, for Iglesia et al. [16], with a Te/XNa catalyst, the bond-shift mechanism involving an α , γ , γ triadsorbed intermediate [22] may account for the three *n*-heptane isomers. Bond-shift reaction, occurs preferentially on platinum catalysts of low and medium dispersion [23], which is our particular case ($D = 34\%$). Since 2-methyl-

hexane can never be formed from ethylcyclopentane ring opening, the fact that it appears in all the range of space–time analyzed indicates that the bond-shift mechanism is operative in our system. This result is not surprising if one consider that PtBa/KL catalyst exhibits a bimodal distribution of metal particles, with larger clusters outside the channels which remain partially active with time, thanks to the stabilizing effect of Ba. Actually, deactivation of PtBa/KL is lower than that observed for Pt/KL catalyst, as it was referenced [19]. Therefore, we think that in our conditions both mechanisms may be operative.

3.1.4. Formation of alkanes C₁–C₆

In all the experiments the reaction product contained small concentrations of C₁–C₆ linear alkanes, formed from *n*-heptane by a nonselective hydrogenolysis on Pt metal [24]. These compounds do not play any significant role in the pathway of toluene formation, although *n*-hexane is certainly a precursor of benzene. The overall yield to C₂–C₅ alkanes versus space–time is represented in a single curve in Fig. 6, while the yields to *n*-hexane and methane are plotted separately, showing that both are primary products. The maximum and the subsequent drop in *n*-hexane yield with space–time are consistent with the fact that it is an intermediate for benzene production. On the other hand, the continuous increase of the methane yield from the beginning of reaction indicates that it is a primary and final product.

Isoalkanes C₆, C₅ and C₄ appear to be secondary products ($r_i = 0$). Hexane isomers (2- and 3-methylpentane) are produced by scission of methylcyclopentane previously formed from *n*-hexane by 1,5 ring closure [14]. The yields of these products exhibit a maximum and then decline probably due to their conversion into benzene. The yields of *i*-pentane and *i*-butane grow in all the range of space–time analyzed, indicating that they are more stable molecules.

3.1.5. Selectivity toward the reaction products

Plots of selectivity to the more significant products versus heptane conversion are given in Fig. 7. Extrapolation of the curves to zero conversion clearly confirms that toluene, ethylcyclopentane, methylcyclohexane and heptenes are primary products (intercept > 2). The fact that methylhexanes and ethylpentane are detected at very low conversions even with very low selectivity led us to conclude that they are likely primary products. In contrast, benzene is a nonprimary product (zero selectivity for $X \rightarrow 0$) and, moreover, its selectivity increases with conversion while the selectivity towards toluene remains roughly constant up to high conversion values and then it slightly decays. This result indicates that transformation of toluene into benzene is only relevant for the higher space–time values, after a high conversion of *n*-heptane is reached. At low conversion it is reasonable to assume that *n*-hexane produces benzene, as it is repeatedly reported in the literature.

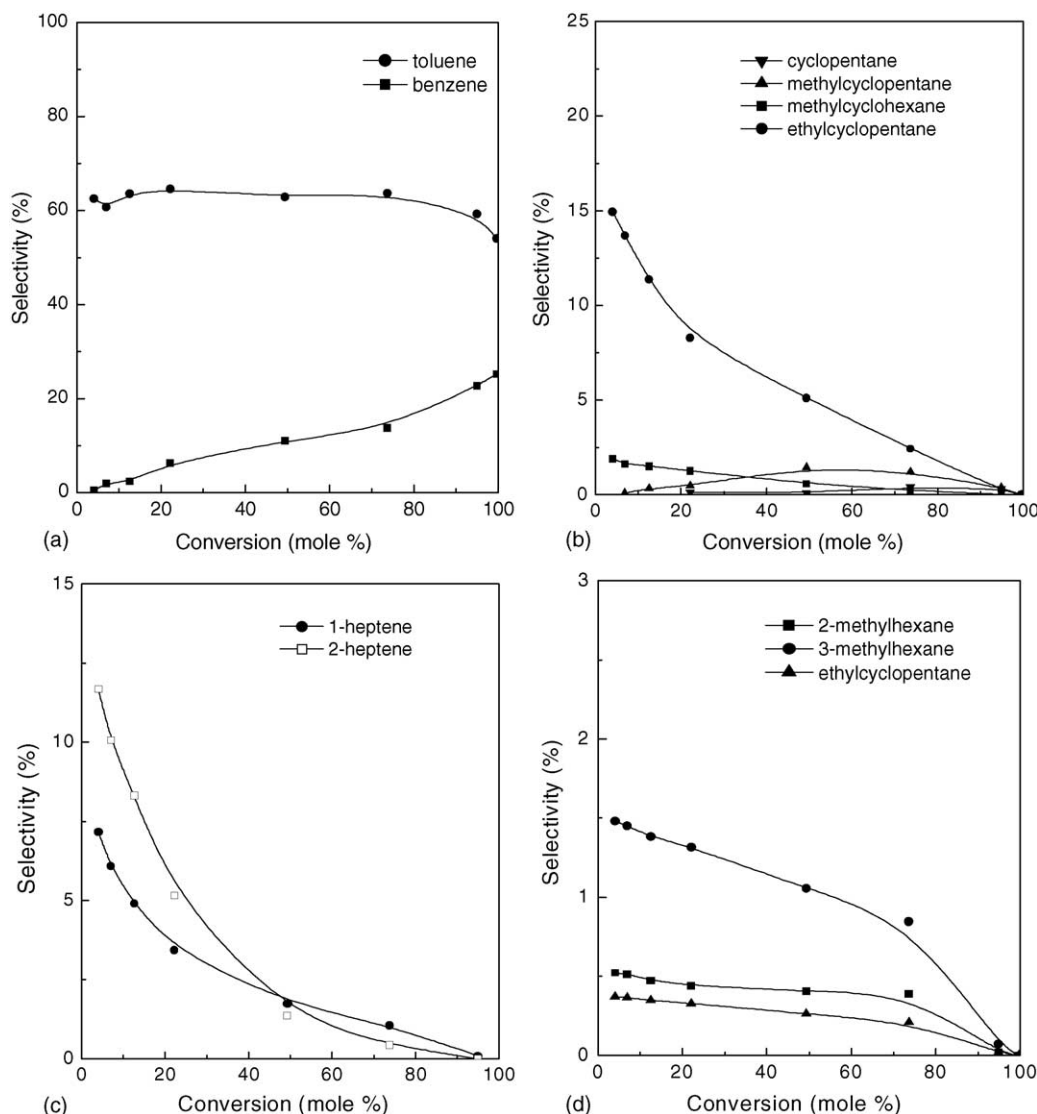


Fig. 7. Selectivity toward the reaction products as a function of the *n*-heptane conversion at 723 K, 100 kPa and H_2/n -heptane = 7.3 mol/mol over Pt/BaKL catalyst: (a) aromatics: toluene (●), benzene (■); (b) cycloalkanes: cyclopentane (▼), methylcyclopentane (▲), methylcyclohexane (■) and ethylcyclopentane (●); (c) heptenes: 1-heptene (●) and 2-heptene (□); (d) heptane isomers: 2-methylhexane (■), 3-methylhexane (●) and ethylcyclopentane (▲).

3.2. Reactivity of the reaction products

From the results analyzed above one can assert that *n*-heptane is transformed over Pt/Ba/KL catalyst following different reactions, namely, cyclization, dehydrogenation, isomerization and hydrogenolysis leading to the identified hydrocarbons. In order to gain insight into the role of the reaction products in the pathway of the overall reaction, additional experiments were carried out at 723 K using separately toluene, benzene, 1- and 2-heptene, methylcyclohexane, ethylcyclopentane, 2- and 3-methylhexane and ethylpentane, as reactants.

The results obtained working at 8 and 30 $g\ h\ mol^{-1}$ are given in Tables 3 and 4, where those corresponding to *n*-heptane under similar experimental conditions have also been included for the purpose of comparison. From

tabulated thermodynamic data [25] we have calculated the values of standard enthalpies (ΔH_r°) and equilibrium constants (K_{eq}) at 723 K for some possible individual reactions involved in the overall process (Table 5).

3.2.1. Toluene and benzene

Conversion of toluene, under conditions of dehydrocyclization, at $W/F = 8\ g\ h\ mol^{-1}$ was practically zero and at 30 $g\ h\ mol^{-1}$ only 6%, with benzene and methane as the only reaction products (Table 3). The yield to benzene (5.1%) is lower than that obtained from *n*-heptane under similar conditions (7.8%). This is an important result because it confirms that another source of benzene, in addition to toluene, do exist. On the other hand, we have experimentally verified that benzene is unreactive at 723 K, indicating that it is a final product of reaction.

Table 3
Reactivity of *n*-heptane, toluene, 1-heptene and methylcyclohexane under conditions of dehydrocyclization

	Compound						
	<i>n</i> -heptane		Toluene		1-Heptene, 8 ^a	Methylcyclohexane	
	8 ^a	30 ^a	8 ^a	30 ^a		8 ^a	30 ^a
Conversion (mol%)	20.5	68.6	0.0	6.0	98.7	86.0	99.8
Yield (mol%) to:							
Methane	0.3	2.3	0.0	0.9	0.3	0.3	2.7
C ₂ –C ₅ alkanes	0.5	5.9	0.0	0.0	1.5	0.0	0.0
Cyclopentane	0.0	0.5	0.0	0.0	0.1	0.0	0.0
<i>i</i> -Hexane	0.3	1.4	0.0	0.0	0.2	0.0	0.0
<i>n</i> -Hexane	0.1	0.7	0.0	0.0	0.3	0.0	0.0
Methylcyclopentane	0.1	1.0	0.0	0.0	0.3	0.0	0.0
Benzene	1.0	7.8	0.0	5.1	1.3	1.1	12.7
2-Methylhexane	0.1	0.4	0.0	0.0	0.4	0.0	0.0
3-Methylhexane	0.4	0.9	0.0	0.0	0.9	0.0	0.0
Ethylpentane	0.1	0.3	0.0	0.0	0.3	0.0	0.0
1-Heptene	0.9	1.3	0.0	0.0	–	0.0	0.0
<i>n</i> -Heptane	–	–	0.0	0.0	69.1	0.0	0.0
2-Heptene	0.9	0.7	0.0	0.0	1.6	0.0	0.0
Methylcyclohexane	0.4	0.4	0.0	0.0	0.9	–	–
Ethylcyclopentane	2.7	2.7	0.0	0.0	4.2	0.0	0.0
Toluene	12.7	42.3	–	–	17.3	84.6	84.4

H₂/hydrocarbon = 7.3 mol/mol, *T* = 723 K and *P* = 100 kPa.

^a *W/F* (g h mol⁻¹).

3.2.2. Heptenes

1-Heptene is highly reactive (*X* = 98.7%, at 8 g h mol⁻¹, Table 3). Its yield to toluene (17.3%) is higher than that obtained from *n*-heptane (12.7%) and the product distribution is qualitatively similar to that obtained in the dehydrocyclization of *n*-heptane, suggesting that it is an intermediate in the formation of toluene from *n*-heptane. It is important to remark that toluene and *n*-heptane (*Y*_{*n*C₇} = 69.1%) are the major reaction products, which

are formed through two parallel reactions, dehydrocyclization and hydrogenation, respectively. The former is endothermic ($\Delta H_{723}^{\circ} = 123.3$ kJ/mol) and the last exothermic ($\Delta H_{723}^{\circ} = -130$ kJ/mol) although both reactions are thermodynamically favored (see Table 5). Furthermore, the fact that the yields to methylcyclohexane and ethylcyclopentane are higher than those obtained from *n*-heptane suggests that 1-heptene is, as well, an intermediate in the cyclization paths and, probably, the first of the series of

Table 4
Dehydrocyclization of *n*-heptane, 2-heptene, ethylcyclopentane, 2-ethylhexane, 3-methylhexane and ethylpentane

	Compound ^a					
	<i>n</i> -Heptane	2-Heptene	Ethylcyclopentane	2-Methyl-hexane	3-Methyl-hexane	Ethyl-pentane
Conversion (mol%)	20.5	98.4	17.7	20.3	22.4	9.5
Yield (mol%) to:						
Methane	0.3	0.3	0.8	0.1	0.6	0.4
C ₂ –C ₅ alkanes	0.5	1.6	0.6	0.0	0.7	0.2
Cyclopentane	0.0	0.1	0.1	0.0	0.1	0.1
<i>i</i> -Hexane	0.3	0.1	0.3	0.0	0.4	0.3
<i>n</i> -Hexane	0.1	0.2	0.1	0.0	0.1	0.1
Methylcyclopentane	0.1	0.4	0.4	0.0	0.2	0.1
Benzene	1.0	1.2	1.6	2.1	4.2	1.3
2-Methylhexane	0.1	0.4	<0.1	–	0.4	<0.1
3-Methylhexane	0.4	0.9	0.7	0.4	–	<0.1
Ethylpentane	0.1	0.3	0.7	0.0	0.6	–
1-Heptene	0.9	1.4	0.0	0.0	0.0	0.4
<i>n</i> -Heptane	–	69.1	0.3	0.0	0.4	1.6
2-Heptene	0.9	–	0.0	0.0	0.1	0.1
Methylcyclohexane	0.4	0.9	0.3	0.5	0.0	–
Ethylcyclopentane	2.7	4.2	–	0.0	0.3	0.8
Toluene	12.7	17.3	11.0	17.2	14.3	4.0

H₂/hydrocarbon = 7.3 mol/mol, *T* = 723 K and *P* = 100 kPa.

^a *W/F* = 8 g h mol⁻¹.

Table 5
Thermodynamic properties for the reaction involved in the dehydrocyclization of *n*-heptane at 723 K

Reaction	ΔH_{723}° (kJ/mol)	K_{eq}
$n\text{-C}_7\text{H}_{16} \rightleftharpoons \text{C}_6\text{H}_6 + 4\text{H}_2$	252.5	1.6×10^5
$n\text{-C}_7\text{H}_{16} \rightleftharpoons \text{C}_5\text{H}_{10} + \text{H}_2$	61.5	7.5×10^{-1}
$n\text{-C}_7\text{H}_{16} \rightleftharpoons \text{C}_6\text{H}_{12} + \text{H}_2$	36.4	1.2×10^5
$n\text{-C}_7\text{H}_{16} \rightleftharpoons 1\text{-C}_7\text{H}_{14} + \text{H}_2$	130.0	5.7×10^{-3}
$\text{C}_5\text{H}_{10} + \text{H}_2 \rightleftharpoons \text{C}_6\text{H}_{12}$	-65.2	1.8
$\text{C}_5\text{H}_{10} + \text{H}_2 \rightleftharpoons \text{C}_6\text{H}_{12}$	-62.7	2.5×10^{-1}
$1\text{-C}_7\text{H}_{14} \rightleftharpoons \text{C}_6\text{H}_6 + 3\text{H}_2$	123.3	2.8×10^7
$\text{C}_6\text{H}_{12} \rightleftharpoons \text{C}_6\text{H}_6 + 3\text{H}_2$	216.1	1.3×10^5

intermediates in the adsorbed phase. Similar results were obtained from 2-heptene (Table 4) indicating that both heptenes are equally reactive.

3.2.3. Methylcyclohexane

Methylcyclohexane (Table 3) is likewise more reactive than *n*-heptane and comparable to 1-heptene, but much more selective toward toluene, because it only produces benzene and methane as byproducts in a small amount. Thus, at 8 g h mol^{-1} the yield to toluene from methylcyclohexane is 84.6% for $X = 86\%$, while the corresponding value from heptenes is 17.3% for $X = 98.7\%$. This means that methylcyclohexane is a more immediate precursor of toluene than heptenes in the sequential path of transformation of *n*-heptane into toluene. It seems that methylcyclohexane, once formed in the adsorbed phase, is irreversibly transformed into toluene ($K_{eq} = 1.84 \times 10^5$) faster than 1-heptene. Obviously, to explain such reaction we can assume the formation of intermediate cycles-C6 more and more deeply dehydrogenated on the surface. Traces of methylcyclohexene were found in the gas phase but methylcyclohexadiene was never detected, because its sequential surface dehydrogenation to toluene is probably faster than its desorption to the gas phase.

The fact that the yield to benzene ($Y_B = 12.7\%$ at 30 g h mol^{-1}) is higher than that reached from toluene ($Y_B = 5.1\%$) is a very meaningful result because it indicates that hydrogenolysis of methylcyclohexane to cyclohexane and its subsequent dehydrogenation is, in addition to the hydrogenolysis of toluene and the dehydrocyclization of *n*-hexane, other route of formation of benzene.

3.2.4. Ethylcyclopentane

Ethylcyclopentane (Table 4) gives a product distribution similar to that of *n*-heptane, but the yield to toluene is lower ($Y_T = 11\%$). Since C5 ring enlargement is not favored on Pt-non-acid catalysts [14], formation of

methylcyclohexane, and hence that of toluene, requires the ring opening of ethylcyclopentane and the formation of heptane isomers. Methylcyclopentane and cyclopentane are formed by hydrogenolysis in the lateral chain. Therefore, ethylcyclopentane is doubtlessly the immediate precursor of 3-methylhexane, ethylpentane, methylcyclopentane and cyclopentane but not of 2-methylhexane, which has to be formed by isomerization of the other heptane isomers.

3.2.5. Heptane isomers

The overall reactivity of heptanes is in the order 3-methylhexane > *n*-heptane > 2-methylhexane \gg ethylpentane (see Table 4) and their respective yield to toluene follow the order 2-methylhexane (17.2%) > 3-methylhexane (14.3%) > *n*-heptane (12.7%) \gg ethylpentane (4.0). The higher dehydrocyclization selectivity from 2-methylhexane indicates that this isomer gives methylcyclohexane more easily than the other heptane isomers. The formation rate of toluene from ethylpentane is, in contrast, much lower because it cannot undergo the C₁-C₆ ring closure but it must be previously isomerized.

3.3. A mechanistic proposal for the dehydrocyclization of *n*-heptane

From the results analyzed above one can assert that *n*-heptane is transformed over the PtBa/KL catalyst through a complex network of parallel and consecutive interconnected reactions depicted in Fig. 8, with a large variety of intermediate compounds. The overall chemical process occurs on the catalyst surface, involving adsorbed species (σ). There are no thermal homogeneous reactions, but only heterogeneous catalysis. The pathway includes reactions of cyclization (CY), dehydrogenation (DH), isomerization (IS) and hydrogenolysis (HL).

The initial stage of the mechanism is the homolytic dissociative adsorption of *n*-heptane through its terminal carbon atom (C₁) on a metallic center, with abstraction of a hydrogen atom by other neighboring metallic center, giving the first reactive intermediate species (σC_7). Since heptenes and methylcyclohexane have been identified as precursors of toluene and they are transformed faster than *n*-heptane it seems that the rate limiting step of the overall process may be the C-H bond rupture to fix the *n*-heptane on the catalyst surface. From this C₁ adsorbed entity, the different paths of the network become determined by the position of the second adsorbed carbon atom in the chain of the σC_7 . Results in Tables 3 and 4 showed that heptene, or rather an alkene-like surface entity, appears as precursor of methylcyclohexane. Thus, it is reasonable to assume that the subsequent adsorption of the C₂ carbon atom on Pt with formation of the first alkene-like intermediate (σC_7^-) should be very favored, in agreement with most of the published results [14]. This species may be transformed following different routes, namely:

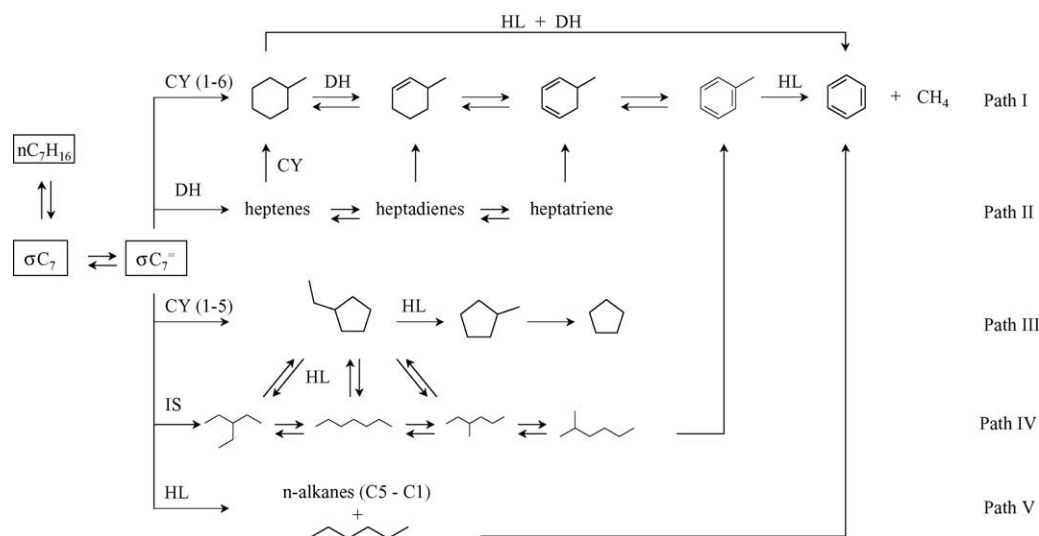


Fig. 8. Reaction pathway for dehydrocyclization of *n*-heptane at 723 K and 100 kPa over the Pt/BaKL catalyst.

- (i) Desorption to the gas phase as heptene.
- (ii) C₁–C₆ ring closure with formation of methylcyclohexane, which may desorb to the gas phase or successively dehydrogenate on the surface to give finally toluene (Path I). This path is very feasible due to the high aromatizing selectivity of the Pt/KL catalyst, which in our particular case has been enhanced by the addition of barium oxide, which increases the electron density of platinum evidenced by FT-IR/CO chemisorption.
- (iii) The species $\sigma\text{C}_7^=$ may be successively dehydrogenated (DH) to heptatriene ($\sigma\text{C}_7^{3=}$) (Path II) and then undergo cyclization (CY) to toluene. Eventually, cyclization of the alkene and/or alkadiene adsorbed species may give the corresponding adsorbed cycle of the Path I. It should be noted that neither heptadienes nor heptatriene were detected in the product, indicating that the reactivity of these intermediates is so high that they react before they desorb, in accordance with the literature data [26].
- (iv) C₁–C₅ closure with formation of ethylcyclopentane, which may desorb to the gas phase or gives raise to different types of compounds and, indirectly, can also lead to toluene (Paths III and IV of the scheme).
- (v) Other less favored reactions from $\sigma\text{C}_7^=$ are the bond shift isomerization (Path IV) via triadsorbed α, α, γ and α, γ, γ molecules [12] and the non-selective hydrogenolysis (Path V).

To meet the *least motion principle* [26] the appearance of toluene as a primary product can be explained assuming that the successive transformations of the intermediates in Paths I and II take place in the adsorbed phase, on the same active site, following a type rake mechanism [27–29]. In this mechanism, the rates of surface reaction of the intermediates are higher than their respective desorption rates. This process goes on until the stable final product (toluene) is formed and desorbed,

even at very low conversions (i.e., for $W/F \rightarrow 0$). The intermediates methylcyclohexane and heptenes formed by the rake mechanism are stable molecules, which can desorb to the gas phase. In contrast, the highly unsaturated adsorbed intermediates are too reactive to be desorbed to the homogenous phase and appearing between reaction products. Experimental evidences of the dehydrocyclization mechanism via unsaturated intermediates have been also discussed in earlier publications [30,31]. It is important to point out, on the other hand, that the mechanism in Fig. 8 is proposed on the basis of results obtained at atmospheric pressure, because at higher pressures it may be different.

4. Conclusions

Dehydrocyclization of *n*-heptane with a monofunctional basic PtBa/KL catalyst has been studied at 723 K and atmospheric pressure, in the range of space-time 1.8–117.0 g h mol⁻¹ and the product distribution analyzed in order to propose a reaction pathway. Toluene, methylcyclohexane, ethylcyclopentane, heptenes, heptane isomers, hexane and methane have been found to be primary products, which are formed from *n*-heptane following a network of parallel and consecutive steps, involving cyclization, dehydrogenation, isomerization and hydrogenolysis reactions on the catalyst surface. Dehydrocyclization of toluene, methylcyclohexane, ethylcyclopentane, (1- and 2-heptene, 2- and 3-methylhexane), ethylpentane and benzene have been also performed at the same temperature, and the results used to clarify the possible routes of transformation of heptane.

Dehydrocyclization of *n*-heptane to toluene takes place through two parallel and eventually interconnected routes from an adsorbed unsaturated $\sigma\text{C}_7^=$ common precursor—Path I: C₁–C₆ ring closure and subsequent progressive

dehydrogenation; Path II: successive dehydrogenation of σC_7^- up to heptatrienes and then cyclization to toluene. Both routes take place via a rake mechanism, in which the initial precursor is sequentially transformed in the adsorbed phase, on the same active site, up to toluene, in such a way that only a few of the total adsorbed intermediates formed appear in the gas phase. The rest of the intermediates are not desorbed due to their high reactivity.

Acknowledgements

The authors gratefully acknowledge the financial support from CICYT, Spain (project MAT1999-0812). J.M.G. thanks CONICET and UNL, Argentina, for the Ph.D. fellowship (project FOMEC 824).

References

- [1] J.R. Bernard, in: L.W. Rees (Ed.), in: Proceedings of the Fifth International Conference on Zeolites, Heyden, London, 1980p. 686.
- [2] C. Besoukhanova, J. Guidot, D. Barthomeuf, M. Breyse, J.R. Bernard, *J. Chem. Soc., Faraday Trans.* 77 (1981) 1595.
- [3] W. Han, A.B. Kooch, R.F. Hicks, *Catal. Lett.* 18 (1993) 219.
- [4] P.V. Menacherry, G.L. Haller, *J. Catal.* 177 (1998) 175.
- [5] E. Iglesia, J.E. Baumgartner, *Stud. Surf. Sci. Catal.* 75 (1993) 993.
- [6] G. Jacobs, C.L. Padro, D. Resasco, *J. Catal.* 179 (1998) 43.
- [7] G.B. McVicker, J.L. Kao, W.E. Gates, J.L. Robbins, M.M.J. Treacy, S.B. Rice, T.H. Vanderspurt, V.R. Cross, A.K. Ghosh, *J. Catal.* 139 (1993) 488.
- [8] S.J. Tauster, J.J. Steger, *J. Catal.* 125 (1990) 387.
- [9] E.G. Derouane, D.J. Vanderveken, *Appl. Catal.* 45 (1988) 15.
- [10] N.D. Triantafillou, J.T. Miller, B.C. Gates, *J. Catal.* 155 (1995) 131.
- [11] G.S. Lane, F.S. Modica, J.T. Miller, *J. Catal.* 129 (1991) 145.
- [12] T. Fukunaga, V. Ponec, *Appl. Catal. A* 154 (1997) 207.
- [13] J.T. Miller, N.G.B. Agrawal, G.S. Lane, F.S. Modica, *J. Catal.* 163 (1996) 106.
- [14] D.S. Lafyatis, G.F. Froment, A. Pasaclaerhout, E.G. Derouane, *J. Catal.* 147 (1994) 552.
- [15] H. Pines, L. Nogueira, *J. Catal.* 70 (1981) 391.
- [16] E. Iglesia, J. Baumgartner, G.L. Price, K.D. Rose, J.L. Robbins, *J. Catal.* 125 (1990) 95.
- [17] B.H. Davis, *Catal. Today* 53 (1999) 443.
- [18] J.M. Grau, L. Daza, X.L. Seoane, A. Arcoya, *Catal. Lett.* 53 (1998) 161.
- [19] J.M. Grau, X.L. Seoane, A. Arcoya, *Catal. Lett.* 83 (2002) 247.
- [20] I. Manninger, Z. Zhan, X.L. Xu, Z. Paál, *J. Mol. Catal.* 66 (1991) 223.
- [21] B.H. Davis, P.B. Venuto, *J. Catal.* 15 (1969) 363.
- [22] J.H. Sinfelt, *Adv. Catal.* 23 (1973) 91.
- [23] F.G. Gault, *Adv. Catal.* 30 (1981) 1.
- [24] G. Leclercq, S. Pretrzyk, M. Peyrovi, M. Karroua, *J. Catal.* 99 (1986) 1.
- [25] D.R. Lide (Ed.), *Handbook of Chemistry and Physics*, CRC Press, New York, 1999.
- [26] O.S. Tee, *J. Am. Chem. Soc.* 91 (1969) 7144.
- [27] X.L. Seoane, P. Boutry, R. Montarnal, *J. Catal.* 63 (1980) 191.
- [28] E.G. Derouane, in: F. Ramôa-Ribeiro, A.E. Rodrigues, L. Deane Rollmann, C. Naccache (Eds.), *Zeolites: Science and Technology*, Martinus Nijhoff Publ., The Hague, 1984p. 515.
- [29] G. Centi, in: R.W. Joyner, R.A. van Santen (Eds.), *Elementary Reaction Steps in Heterogeneous Catalysis*, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1993p. 93.
- [30] Z. Paál, P. Tétényi, *J. Catal.* 30 (1973) 350.
- [31] Z. Paál, *J. Catal.* 105 (1987) 540.