Conversion of Industrial Feedstock mainly with Butanes and Butenes over HZSM-5 and Zn/HZSM-5 (nitrate) Catalysts

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The activity and selectivity in the aromatization of $C_{/C_{q}}$ hydrocarbons on Zn/HZSM-5 (wt% 1.39 Zn) (nitrate) prepared by ion exchange compared with that on HZSM-5 was been investigated. The experimental results show that the conversion of hydrocarbons and the selectivity to aromatics BTX on the bifunctional Zn/HZSM-5 (nitrate) catalyst are higher than that on monofunctional HZSM-5. On HZSM-5, protons (Bronsted acid sites) and on Zn/HZSM-5, both Zn cations and protons intervene in alkanes dehydrogenation and further in dehydrocyclo-oligomerization reactions that form C_6 - C_9 aromatics. In the liquid product, the aromatics represent an average value of 30 wt%, with more xylenes, on HZSM-5 catalyst after 24 h time on stream at 450°C and 8 atm., and ~70 wt% with more toluene, on Zn/HZSM-5 catalyst, after 52h time on stream at 450°C and atmospheric pressure. The aromatization process is accompanied by oligomerization (more C_9 - C_{10} and $>C_{10}$ aliphatic hydrocarbons) especially on HZSM-5 catalyst.

Keywords: aromatization, butanes, butenes, zinc exchanged HZSM-5.

The transformation of light hydrocarbons C_2-C_4 (alkanes, alkenes and their mixtures) into high value aromatic – rich liquid hydrocarbons by direct catalytic route is an area of great industrial relevance and also of academic interest for the production of benzene, toluene and xylenes (BTX) [1]. The main reason for the production of aromatics is the application of aromatics as high octane blending components for gasoline (application that tends to decrease because of carcinogenic nature of benzene, especially) and the use as a base chemical in a number of petro-chemical and chemical processes [2].

The aromatic hydrocarbons are produced from coal by coking and from crude oil by catalytic reforming or hydro reforming of heavy naphtha, by naphtha pyrolisis and by catalytic cracking FCC [3, 4]. 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) represents a new attractive way of producing BTX aromatics. The conversion of light alkanes into aromatics (with low selectivity to BTX) was first described in 1970 by Csicsery, using bifunctional catalysts such as Pt on alumina or metal oxide on alumina [5].

Aromatization of light hydrocarbons into aromatics over zeolite catalysts, in particular on middle-porous ZSM-5 (MFI) has attracted much attention in the past decades [6–20]. The properties that make ZSM-5 critical 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 micro pores and/or cavities size and shape. The structure 3-D of ZSM-5 zeolite is characterized by two dimensional types of intersecting channels (2-D pore system) with 10member ring (MR) openings: one type is sinusoidal (zigzag) with a near-circular (0.53x0.56 nm) openings and the other one is straight with an elliptical (0.51x0.55 nm) openings [21, 22]. The channel intersections have a diameter of 0.89 nm and are the locus of strong acid sites and of aromatic C₆-C₈ hydrocarbons formation. Due to the shape-selective properties of the ZSM-5

^oDue 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 [23].

Already a few commercial processes have been announced based on HZSM-5 (M2 Forming process – Mobil Oil, and M-Forming process – Mobil [24-26], on Ga/HZSM-5 (Cyclar-BP/UOP [27-31] – Cyclization of light hydrocarbons to aromatics - and Z-Forming from Mitsubishi Oil and Chiyoda [32]), on Zn/HZSM-5 (Alpha process of Asahi Chemical and Petrochemical [33]), on monofunctional Pt/K(Ba)L (Aromax[™] process – Chevron – Phillips Chemical Co. [34] and RZ- Platforming process – UOP [35, 36] and Aroforming from IFP and Salutec based on metal oxides-HZSM-5 [37,38].

ZSM-5 (MFI) zeolite was discovered in the late 1965's by Mobil researchers and was patented in 1972 [39, 40]. Many studies have focused on the ability of the monofunctional acid catalyst (HZSM-5) to convert light hydrocarbons to BTX [7-10, 14-16, 19, 20, 25, 26, 41-48]. 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 (\leq 30%). Aromatization over HZSM-5 is accompanied by substantial cracking of C – C bond of alkanes with a

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production of 3 moles of small alkanes per one mole of aromatics.

The enhancement of light alkanes conversion to aromatics has been demonstrated by using metalcontaining HZSM-5 catalysts instead of HZSM-5. The catalysts investigated contain as dehydrogenating metal: Pt [9, 11, 15, 34-37], Ga [7, 9-12, 14-20, 23, 27-32, 41, 44-48], Zn[7, 10, 14-19, 33, 40-46, 49-66], Pd, Ge, Ni, Fe, Cu, Mo, Co, Ru, Re, Ag; two metals: Pt-Sn, Pt-Re, Pt-Ge, Pt-Ga, Pt-Zn, Zn-Ni, Zn-Cu, Zn-Ga, Zn-In, Zn-Na; oxides MO (M = Zn, Cu, Ni); oxides MO₂ (M = Sn, Zr, Ce) [60], oxides M_2O_3 (M = Ga, Fe, Cr, La, Y, In, Nd, Tl) [61, 62].

The catalytically active species (metal, metal ion, metal oxide) facilitate the heterolytic cleavage of the C–H bond of the adsorbed alkanes (dehydrogenation of alkanes) and accelerate the combination of surface hydrogen atoms formed via the dehydrogenation and dehydrocyclization process and their removal as molecular hydrogen.

Particular attention was directed to the utilization of Pt, Ga and Zn for the aromatization of light alkanes, especially in the combination with HZSM-5. Pt exhibit great dehydrogenation activity of light alkanes, but is, also, an active hydrogenollysis catalyst of oligomers and cyclic compounds and is expensive. Ga has the advantage of the lower volatility under reduced atmosphere at high temperature and of the moderate or low activity in hydrogenollysis. The poisonousness and the high price of gallium salt have a limiting role. Zn ion in the di-cation state, Zn²⁺, with a closer d¹⁰ electronic configuration exhibit a good dehydrogenation activity and aromatization selectivity, seems to be stable in cationic exchange position (not in the form of ZnO) and remain unreduced under the alkanes conversion conditions.

Use of a Zn-based HZSM-5 catalyst instead of Ga-based HZSM-5 catalyst might be preferential from the environmental point of view (is a low-waste catalyst) and from technological (profitable) and economical (cheaper) aspects.

The dehydrogenation metal may be incorporated into the HZSM-5 zeolite structure by aqueous ion exchange using solution of salts, by solid-state ion exchange involving thermal treatment, chemical vapor deposition, sublimating volatile compounds onto zeolites, mechanical mixing of metal oxide with HZSM-5 zeolite and by isomorphous substitution in the framework during the hydrothermal synthesis.

The purpose of this study is to develop, characterizes and tests the performances of the fresh and reactivated zinc ion exchanged HZSM-5 zeolite catalyst for the conversion of butanes-butenes technical mixture to light aromatic hydrocarbons. The objectives of this work are to study the catalytic activity and selectivity of Zn/HZSM-5 catalyst, in which the NaZSM-5 zeolite was synthesized from alkaline media in presence of ethylene glycol, the role of butenes in co-aromatization of small alkanes and the effect of time on stream (TOS) on conversion of butanes-butenes mixture under fixed-bed down-flow conditions at 450°C, 8 atm. for HZSM-5 and atmospheric total pressure for Zn/HZSM-5 and at a space velocity of 1 h⁻¹.

Experimental part

NaZSM-5 zeolite synthesis

The reactant materials used in hydrothermal synthesis were sodium silicate solution (29.63 wt% SiO₂, 9.55 wt% Na₂O, 60.82 wt% H₂O), aluminum sulphate, Al₂(SO₄)₃. 18H₂O (15 wt% Al₂O₃), sulphuric acid (96 wt% H₂SO₄),

ammonium hydroxide solution (25 wt% NH₃), ethylene glycol and demineralized water.

NaZSM-5 zeolite used in this work was synthesized according to a method described in the patent [70]. The NaZSM-5 zeolite having SiO₂/Al₂O₃ molar ratio of 36.02 was crystallized from a hydrogel with molar composition 6.49 Na₂O-Al₂O₃-58.92 SiO₂-29.43 EG-1832 H₂O having a molar ratio HO⁻_{free}/SiO₂=0.21. HO⁻_{free} are the HO⁻ ions not neutralized by H⁺ ions added indirectly by means of aluminum sulphate and directly by means of sulphuric acid. The synthesis run was carried out at 180 ± 5°C for 24 h in a Teflon-lined stainless steel autoclave under intermittent stirring and autogenously pressure. The solid material was filtered, washed with demineralized water, dried at 110°C for 6h and heated in air at 550°C for 6h to burn off the organic additive and to calcined.

The calcined sample was characterized by X-ray diffraction (XRD) to identify the zeolite structure type, phase purity, degree of crystallinity and crystallite size. The XRD measurements was performed using a Philips PW 1830 computerized-diffractometer with CuK_{α} radiation and Ni filter with a scan rate of 0.02° s⁻¹ in the 20 range of 6-30°. The surface morphology and the size of the crystals of calcined NaZSM-5 zeolite was studied by SEM (Microspec WDX-2A) using a 30 kV accelerating potential. The chemical composition of the calcined NaZSM-5 sample was analyzed by wet method after dissolving in HF solution: aluminum concentration (Al₂O₃) was determined by the chelatometric titration using EDTA and Zn standard solution, sodium concentration (Na₂O) by flame photometry using a Karl Zeiss Jena Phlamenphotometer and SiO, by difference between the calcined weight of sample at 950°C and weight of calcined residuum at 950°C after the treatment with HF solution.

Catalyst Zn/HZSM-5 preparation

First, the ammonium form, NH₄ZSM-5 was obtained by ion exchange of NaZSM-5 zeolite, three times under stirring, with 1M NH₄NO₃ solution (solid (g) : solution (mL) ratio of 1:5) at 80°C for 3h each time. The NH₄ZSM-5 was filtered, washed, dried at 110°C for 6h and calcined in air at 550°C for 6h to get protonic HZSM-5 zeolite. The HZSM-5 zeolite was converted in the Zn/HZSM-5 form by treating it with 0.1 M Zn(NO₃)₂ aqueous solution (solid : solution = 1g : 5 mL) two times under stirring at 80°C for 6h each time. The Zn/HZSM-5 sample was washed, dried at 110°C for 6h and calcined in air at 450°C for 6h.

The zinc contained in the sample was 1.39 wt% (1.73 wt% as ZnO). The structure of HZSM-5 and Zn/HZSM-5 samples was checked up by X-ray diffraction, the specific surface area was determined applying the BET method using a Carlo-Erba Sorptomatic Series 1800 instrument at -196°C and the total acidity (Bronsted and Lewis) of HZSM-5 and Zn/HZSM-5 catalysts have been carried out by ammonia TPD method.

The catalyst granules were obtained by extrusion the mixture of HZSM-5 and Zn/HZSM-5 powder with 20 wt% γ -Al₂O₃ Before using, HZSM-5 was activated in air at 550°C for 6h and Zn/HZSM-5 catalyst in nitrogen at 475°C for 6h.

Catalytic experiments

The catalytic experiments were carried out in a continuous flow fixed-bed stainless-steel reactor (Twin Reactors System Naki) (with 25 mm internal diameter) at 8 atm pressure (over HZSM-5) and at atmospheric pressure (over ZnHZSM-5) at 450°C and a space velocity (WHSV) of 1 h⁻¹ without recirculation of resulted gaseous products. The catalyst charge was 100 cm³ and the time of stream

was ~24h for HZSM-5 (five tests) and ~52h for Zn/HZSM-5 (ten tests). After each test, the catalyst was regenerated at 475° C for 8h in nitrogen with 2% oxygen flow. The effluents from the reactor were cooled in a condenser and the liquid and the gaseous fractions collected after 4 h were analyzed gas chromatographic: a GC Carlo Erba Mega using a fused silica capillary column (25 m length and 0.32 mm i.d.) with SEE 52 stationary phase and FID for liquid phase, and a GC Carlo Erba Model C, using a column (6 m length) with squalane and dimethyl sulpholane for gaseous phase.

Results and discussions

X-ray diffraction analysis

The diffraction pattern of the starting Pentasil NaZSM-5 with SiO₂/Al₂O₃ = 36.02 in the region of 2θ = 6 - 30s is presented in figure 1(a). From the diffractogram, the positions of diffraction lines $(2\theta_{hkl})$, the calculated d_{hkl} values $(n\theta l=2dsin\theta)$ and the corresponding relative intensities (I/I_0) agree very well with the reported values for ZSM-5 (MFI) zeolite [22, 71].

The zeolite have a high degree of crystallinity (99.6%) derived from the high intensities of the XRD lines in the region $22.5 - 25^{\circ}2\theta$, based on a standard ZSM-5 crystallized in presence of tetrapropyl ammonium hydroxide:



Desorbed ammonia, mmol/g

2nd peak

(HT)

0.282

0.144

Total

acidity

0.900

0.782

No other diffraction peaks were found in this region (6- $30^{\circ}2\theta$), which means the pure ZSM-5 was obtained.

The XRD patterns of HZSM-5 and of zinc-exchanged HZSM-5 (not presented) are similar to NaZSM-5; the ion exchange process and thermal treatment not producing any damage to the zeolite network. The Zn/HZSM-5 sample exhibits no diffraction peaks at $2\theta = 31.60^{\circ}$, 34.2, 36.1 and 56.6° which are characteristic for ZnO indicating that the zinc is present as Zn^{2+} highly dispersed in the zeolite matrix.

Morphology of the NaZSM-5 sample

The scanning electron micrograph of the NaZSM-5 sample is shown in figure 1(b). It can be seen the well developed hexagonal-shaped crystals with crystal size of $3.5 - 4.3 \,\mu\text{m}$ in length and 2.1 - 2.86 m in width and the no crystalline material is absent.

Elemental analysis and specific surface area

The chemical composition of calcined NaZSM-5 zeolite as well as texture parameters is presented in table 1.

Acidity and strength distribution

The acidity of the HZSM-5 and Zn/HZSM-5 catalysts was evaluated by using temperature programmated desorption (TPD) of ammonia technique and the NH₃-spectra TPD (amount of ammonia desorbed, mmol/g, vs temperature of desorption, °C). Being a small molecule, ammonia (kinetic diameter 2.62 A) can reach all the acid sites in a zeolite. The total amount of acid sites (Bronsted protic and Lewis aprotic acid sites) and the acid strength (expressed as the maximum temperature of ammonia desorption) are summarized in table 2.

Both catalysts give two humps (peaks), one at low temperature (LT) (T < 300°C) and the other one at high temperature (HT) (T > 300°C). The low region with $T_{max} = 1000$ 200 - 220°C correspond to the low strength of Lewis and weak Bronsted acid sites and consists of the physisorbed ammonia (ammonia is coordinative bonded to the terminal silanol groups). The high region with T_{rr} $= 420^{\circ}C$ correspond to the moderate and high strength of Bronsted acid sites and consists of the chemisorbed ammonia (ammonia forms ammonium ions hydrogen-bonded to oxygen of the framework).

Cations exchange of NaZSM-5 with protons (H⁺ ions) forms hydroxyl groups resulting in a bridging a" Si-OH-Al a" structure. These groups known as Bronsted acid sites are in a dissociation equilibrium, like mineral acids in solution: [72]

(high temperature) (low temperature)

Table 1 CHEMICAL COMPOSITION OF CALCINED NAZSM-5 ZEOLITE AS WELL AS TEXTURE PARAMETERS

Table 2 QUANTITATIVE RESULTS OF AMMONIA DESORBED (TOTAL ACIDITY) AND THE MAXIMUM TEMPERATURE OF DESORPTION (ACID STRENGTH)

0.638 REV. CHIM. (Bucharest) ◆ 66 ◆ No. 5 ◆ 2015

1st peak

(LT)

0.618

Catalyst

HZSM-5

Zn/HZSM-5

http://www.revistadechimie.ro

T_{max},

1st peak

220

200

⁰C

2nd peak

420

420

Cations exchange of HZSM-5 with multivalent cations or transition metal ions (Zn²⁺) forms weak and moderate strong acid sites, especially Lewis acid sites. Lewis acid sites can be also generated by dehydration from two acidic hydroxyl groups at temperature higher than 480°C, by presence of hydroxyl nests [73].



The total acidity of ZSM-5 catalysts is due to the number of acid sites (proportional to the Al content of framework) and to the strength of acid sites (determined by the number of Al atoms that are adjacent to a proton as second-nearest neighbors). The sites (protons) corresponding to framework bridged hydroxyl groups surrounded by less than three-nearest neighbors are moderate acid sites and are mostly Bronsted acid sites. The sites corresponding to protons surrounded by three Al atoms as second-nearest neighbors are weak acid sites and are mostly of Lewis type. Each Al atom has four Si atoms as nearest neighbors (Lowenstein's rule). The catalytic activity of zeolite catalyst takes into consideration the total number of acid sites, the ratio of Bronsted to Lewis sites and the acid strength distribution of each types of site.

Table 3 presents the feedstock composition and reaction conditions of aromatization for five cycles (with intermediate regeneration) on HZSM-5 catalyst.

Conversion of mixed butanes/butenes feedstock to aromatics over HZSM-5 takes place with low selectivity to BTX, the reactants forming predominantly the cracking products.

The change in the gaseous product distribution and of liquid phase over HZSM-5 with time on-stream in the transformation of butanes and butenes are presented in figure 2.

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-C4	0.39	0.30	0.12	0.07	-			
$tr2-C_4^{=}$	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			

TOS : ~24 h; temperature: 450°C; 8 atm. pressure; WHSV = 1 h⁻¹; catalyst; 100 cm³; regeneration of catalyst after each test: 475°C for 6h in nitrogen flow with 2% oxygen.



 $\bullet -\Sigma C_4; \bullet -\Sigma C_4^=; \blacktriangle C_1 + C_2; \ast -C_3$



The concentration of butanes (n+i) 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 $(1-C_4^{=}, \text{trans-2-}C_4^{=})$ and cis-2-C₄⁼) 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% (vol) after 4 h 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 visible for first 12h run, after that aliphatic $C_5 - C_{10}$ are formed.

Catalytic performance of Zn/HZSM-5 catalyst in $C_4/C_4^{=}$ hydrocarbons aromatization

The industrially feedstock composition and the conditions of aromatization on the ion exchanged Zn/HZSM-5 during of the ten catalytic tests are given in table 4.

Aromatization of a mixture containing 57.41%(vol) butanes and 30.87%(vol) butenes (feedstock no.1) over Zn/HZSM-5 takes place with high selectivity to aromatics BTX and with production of molecular hydrogen. The changes in the gaseous product distribution over Zn/HZSM-

Table 3BUTANES-BUTENES FEEDSTOCKCOMPOSITION AND CONDITIONS OFAROMATIZATION ON HZSM-5 CATALYST

Fig. 2. Gaseous phase composition and liquid phase composition *vs* time on stream over HZSM-5 catalyst in butane/ butenes conversion, test no. 4

Feedstock	Test number										
composition	1	2	3	4	5	6	7	8	9	10	
(vol.%)											
C ₃	1.08	0.28	0.89	0.62	0.42	0.24	0.26	0.31	0.30	0.57	
n-C ₄	9.67	2.90	5.72	5.40	12.02	10.58	11.42	12.52	11.36	14.63	
i-C4	57.34	49.34	51.91	52.53	44.85	36.10	31.33	33.21	35.24	38.52	
$1 - C_4^{=}$	9.78	16.20	10.57	16.97	12.59	16.07	17.90	16.53	15.85	13.39	
$i-C_4^{=}$	11.03	26.28	26.00	19.34	24.39	30.33	31.78	29.42	30.16	12.63	
$tr2-C_4^{=}$	6.72	2.77	3.15	3.54	4.42	4.64	5.16	5.61	5.23	11.86	
$cis-2-C_4$ ⁼	3.34	1.71	1.64	1.35	1.20	2.05	2.12	2.36	1.84	7.53	
TOG 50	1		500G .	1	+	TTTY	** ***		100	3	

TOS : 52 h; temperature: 450°C; atmospheric pressure; WHSV = 1 h^{-1} ; catalyst; 100 cm³; regeneration of catalyst after each test: 475°C for 6h in nitrogen flow with 2% oxygen.



5 with time on-stream (from four to four hours), test no.1 in comparison with the test no.10, are shown in figure 3.

The concentration of butenes decreased from 30.87 vol. to 1.22 vol.% after first 4h of reaction and remain at values smaller than 2.0% after 5h of reaction. The concentration of butanes (n+i) decreased from 67.01% to 15.03% after 8h of reaction, after that is continuously increasing without to rise above the initial concentration. It is evident that after about 470h of catalytic reaction and nine regeneration steps at 475^sC the catalytic activity and selectivity to aromatics BTX are present. The hydrogen molecular concentration exceeds the butanes concentration during the first 40h of reaction in test no.1 and after 24h of reaction in test no.10. The thermal treatments and the partial removal of coke deposited can be the reason for this diminution but the zinc is still present in the catalyst. The main gaseous hydrocarbon over Zn/HZSM-5 is propane (20 vol. %) nearby $C_2 - C_2^{=}$, less than over HZSM-5 (about 60 vol. %).

The aromatic hydrocarbon distribution in the liquid phase corresponding to catalytic tests no.1 and no.10 is plotted in figure 4.

The produced aromatic hydrocarbons were mainly toluene (~40 wt.%) and xylenes (~21 wt%); the benzene in the aromatics was about 9 wt% greater than over HZSM-5. The aliphatic hydrocarbons C_5-C_{10} fraction in the liquid phase is increasing from ~ 13 wt% after 4h of reaction to ~23 wt% after 52h of reaction and is based on C_9 and C_{10} hydrocarbons. The formation of aliphatic hydrocarbons with more than 10 carbon atoms (> C_{10}) is limited to about 6



Table 4BUTANES-BUTENES FEEDSTOCKCOMPOSITION AND CONDITIONS OFAROMATIZATION ON ZN/HZSM-5CATALYST

Fig.3. Gaseous phase composition *vs.* TOS over Zn/HZSM-5 catalyst: $\bullet -\Sigma C_4$; $\bullet -\Sigma C_4 = : \bullet -C_2 + C_2 = : *-C_3 : o-H_2$

wt%. In the liquid product of all catalytic tests is present naphthalene in a concentration below 1.0 wt%.

The average output of aromatic hydrocarbons BTX during the five catalytic experiments over HZSM-5 catalyst is presented in figure 5.

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.

In figure 6 is presented the average output of aromatics BTX during the ten catalytic experiments over Zn/HZSM-5. The average output of aromatic hydrocarbons BTX over Zn/HZSM-5 bifunctional catalyst represents more than 70 wt% in the liquid phase in all ten catalytic tests.

Aromatization of multicomponent feedstock is complex, involving a large number of heterogeneous reactions. It is generally agreed that the aromatization of low molecular weight alkanes can be represented as a three stage process: 1) alkanes conversion into small alkenes, $C_2^{=}$ - $C_4^{=}$; 2) alkenes oligomerization and cracking, and 3) aromatization of small alkenes into C_6 - C_{10} aromatic hydrocarbons. The relevant reactions consist of: a) alkanes C-H bond activation through a pentavalent carbonium ion and of alkenes C-H through a trivalent carbonium ion (through protonation); b) dehydrogenation of carbonium ion to carbenium ion and finally to small alkenes, $C_2^{=}$ - $C_4^{=}$; c) oligomerization of small alkenes to higher alkenes, C_6 - C_{10} , d) rapid isomerization, e) β -scission; f) dehydrogenation of higher alkenes to dienes; g) cyclization of dienes to cyclic alkenes; h) dehydrogenation of cyclic alkenes to

> Fig. 4. Distribution of hydrocarbons in liquid phase: $\bullet -\Sigma$ Ar; $\bullet --C_5-C_{10}$; $\bullet -> C_{10}$; *-B; o-T; x-X+EB



cyclic dialkenes and finally to aromatics, C_6 - C_{10} [15, 41, 47, 48, 76].

In presence of HZSM-5 catalyst, the first stage of alkanes transformation proceeds via two routes: protolytic cracking route of C–C and C–H bonds in the alkanes molecules on strong acid sites to very unstable carbonium ion that collapse to give alkanes (or H₂) and adsorbed carbenium ions, and hydrogen transfer route (dehydrogenation) between the alkanes with the alkenic intermediates adsorbed on the Bronsted acid strong sites resulting new alkanes as side products [7, 18, 41, 48, 74-77]. The second stage, alkenes interconversion, includes alkenes isomerization, oligomerization and cracking steps. The third stage, alkenes aromatization, proceeds via a sequence of cyclization and hydrogen transfer with formation of aromatics and alkanes.

Monofunctional HZSM-5 catalyst exhibits preferentially high cracking, isomerization and β -scission reactivity that lead to loss of carbon atoms to undesirable products [14]. Hydrogen rejection from surface occurs by hydrogen transfer to alkanes which limits the aromatics yield that can be obtained on HZSM-5.

It is well known that the acidity of the surface of the catalyst has a decisive effect on the activity of the catalyst. The acidity is influenced by the type of the acid sites, such as the Bronsted (protic acid sites) and Lewis (aprotic acid sites) sites as well as the number and the strength of the acid sites. The type and concentration of acid sites are controlled by the location of Al atoms at the framework [AlO₄]⁻ and non-framework position. The total amount of acid sites (Bronsted and Lewis) of the HZSM-5 and Zn/HZSM-5 and the acid strength expressed as the maximum temperature of ammonia desorption are summarized in table 2. Bronsted sites can form both carbenium and carbonium ion intermediates whereas Lewis sites produce only carbenium ions.

The HZSM-5 catalyst contain predominantly Bronsted strong acid sites related to aluminum located in the framework and Bronsted weakly acid sites related to some silanol groups and Lewis acid sites related to the extraframework aluminum (AlO⁺ species) or distorted aluminum in framework. The HZSM-5 catalyst is solid Bronsted super acids, which at high temperature (~500°C) can even protonate alkanes. The acid strength of HZSM-5 catalyst is enhanced by the presence of extra-framework aluminum which is easy generated during the synthesis of



Fig. 6. The aromatics average output over Zn/HZSM-5 catalyst (450°C, atm pressure, WHSV = 1 h⁻¹)

ZSM-5 by non-template method. The total acidity of HZSM-5 catalyst determined by ammonia-TPD method have the value of 0.900 mmol/g and the high strength (mostly Bronsted acid sites) to the region with $T_{max} = 420$ °C (0.282 mmol/g). The strength of the Bronsted acid sites is strong in HZSM-5 catalyst and the conversion of alkenes and alkanes to small alkenes takes place via acid cracking and hydrogen-transfer reactions.

The total acidity of zinc ion-exchanged HZSM-5 (50%) is lower (0.782 mmol/g) and the strength of acid sites in the region with $T_{max} = 420$ °C is only 0.144 mmol/g. After the zinc incorporation by ion exchange method the concentration of Bronsted acid sites decreases and the amount of Lewis sites increases [14, 49]. Zn/HZSM-5 catalyst contains medium acidity that minimizes the occurrences of cracking reactions. Zinc incorporated in HZSM-5 zeolite through ion exchange is very well dispersed and is stable in isolated cationic (Zn^{2+}) positions with tetrahedral symmetry and of ZnOH+ not thermally stable either compensating the charge of two Al tetrahedral (O- $Zn^{2+}O$) or legated to one internal silanol or OH group (= Si-OZn) [53,74]. In the case of Zn/HZSM-5 catalyst the alkanes dehydrocyclo-dimerization 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. Zinc cations as Lewis acid sites promote alkanes dehydrogenation (heterolytic cleavage of the C-H bond) to alkenes (dehydrogenation function) and oligomers dehydrogenation to oligomers with one or more double bonds, decrease β -scission rates and the residence time of alkenes within oligomerization/ β -scission cycles[16], exert strong hydrogen attracting action and promote removal of hydrogen atoms adsorbed as hydrogen molecular [16, 18, 40, 41], prevents hydrogenation of alkenes required in cyclization and consequently, enhances aromatization [41,74]. The ZnK-edge X-ray absorption studies and TPR studies show that Zn2+ cations in Zn/HZSM-5 do not reduce to zerovalent species (Zn^0) [14, 52].

Butanes-butylenes mixtures conversion over HZSM-5 and Zn/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 and Lewis acid sites with acidic OH groups located at channel intersections.

Bifunctional catalyst Zn/HZSM-5 exhibits high selectivity to aromatics BTX in the aromatization of butanes-butenes mixture, due to dehydrogenation of alkanes to alkenes and dehydrocyclization of alkenic oligomers to naphthenic intermediates on exchanged Zn^{2+} cations (Lewis strong acid sites), and of alkenes interconversion and aromatic formation on acid OH groups (Bronsted strong acid sites). The average output of aromatics BTX in the liquid phase represent more than 70 wt% and the formation of toluene (~40 wt. %) and xylenes (~21 wt.%) are of preference. The significant production of aromatics is explained by the enhanced production of alkenes by the effective dehydrogenating action of zinc on alkanes.

The high Bronsted acidity of HZSM-5 catalyst is responsible for the high percentage of C_5 - C_{10} aliphatic hydrocarbons (~80 wt% after 24h TOS), in comparison with Zn/HZSM-5 catalyst (~25 wt% after 52 h TOS).

The product distribution (gaseous and liquid) in the conversion of butanes-butenes mixtures at 450°C and 8 atm. and atmospheric pressure over HZSM-5 and Zn/HZSM-5 catalysts is changing with time on-stream. The HZSM-5 catalyst deactivates fast and Zn/HZSM-5 catalyst is 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 protonation to carbenium ions from a Bronsted acid site and then activate butanes through hydride abstraction.

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

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