# Conversion of $C_4 - C_4$= Technical Fraction Over Zinc – Copper ZSM-5 Catalyst

**IULEAN ASAFTEI[1], NICOLAE BILBA[1], ION SANDU*[2]**

[1] "Al. I. Cuza" University of Iasi, Faculty of Chemistry, Laboratory of Materials Chemistry, 11 Carol I Blv., 700506, Romania
[2] ARHEOINVEST Interdisciplinary Platform, "Al. I. Cuza" University of Iasi, 22 Carol I Blv., 700506, Romania

*The catalytic activity and product distribution over Zn-Cu-HZM-5 and HZSM-5 catalysts during the $C_4 - C_4^=$ conversion, have been studied. The experimental results show that the conversion of hydrocarbons and the selectivity to aromatics BTX on the bifunctional Zn-Cu-HZSM-5 catalyst are higher than that on monofunctional HZSM-5. On HZSM-5, protons (Bronsted acid sites) and on Zn-Cu-HZSM-5, both $Zn^{2+}$/ $Cu^{2+}$ cations and protons intervene in alkanes dehydrogenation and further in dehydrocyclooligomerization reactions that form $C_6$-$C_8$ aromatics; the aromatic products (principally toluene, xylenes and benzene) concentration of liquid products varied with the time on stream of the process. The initial aromatization process described as dehydrocyclodimerization of alkanes and alkenes, principally to aromatics BTX and molecular hydrogen is accompanied by an oligomerization, isomerisation, cracking and alkylation process to form finally in the liquid product an excessively mixture of iso- and n- $C_5 - C_{10}$ aliphatic hydrocarbons and > $C_{10}$.*

*Keywords: aromatization, Zn-Cu-HZSM-5, $C_4 - C_4^=$ technical fraction*

The MFI zeolite has the greatest interest due to its unique two-dimensional pore system and relatively slow deactivation [1]. One of the catalytic processes in which the modified ZSM-5 catalysts have proved their superiority is that of conversion of light alkanes ($C_2 - C_7$) and alkenes ($C_2^=$- $C_4^=$) into more useful compounds, such as BTX. The main reason for the production of aromatics is the application of aromatics as a base chemical in a number of petrochemical and chemical processes.

The aromatization of light alkanes contained in non-associated natural gas, in associated gas (as petroleum casing-head gas) and from petroleum refining processes (as liquefied petroleum gas, LPG) represent a new attractive way of producing BTX aromatics. Already a few commercial processes have been announced based on: HZSM-5 (M2 Forming Process – Mobil Oil [2, 3] and M-Forming Process – Mobil) [4]; Ga/HZSM-5 (Cyclar-BP/UOP [5, 6] and Z-Forming from Mitsubishi Oil and Chiyoda [7]; Zn/HZSM-5 (Alpha process of Asahi Chemical and Petrochemical) [8]; Pt/K(Ba)L (Aromax™ process – Chevron – Phillips Chemical Co. [9]; RZ- Platforming process – UOP [10, 11]; Aroforming from IFP; Salutec based on metal oxides-HZSM-5 [12, 13].

The conversion of light alkanes into aromatics (with low selectivity to BTX) was first described in 1970 by Csicsery, [14] using bifunctional catalysts such as Pt on alumina or metal oxide on alumina.

The properties that make ZSM-5 crucial for industrial applications are its high thermal and acid stability, high selectivity, high activity and coke resistance in many catalytic conversions. Activity is mostly determined by the zeolite Bronsted acid sites and by the active metal-phase supported by zeolite and selectivity is due to the zeolite microspores and/or cavities size and shape. The structure of ZSM-5 zeolite is characterized by two dimensional types of intersecting channels (2-D pore system) with 10-member ring (MR) openings: one type is sinusoidal (zigzag) with near-circular openings (0.53x0.56 nm) and the other one is straight with elliptical openings (0.51x0.55 nm) [15]. The channel intersections have a diameter of 0.89 nm and are the locus of strong acid sites and of aromatic $C_6$-$C_8$ hydrocarbons formation. Due to the shape-selective properties of the ZSM-5 framework (determined by product shape selectivity or/and transition state selectivity), mainly small aromatics (BTX) are formed and activation on account of coke deposition is relatively slow, because no appreciable amounts of polyaromatics can be formed [16].

Many studies have focused on the ability of the monofunctional acid catalyst (HZSM-5) to convert light hydrocarbons to BTX [17-32]. HZSM-5 catalysts are not the best dehydrogenating catalysts because the hydrogen rejection from catalyst occurs by hydrogen transfer to olefins which limits the aromatics selectivity. Aromatization over HZSM-5 is accompanied by substantial cracking of C-C bond of alkanes with a production of 3 moles of small alkanes per one mole of aromatics.

The selectivity toward aromatics can be increased significantly if the light alkanes and alkenes aromatization reaction is carried out over Ga-HZSM-5 [17-39] or Zn-HZSM-5 [17-23, 26, 34-57]. The Zn-HZSM-5, have on essential instability because of easily evaporation of zinc at around 500-520°C. Introduction of Cu led to increase the hydrogenation /dehydrogenation activity at high temperature. The present work deals with the results obtained by investigation of aromatization of technical fraction $C_4^=$ - $C_4$ on HZSM-5 and Zn-Cu-HZSM-5 catalysts.

## Experimental part

### *NaZSM-5 zeolite synthesis*

NaZSM-5 zeolite (Si/Al = 36,02; 2,65 wt.% $Na_2O$), was synthesized by hydrothermal crystallization from alkaline media containing sodium silicate (29.63 wt.% $SiO_2$, 9.55 wt.% $Na_2O$, 60.82 wt.% $H_2O$, pycnometric density 1.443 kg dm$^{-3}$), aluminum sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$ (15 wt.% $Al_2O_3$), sulphuric acid (96 wt.%, 1.835 kg dm$^{-3}$), ethylene glycol (1.1132 kg dm$^{-3}$) as a gel modifier and as a void filler, deionizer water and ammonium hydroxide (25 wt.% $NH_3$) to control the pH of the gel (11.0 – 11.5). All chemicals are Romanian technical products and were used as received [58]. The gel was allowed to crystallize in Teflon – lined

---

* email: sandu_i03@yahoo.com , Tel. +40 232 201662

autoclave at180 ± 5°C for 24h with stirring. The product was then filtered, washed, and dried at 110°C for 6h and calcined at 550°Cin air for 6h. The purity and crystallinity of Na-ZSM5 was checked by X- ray diffraction.

*Catalysts preparation*

The HZSM-5 form was obtained by triple ion – exchange with 1M $NH_4NO_3$ at 80°C for 4h and by calcinations in air at 550°C for 6h. Zeolite HZSM-5 was converted to Zn-HZSM-5 by process of ion exchanges two times with 0.1 M $Zn(NO_3)_2$ aqueous solution (solid : solution = 1g : 5 mL) under stirring at 80°C for 6h each time. The Zn-HZSM-5 sample was filtered, washed, free from $NO_3^-$ ions, dried at 110°C for 6h and calcined at 450°C in air for 6h. The zinc contained in the sample was 1.73wt% at ZnO. The Zn-Cu-HZM-5 zeolite (1.73 ZnO wt% and 0.64 wt % CuO) was prepared by ion – exchange of the prepared Zn-HZSM-5 sample using 0.1 M $Cu(NO_3)_2$ solutions under stirring at 80°C for 6h. The product was filtered, washed, dried at 110°C for 6h and calcined in air at 550°C for 6h. The HZSM-5 and mixture of Zn-Cu-HZSM-5 powders with 20 % wt, g - $Al_2O_3$ as binder was extruded and then cut into short cylinders, dried at 110°C for 6h and calcined at 475°C in air for 6 h.

*Characterization*

The structure type, phase purity and degree of crystallinity were determined by X-ray powder diffraction pattern which were obtained on a Philips PW 1830 diffractometer using Ni filtered Cu $K_\alpha$ radiation at a scanning speed of 0.02° $s^{-1}$ in the range of 6–45, 2θ. XRD powder pattern of the Na-ZSM-5 sample exhibit only diffraction lines proper to MFI structure and high crystallinity (fig. 1). The pattern confirms that the synthesized zeolite has the structure identical to MFI-type zeolite [15]. The parent NaZSM-5 has a high crystallinity derived from the high intensities of the XRD reflections in the range of 22.5 – 25° (2θ). No other diffraction lines were found in the XRD pattern.

The morphology and size of the individual crystals were obtained by scanning electron microscopy (SEM) with a Microspec WDX-2A using a 25 kV accelerating potential. The SEM image of parent NaZSM-5 is presented in figure 2. It reveals the welldefined morphology of crystals indicating highly crystalline material.

The acidity and strength distribution on HZSM-5 and Zn-Cu-HZSM-5 catalysts were measured using Temperature Programmed Desorption (TPD) technique using ammonia. A known weight of the sample was activated in a dry $N_2$ at 500°C for 4h then cooled to 80°C when ammonia was admitted. The amount of ammonia desorbed from 100°C to 800°C (at a heating rate of 10°C/min) was quantitatively monitored by absorption in 1M HCl. The ammonia desorbed represents the total acidity (weak and strong) of the sample. The TPD ammonia desorption presents two peaks, one at low temperature (LT) and one at high temperature (HT) (table 1) Temperature peak correspond to higher acid strength and is done to ammonia bound to strong structural Brönsted sites (Si – O – Al bridging OH), and possible to strong Lewis sites (≡ Al and ≡ $Si^+$). Low temperature peak correspond to less acidic sites (terminal OH groups, cationic sites $M^{n+}$, $AlO^+$). The temperature and the amount of desorbed ammonia give information about strength and number of the acid sites.

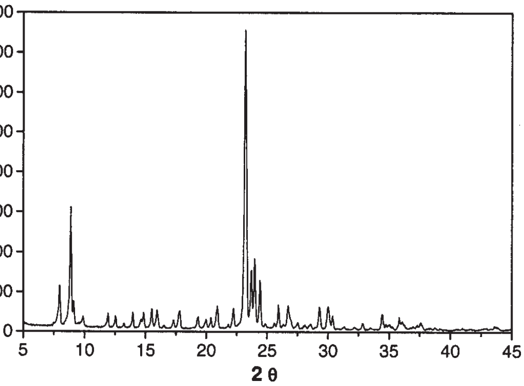


Fig.1. X-ray diffraction pattern of NaZSM-5 zeolite

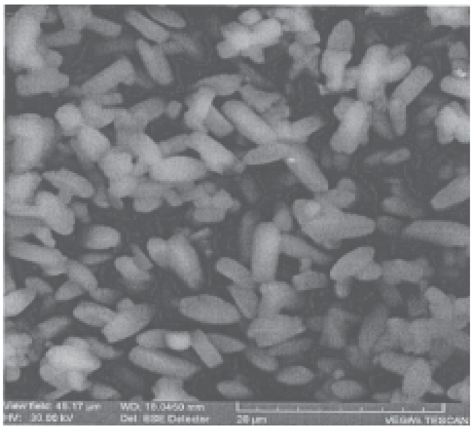


Fig.2. SEM image of parent NaZSM-5 zeolite

The BET specific surface area applying the BET equation was determined using a Carlo – Erba Sorptomatic Series 1800 instrument at -196°C and at sub-atmospheric pressure with nitrogen as the analysis gas.

The values of the BET specific surface area and acidity of the HZSM-5 and Zn – Cu – HZSM-5 catalysts are presented in table 1.

The incorporation of the $Zn^{2+}$ and $Cu^{2+}$ ions into cationic positions affects the acidity of the HZSM-5 zeolite, decreasing the number of Brönsted strong acid sites and increasing the Lewis acid sites.

*Catalytic performance*

The catalytic activity of HZSM-5 and Zn-Cu-HZSM-5 for $C_4 – C_4^=$ technical fraction conversion at 450°C and 8 atm. (HZSM-5) and under atmospheric pressure (Zn-Cu-HZSM-5), with WHSV 1$h^{-1}$, to aromatics BTX, in a fixed-bed continuous flow stainless – steel reactor (a commercial Twin Reactor System Naky Metrimpex, Hungary) was studied. The catalysts were pre-treated with $N_2$ for 1h at 450°C to remove the adsorbed impurities and the moisture.

The reaction products were separated into liquid and gas fractions through an ice – trap. Composition of products was obtained with two gas chromatographs (GC Carlo Erba,

**Table 1**

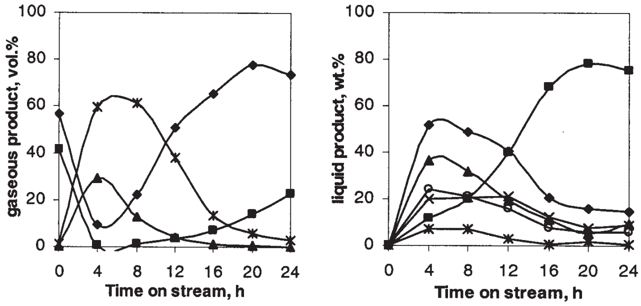
PHYSICO-CHEMICAL CHARACTERISTICS OF THE STUDIED CATALYST

| Sample | BET surface area, $m^2$/g | Acidity, mmol. $NH_3$/g | | Total acidity |
|---|---|---|---|---|
| | | low-peak<br>LT $_{180°C}$<br>80-300°C | high-peak<br>HT$_{450°C}$<br>300-600°C | |
| HZSM-5 | 296 | 0,618 | 0,282 | 0.900 |
| Zn/Cu-HZSM-5 | 271 | 0.737 | 0.126 | 0.863 |

| Feedstock composition | Test number | | | | |
|---|---|---|---|---|---|
| %(vol) | 1 | 2 | 3 | 4 | 5 |
| $C_2$ | 0.015 | 0.015 | 0.03 | - | - |
| $C_3$ | 0.76 | 0.764 | 1.07 | 1.11 | - |
| i-$C_4$ | 22.46 | 22.46 | 35.39 | 23.84 | 27.49 |
| n-$C_4$ | 27.20 | 27.20 | 26.85 | 32.69 | 34.31 |
| i-$C_5$ | 0.03 | 0.03 | 0.02 | 0.25 | 0.29 |
| 1-$C_4^=$ | 29.15 | 29.15 | 22.13 | 22.33 | 19.02 |
| i-$C_4^=$ | 0.39 | 0.30 | 0.12 | 0.07 | - |
| tr.-2-$C_4^=$ | 11.45 | 11.45 | 8.90 | 12.66 | 11.20 |
| cis-2-$C_4^=$ | 6.62 | 6.62 | 4.65 | 6.57 | 6.09 |
| 1,3-$C_4^{==}$ | 1.73 | 1.73 | 0.58 | 0.33 | 0.31 |

Temperature: 450°C; 8 atm. pressure; WHSV=1 $h^{-1}$; catalyst; 100 $cm^3$; regeneration of catalyst after each test: 475°C for 6h in nitrogen flow with 2% oxygen.

**Table 2**
BUTANES-BUTENES FEEDSTOCK COMPOSITION AND CONDITIONS OF AROMATIZATION ON HZSM-5 CATALYST



◆–Σ $C_4$; ■–Σ $C_4^=$; ▲–$C_1$+$C_2$; ✱–$C_3$ ◆– Σ Ar ; ■–$C_5$–$C_{10}$ ; ▲–> $C_{10}$; ✱–B;

○–T; x–X+EB

Fig.3. Gaseous phase composition and liquid phase composition vs. time on stream over HZSM-5 catalyst in butane-butenes conversion; Test No.4

model C and Vega) using a fused silica capillary column (25 m length and 0.32 mm i.d.) with SE-52 stationary phase and flame ionization detector (FID) for liquid phase and a column (6m length) with squalane and dimethylsulpholane and a thermal conductivity detector (TCD) for gaseous phase, respectively.

## Results and discussions

### *Catalytic performance of HZSM-5 catalyst in $C_4$- $C_4^=$ hydrocarbons aromatization*

Conversion of mixed butanes-butenes to aromatics over HZSM-5 takes place with low selectivity to BTX, the reactants forming predominantly the cracking products. The operating conditions (temperature 450°C, WHSV 1 $h^{-1}$ and pressure 8 atm.) were in advance selected to obtain the high yield of liquid product during the catalytic tests.

Table 2 presents the feedstock composition and reaction conditions of aromatization for five cycles (with intermediate regeneration) on HZSM-5 catalyst.

The change in the gaseous and liquid products distribution over HZSM-5 with time on-stream (TOS) in the conversion of butanes and butenes are presented in figure 3.

The concentration of butanes (n-+i-$C_4$) decreased from 56.53 vol. % to 9.16 vol. % in the first 4h of reaction, after that is continuously increasing going beyond the feedstock after 16h. The concentration of butenes (1-$C_4^=$, *trans*-2-$C_4^=$ and *cis*-2-$C_4^=$) decreased from 41.63 vol. % to 0.84 vol. % in the first 4h, and to 3.32 vol. % after 12h of reaction. The forming of methane and ethane ($C_1$ + $C_2$) reach the maximum value (29.50%) after 4h of reaction and the forming of propane ($C_3$) after 8h of reaction (61.68 vol. %); their production is connected to aromatic hydrocarbons formation. The molecular hydrogen was not detected in the gaseous phase.

The catalytic activity and selectivity to aromatic hydrocarbons is maximum for the first 8 h run; after that aliphatic $C_5$ – $C_{10}$ are progressively formed.

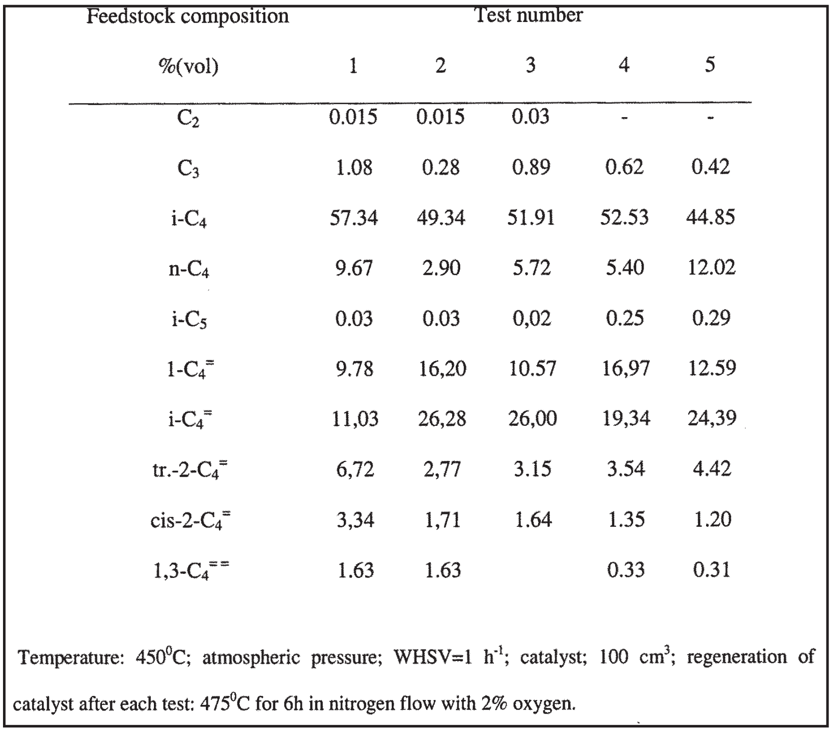
### *Catalytic performance of Zn-Cu-HZSM-5 catalyst in $C_4$- $C_4^=$ hydrocarbons aromatization*

Five catalytic tests at 450°C, using the butanes – butenes technical fraction were performed on Zn-Cu-HZSM-5. The industrially feedstock composition and the conditions of aromatization over ion exchanged Zn-Cu-HZSM-5 during of five catalytic tests are given in table 3. The average yields in liquid product in the five tests were ~37.5 wt %. The liquid product contained over 68.0 wt % aromatic hydrocarbons.

The operating conditions (temperature 450°C, WHSV 1 $h^{-1}$ and atmospheric pressure) were in advance selected to obtain the high yield of liquid product during the catalytic tests.

The dependence of component concentration on TOS in the gaseous and liquid product on Zn-Cu-HZSM-5 during $C_4$ – $C_4^=$ conversion is presented in figures 4 and 5. Butenes are consumed almost totally during the whole test, while the butanes are consumed during the first 4 h of reaction,

**Table 3**
BUTANES-BUTENES FEEDSTOCK
COMPOSITION AND CONDITIONS OF
AROMATIZATION ON Zn-Cu-HZSM-5 CATALYST



| Feedstock composition %(vol) | Test number 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $C_2$ | 0.015 | 0.015 | 0.03 | - | - |
| $C_3$ | 1.08 | 0.28 | 0.89 | 0.62 | 0.42 |
| $i\text{-}C_4$ | 57.34 | 49.34 | 51.91 | 52.53 | 44.85 |
| $n\text{-}C_4$ | 9.67 | 2.90 | 5.72 | 5.40 | 12.02 |
| $i\text{-}C_5$ | 0.03 | 0.03 | 0,02 | 0.25 | 0.29 |
| $1\text{-}C_4^=$ | 9.78 | 16,20 | 10.57 | 16,97 | 12.59 |
| $i\text{-}C_4^=$ | 11,03 | 26,28 | 26,00 | 19,34 | 24,39 |
| $tr.\text{-}2\text{-}C_4^=$ | 6,72 | 2,77 | 3.15 | 3.54 | 4.42 |
| $cis\text{-}2\text{-}C_4^=$ | 3,34 | 1,71 | 1.64 | 1.35 | 1.20 |
| $1,3\text{-}C_4^{==}$ | 1.63 | 1.63 | | 0.33 | 0.31 |

Temperature: 450°C; atmospheric pressure; WHSV=1 $h^{-1}$; catalyst; 100 $cm^3$; regeneration of catalyst after each test: 475°C for 6h in nitrogen flow with 2% oxygen.

after which their concentration increases continuously. Among butanes, the i-butane is most consumed, its concentration in gases decreasing from 44.85 vol. % down to 9.35 vol. % after 4 h. The propane and ethane formation takes place the first hours of reaction, after that their concentration decreases with the decrease of their catalytic activity.

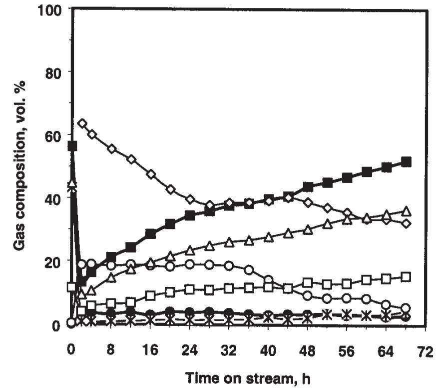


Fig.4. Gas composition vs. time on stream in the $C_4$-$C_4^=$ conversion over Zn-Cu-HZSM-5 at 450°C and atmospheric pressure; (Symbols (·) $\Sigma C_4^=$; (□.) n-$C_4$; (Δ) i-$C_4$; (o) $C_3$-$C_3^=$; (*) $C_2$-$C_2^=$; (■)" $C_4$; (◊) $H_2$ + $C_1$; $\Sigma C_4^=$ = (1+*iso*+*trans*+*cis*)-butene)); Test No.5

In the liquid product resulted on Zn-Cu-HZSM-5 aromatic hydrocarbons are predominant together with the "oligo" fraction which contains mostly alkanes and alkenes in the iso- series.

The corresponding liquid product contains over 75 wt. % mononuclear aromatic hydrocarbons for 40h of reaction, distributes in the order:

toluene > xylenes and ethyl benzene» benzene.

Zinc / cooper dehydrogenation function acts in both steps, the dehydrogenation of i-butane (especially) and the dienes formation and then dehydrogenation of naphtenes to aromatic hydrocarbons. The average output of aromatics BTX over HZSM-5 monofunctional catalyst do not go beyond 30 wt% in the liquid phase and the formation of xylenes and toluene is of preference.

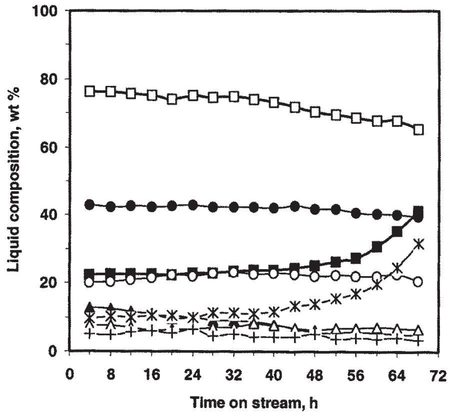


Fig.5. Liquid composition vs. time on stream in the $C_4$-$C_4^=$ conversion over Zn-Cu-HZSM-5 at 450°C and atmospheric pressure; (Symbols: (■)Σ "oligo"; (*)Σ *i* ($C_5$-$C_{10}$); (□) ΣAr; (Δ) Σn($C_5$-$C_{10}$); (+) >$C_{10}$; (o) Xylenes; (•) Toluene; (▲) Benzene); Test no.5

In figure 6 is presented the average output of aromatics BTX during the five catalytic experiments over Zn-Cu-HZSM-5. The average output of aromatic hydrocarbons BTX over Zn-Cu-HZSM-5 bifunctional catalyst represent more than 68 wt% in the liquid phase in for catalytic tests.

In the liquid product resulted on Zn-Cu-HZSM-5 aromatic hydrocarbons are predominant together with the "oligo" fraction which contains mostly alkanes and alkenes in the iso- series.

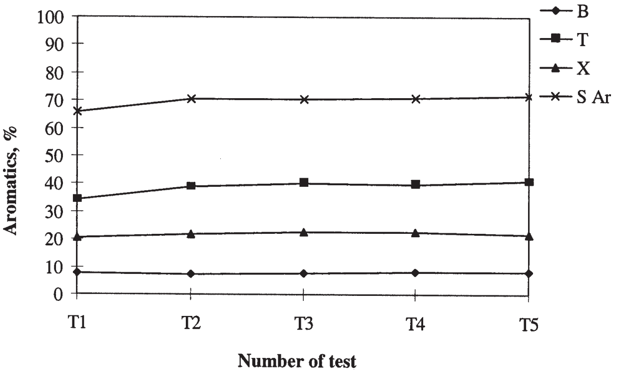
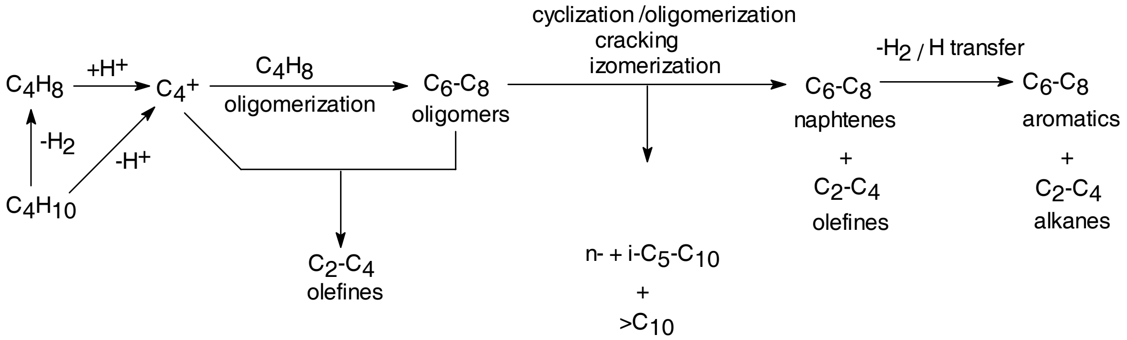


Fig.6. The aromatics average output over Zn-Cu-HZSM-5 catalyst (450°C, atm. pressure, WHSV =1 $h^{-1}$)



Scheme 1

Zn-Cu-HZSM-5 catalyst contains medium acidity that minimizes the occurrences of cracking reactions. Zn and Cu incorporated in HZSM-5 zeolite through ion exchange is very well dispersed and is stable in isolated cationic ($Zn^{2+}$, $Cu^{2+}$) positions with tetrahedral symmetry. In the case of Zn-Cu-HZSM-5 catalyst the alkanes dehydrocyclodimerization proceed via bifunctional pathways involving exchanged cations for dehydrogenation of alkanes and dehydrocyclization of alkenic oligomers and acidic OH groups for alkenes interconversion and aromatic formation. $Zn^{2+}$ and $Cu^{2+}$ cations as Lewis acid sites promote the alkanes dehydrogenation (heterolytic cleavage of the C – H bond) to alkenes (dehydrogenation function), oligomers dehydrogenation to oligomers with one double bond, decrease β-scission rates, exert strong hydrogen attracting action and promote removal of hydrogen atoms adsorbed as hydrogen molecular, prevents hydrogenation of alkenes required in cyclization and consequently, enhances aromatization.

Alkanes are activated by a monomolecular or a bimolecular mechanism depending on the reaction conditions (temperature, surface concentration of reactants and conversion) [59]. The zinc and Zn/Cu species are efficient in the increase of aromatization selectivity since they activate the C H bonds and promote the dehydrogenation as well as the migration of hydrogen atom by hydrogen transfer.

At the same time alkenes $C_4^=$ react much faster than the alkanes $C_4$ in presence of protonic sites of zeolite yielding the carbenium ions which may add to another molecule of alkenes to yield a new carbenium ion.

Butanes-butylenes mixtures conversion over HZSM-5 and Zn-Cu-HZSM-5 occurs via a complex sequence of cracking, dehydrogenation, oligomerization, isomerization, cyclization, β-scission and H transfer (scheme 1).

## Conclusions

Monofunctional acid catalyst HZSM-5 exhibits a low selectivity to aromatics BTX in the catalytic aromatization of butanes-butenes mixture, due to preferentially cracking, isomerization, and β-scission reactivity. The average outputs of aromatics BTX do not go beyond 30 wt% in the liquid phase and the formation of xylenes and toluene is of preference. In the HZSM-5 are present Bronsted with acidic OH groups located at channel intersections and/or Lewis acid sites.

Bifunctional zeolite Zn-Cu-HZSM-5 is very active and selective catalyst in the aromatization of $C_4 – C_4^=$ technical fraction. The incorporation of Zn (II) and Cu (II) into cationic positions promotes a decrease of the number of Brönsted acid sites and an increase of Lewis acid sites that are able to abstract hydride from the adsorbed hydrocarbons molecules and partial catalyze the formation of hydrogen gas. Zn/Cu species is active in dehydrogenation / hydrogenation reactions responsible for formation of hydrogen gas and aromatics BTX.

The product distribution (gaseous and liquid) in the conversion of butanes-butenes mixtures at 450°C and atmospheric pressure over Zn-Cu-HZSM-5 modified catalyst and HZSM-5 (8 atm.) is changing with time on-stream. The HZSM-5 catalyst deactivates fast and Zn-Cu-HZSM-5 catalysts are able to sustain activity and selectivity for a longer period.

The presence of butenes in the butanes feed exercise the activation of butanes: it is thought that butenes are protonate to carbenium ions from a Bronsted acid site and then activate butanes through hydride abstraction.

The catalytic aromatization reactions over Zn-Cu-HZSM-5 catalysts can upgrade the low-value light hydrocarbon byproduct streams from refinery and cracker operations, producing aromatics BTX and hydrogen as co-product.

## References

1.CHEN, N.Y., GARWOOD, W.E., DWYER F.G., in „Shape Selective Catalysis in Industrial Applications”, Marcel Dekker, Inc., Eds., New York, 1989, p. 206.
2.MADIKIZELA-MNQANQENI, N. N., Catal. Today, 143, 2009, p.126.
3.CHEN, N. Y., YAN, T. Y., Ind. Eng. Chem. Process Des. Dev., 25, 1986, p.151.
4.CHEN, N. Y., GARWOOD, W. E., HECK, R. H., Ind. Eng. Chem. Proc., 26, 1987, p.706.
5.MOWRY, J. R., ANDERSON, R. F., AND JOHNSON, J. A., Oil Gas J., 83, 1985, p.128.
6.UOP LLC. Cyclar Process. Des Plaines: UOP 2001; Cyclar TM Process, Brochure, UOP website. See: http://www.uop.com/objects/46%20cyclar:pdf
7.SAITO, S., HIRABAYASHI, K., SHIBATA, S., KONDO, T., ADACHI, K., NPRA Annual Meeting, March 22-24, 1992; Z-Forming Process, Mitshubishi Oil Co. Ltd. and Chiyoda Corp., May, 1994.
8.NAGAMORI, Y., KAWASE, M., Micropor. Mesopor. Mater., 21, 1998, p.439.
9.SWIFT, J. D., MOSER, M. D., RUSS, M. B., HAIZMANN, R. S., Hydrocarbon Technol. Int., 1995, Autumn, 86.
10.TAMM, P. W., MOHR. D. H., WILSON, C. R., Stud. Surf. Sci. Catal., 38, 1988, p.335.
11.UOP LLC: RZ – Platforming Process. Des Plaines: UOP, 1999.
12.ROOSEN, G. N., ORIEVX, A., ANDREWS, J., Dewitt’s Houston Conf. March 1989.
13.MANK, L., MINKKINEN, A., SHADDICK, R., in: HARRISON, P., (Ed.), Hydrocarbon Tech. Int., Sterling Publication, London, 1992, p.69.
14.CSICSERY, S. M., J. Catal., 17, (1970). p.207; 17, p.315; 18, p. 30.
15.BAERLOCHER, CH., MCKUSKER, L. B., OLSON, D. H., “Atlas of Zeolite Framework Types”, 6th Revised Ed.: Elsevier, Amsterdam, 2007, p. 212.
16.GOSLING, C. D., WILCHER, F. P., SULLIVAN, L., MOUNTFORD, R. A., Hydrocarbon Process. Int. Ed., 70, 1991, p.69.
17.SCURRELL, M. S., Appl. Catal., 41, 1988, p. 89.
18.DASS D. V., ODELL, A. L., J. Catal., 113, 1988, p. 259.
19.SEDDON, D., Catal. Today, 6, 1990, p. 351.
20.ONO, Y., Catal. Rev., 34, 1992, p.179.
21.BISCARDI, J. A., IGLESIA, E., Catal. Today, 31, 1996, p. 207.

22.MERIAUDEAU, P., NACCACHE, C., Catal. Rev. Sci. Eng., 39**,** 1997, p.5.
23.BISCARDI, J. A., IGLESIA, E., J. Catal., 182, 1999, p.117.
24.CAEIRO, G., CARVALHO, R. H., WANG, X., LEMOS, M.A.N.D.A., LEMOS, F., GUISNET, M., RIBEIRO, F. R., J. Molec. Catal. A: Chemical, 255, 2006, p.131.
25.BHAN, A., DELGAS, W. N., Catal. Rev., 50, 2008, p.19.
26.KITAGAWA, H., SENDODA, Y., ONO, Y., J. Catal., 101, 1986, p.12.
27.ONO, Y., KITAGAWA, H., SENDODA, Y., J. Chem. Soc., Faraday Trans.1, 83, 1987, p.2913.
28.ONO, Y., KANAE K., J. Chem. Soc., Faraday Trans., 87, 1991, p.663.
29.ONO, Y., KANAE K., J. Chem. Soc., Faraday Trans., 87, 1991, p.669.
30.GUISNET, M., GNEP, N. S., AITTALEB, D., DOYEMET, J. Y., Appl. Catal. A: General, 87, 1992, p.255.
31.FRICKE, R., KOSSLICK, H., LISCHKE, G., RICHTER, M., Chem. Rev., 100, 2000, p.2303.
32.LUBANGO, L. M., SCURRELL, M. S., Appl. Catal. A: General, 235, 2002, p.265.
33.KANAI, J., KAWATA, W., J. Catal., 114, 1988, p.284; Appl. Catal. A: General, 55, 1989, p.115.
34.GNEP, N. S., DOYEMET, J. Y., GUISNET, M., Stud. Surf. Sci. Catal., 46, 1989, p.253.
35.LUKYANOV, D. B., GNEP, N. S., GUISNET, M. R., Ind. Eng. Chem. Res., 34, 1995, p.516.
36.MOLE, T., ANDERSON, J. R., CREER, G., Appl. Catal. A: General, 17, 1985, p.141.
37.MOWRY, J.R., MARTINDALE, D.C., HALL, A.H.P., Arabian J. Sci. Eng., 10, 1985, p. 367.
38.GUISNET, M., GNEP, N.S., ALARIO, F., Appl. Catal**.,** A 89, 1992, p.1.
39.INUI, T., Stud. Surf. Sci. Catal., 195 B, 1997, p.1441.
40.BISCARDI, J. A., MEIZNER, G. D., IGLESIA, E., J. Catal., 179, 1998, p.192.
41.EL-MALKI, EL-M., VAN SANTEN, R. A., SACHTLER, W. M. H., J. Phys. Chem. B, 103, 1999, p.4611.
42.DEGNAN, T. F., CHITNIS, G. K., SCHIPPER, P. H., Micropor. Mesopor. Mater., 35-36, 2000, p.245.
43.HAGEN, A., ROESSNER, F., Catal. Rev., 42, 2000, p.403.
44.FRASH, M. V., VAN SANTEN, R.A., Phys. Chem. Chem. Phys., 2, 2000, p.1085.
45.URDA, A., TEL'BIZ, G., SANDULESCU, I., Stud. Surf. Sci. Catal., 135, 2001, p.4017.
46.NICOLAIDES, C. P., SINCADU, N. P., SCURRELL, M. S., Catal. Today, 71, 2002, p.429.
47.URDA, A., ZAVOIANU, R., SANDULESCU, I., Rev. Chim.(Bucharest), **54**, 2003, p.619.
48.SMIESCOVA A., ROJASOVA, E., HUDEC, P., SABO, L., Appl. Catal. A: General, 268, 2004, p.235; React. Kinet. Catal. Lett., 82**,** 2004, p.227.
49.VISWANADHAM, N., MURALIDHAR, G., PRASADA RAO, T. S. R., J. Molec. Catal. A: Chemical, 223, 2004, p.264.
50.KALYAGIN, YU. G., ORDOMSKY, V. V., KHIMYAK, Y. Z., REBROV, A. I., FAJULA, F., IVANOVA, I. I., J. Catal., 238, 2006, p.122.
51.PUJADO, P.R., RABO, J.A., ANTOS, G.J., GEMBICKI, S.A., Catalysis Today, 13, 1992, p. 113.
52.OSAKO, K., NAKASHIRO, K., ONO, Y., Bull. Chem. Soc. Jpn**.,** 66, 1993, p. 755.
53.HAMID, S.B.A., DEROUANE, E.G., MÉRIAUDEAU, P., NACCACHE, C., YARMO, M..A., Stud. Surf. Sci. Catal., 84, 1994, p. 2335.
54.BILBA, N., ASAFTEI, I., IOFCEA, GH., NAUM, N., in „Proceedings of the 12th Int. Zeolite Conf".; TREACY M.M.J., MARCUS B.K., BISHER M.E., HIGGINS J.B., Eds.; Materials Research Society, Baltimore, USA, 1998, p. 2759.
55.BILBA, N., ASAFTEI, I., IOFCEA, GH, PADURARIU, D. M., PAVEL, C. C., Proceedings of the 13th International Zeolite Conference, Montpellier, France, 8-13 July, 2001, 24-P-30, GALARNEAU, A., Di RENZO, F., FAJULA, F., VEDRINE, J., (Eds.), Studies in surface Science and Catalysis, 135, 2001.
56.ASAFTEI, I. V., BILBA, N., SANDU, I., Rev. Chim.,(Bucharest), **64**, no. 5, 2013, p.509.
57.ASAFTEI, I. V., BILBA, N., SANDU, I., Rev. Chim. (Bucharest), **64**, no. 8, 2013, p.836.
58.BILBA, N., BILBA, V. D., VASILE, A., CRUCEANU, M., ABABI, V., Brevet RO, 96 844 (1988).
59.HAAG W.O., in „Proceedings of the 6th Int. Zeolite Conf."., OLSON D.H., BISIO A., Eds.; Butterworths: Surrey, UK, 1984, p. 466.

Manuscript received: 2.12.2013