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Aromatization of industrial feedstock mainly with butanes and butenes over HZSM-5 and Zn/HZSM-5 catalysts

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Abstract: The activity and selectivity in the aromatization of $C_4/C_4^=$ hydrocarbons on Zn/HZSM-5 (wt% 1.39 Zn) prepared by ion exchange compared with that on HZSM-5 was investigated. The experimental results show that the conversion of hydrocarbons and the selectivity to aromatics BTX on the bifunctional Zn/HZSM-5 catalyst are higher than that on monofunctional HZSM-5. On HZSM-5, protons (Brönsted acid sites) and on Zn/HZSM-5, both Zn cations and protons intervene in alkane dehydrogenation and further in dehydrocyclooligomerization 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 ºC and 8 atm, and 70 wt% with more toluene, on Zn/HZSM-5 catalyst, after 52 h time on stream at 450 ºC 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.

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Introduction

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[1] is an area of great industrial relevance and also of academic interest for the production of benzene, toluene and xylenes (BTX). 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 petrochemical and chemical processes.[2]

The aromatic hydrocarbons are produced from coal by coking and from crude oil by catalytic reforming or hydroreforming of heavy naphtha, by naphtha pyrolysis 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,[5] using bifunctional catalysts such as Pt on alumina or metal oxide on alumina.

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. The activity is mostly determined by the zeolite Brönsted acid sites and by the active metal-phase supported by zeolite and selectivity is due to the zeolite micropores and/or cavities size and shape. The 3-D 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 (0.53×0.56 nm) openings and the other one is straight with elliptical (0.51×0.55 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 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.[23]

A few commercial processes[24] have already been announced based on HZSM-5 (M2 Forming process – Mobil Oil[25] and M-Forming process – Mobil[26]), on Ga/HZSM-5 (Cyclar-BP/UOP[27-31] – **Cycl**ization of light hydrocarbons to **ar**omatics - 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[39] and was patented in 1972.[40] Many studies have focused on the ability of the monofunctional acid catalyst (HZSM-5) to convert light hydrocarbons to BTX.[7-10,14-16,19,20,25,26,41,42,45-48] 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 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 metal-containing HZSM-5 catalysts instead of HZSM-5. The catalysts investigated contain as dehydrogenating metal: Pt;[9,11,15,34-37,63,67] 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 MO_2 (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 alkane (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 exhibits great dehydrogenation activity of light alkanes, but is, also, an active hydrogenolysis 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 hydrogenolysis. The poisonousness and the high price of gallium salt have a limiting role. Zn ion in the di-cation state, Zn^{2+}, with a closer d^{10} electronic configuration exhibits a good dehydrogenation activity and aromatization selectivity, seems to be stable in cationic exchange position (not in the form of ZnO) and remains unreduced under the alkane conversion conditions.

The use of a Zn-based HZSM-5 catalyst instead of Ga-based HZSM-5 catalyst might be preferential from environmental point of view (is a lowwaste catalyst) and due to 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, characterize and test the performances of the fresh and reactivated zinc ion exchanged HZSM-5 zeolite catalyst for the conversion of butanes-butenes 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 ºC, 8 atm and atmospheric total pressure and at a space velocity of 1 h^{-1}.

Experimental

NaZSM-5 zeolite synthesis

The reactant materials used in hydrothermal synthesis were sodium silicate solution (29.63 wt% SiO_2, 9.55 wt% Na_2O, 60.82 wt% H_2O), aluminum sulphate, $Al_2(SO_4)_3 \cdot 18H_2O$ (15 wt% Al_2O_3), sulphuric acid (96 wt% H_2SO_4), ammonium hydroxide solution (25 wt% NH_3), 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 SiO_2/Al_2O_3 molar ratio of 36.02 was crystallized from a hydrogel with molar composition of 6.49 Na_2O-Al_2O_3-58.92 SiO_2-29.43 EG-1832 H_2O having a molar ratio $HO^{-}_{free}/SiO_2=0.21$. 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 ºC for 24 h in a Teflon-lined stainless steel autoclave under intermittent stirring and autogeneous pressure. The solid material was filtered, washed with demineralized water, dried at 110 ºC for 6 h and heated in air at 550 ºC for 6 h to burn off the organic additive and to calcine.

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 were performed using a Philips PW 1830 computerized-diffractometer with CuK_{α} radiation and Ni filter with a scan rate of 0.02º s^{-1} in the 2θ range of 6-30º. The surface morphology and the size of the crystals of calcined NaZSM-5 zeolite were studied by SEM (Microspec WDX-2A) using a 30 kV accelerating potential. The chemical composition of the calcined NaZSM-5 sample was analyzed by the wet method after dissolving in HF solution: aluminum concentration (Al_2O_3) was determined by the chelatometric titration using EDTA and Zn standard solution, sodium concentration (Na_2O) by flame photometry using a Karl Zeiss Jena Phlamenphotometer and SiO_2 by difference between the calcined weight of sample at 950 ºC and weight of calcined residuum at 950 ºC after the treatment with HF solution.

Catalyst Zn/HZSM-5 preparation

First, the ammonium form, NH_4ZSM-5 was obtained by ion exchange of NaZSM-5 zeolite, three times under stirring, with 1M NH_4NO_3 solution (solid (g) : solution (mL) ratio of 1:5) at 80 ºC for 3 h each time. The NH_4ZSM-5 was filtered, washed, dried at 110 ºC for 6 h and calcined in air at 550 ºC for 6 h 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 $Zn(NO_3)_2$ aqueous solution (solid : solution = 1g : 5 mL) two times under stirring at 80 ºC for 6 h each time. The Zn/HZSM-5 sample was washed, dried at 110 ºC for 6 h and calcined in air at 450 ºC for 6 h.

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 ºC and the total acidity (Brönsted and Lewis) of HZSM-5 and Zn/HZSM-5 catalysts by ammonia TPD method.

The catalyst granules were obtained by extrusion of the mixture of HZSM-5 and Zn/HZSM-5 powder with 20 wt% γ-Al_2O_3. Before used, HZSM-5 was activated in air at 550 ºC for 6 h and Zn/HZSM-5 catalyst in nitrogen at 475 ºC for 6 h.

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 ºC and a space velocity (WHSV) of 1 h^{-1} without recirculation of resulted gaseous products. The catalyst charge was 100 cm^3 and the time of stream was 24 h for HZSM-5 (five tests) and 52 h for Zn/HZSM-5 (ten tests). After each test, the catalyst was regenerated at 475 ºC for 8 h 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 by gas chromatography with 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.

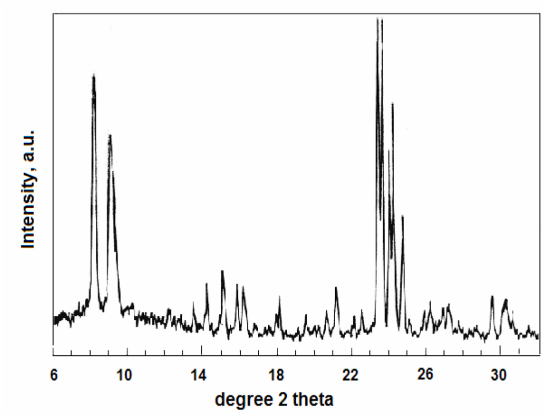
Results and discussion

X-ray diffraction analysis

The diffraction pattern of the starting pentasil NaZSM-5 with SiO_2/Al_2O_3 = 36.02 in the region of 2θ = 6 - 30º is presented in Figure 1. From the diffractogram, the positions of diffraction lines ($2\theta_{hkl}$), the calculated d_{hkl} values ($n\lambda=2d\sin\theta$) and the corresponding relative intensities (I/I_0) agree very well with the reported values for ZSM-5 (MFI) zeolite.[22,71]

The zeolite has a high degree of crystallinity (99.6%) derived from the high intensities of the XRD lines in the region 22.5 – 25º 2θ, based on a standard ZSM-5 crystallized in presence of tetrapropyl ammonium hydroxide:

$$\text{Crystallinity}(\%)=\frac{\sum I_{hkl}-\text{sample}}{\sum I_{hkl}-\text{standard}}100$$



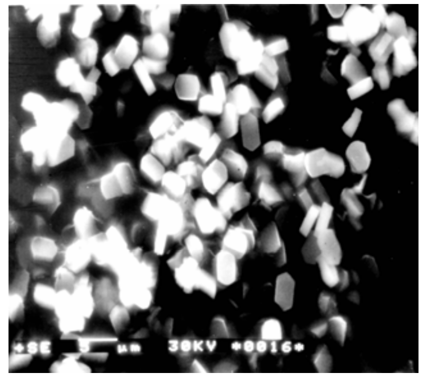


Figure 1. Powder X-ray diffraction pattern and SEM micrograph of calcined NaZSM-5.

No other diffraction peaks were found in this region ($6\text{-}30^0\ 2\theta$), 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 are not producing any damage to the zeolite network. The Zn/HZSM-5 sample exhibits no diffraction peaks at $2\theta = 31.60^o$, 34.2^o, 36.1^o and 56.6^o 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. It can be seen the well developed hexagonal-shaped crystals with crystal size of 3.5 - 4.3 µm in length and 2.1 – 2.86 µm in width and that no crystalline material is absent.

Elemental analysis and specific surface area

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

Table 1. The chemical composition of calcined NaZSM-5 zeolite and texture parameters.

Oxidic composition, wt%	SiO_2	Al_2O_3	Na_2O	SiO_2/ Al_2O_3 molar ratio	Zn/ZnO
NaZSM-5	92.92	4.38	2.70	36.02	-
ZnHZSM-5			-	36.02	1.39/1.73
Specific surface area, m^2g^{-1}	NaZSM-5		HZSM-5	ZnHZSM-5	
	302.5		291	273	
Static adsorption capacity after 24 h	H_2O		Benzene	n-hexane	
NaZSM-5	11.75		12.7	10.24	

Acidity and strength distribution

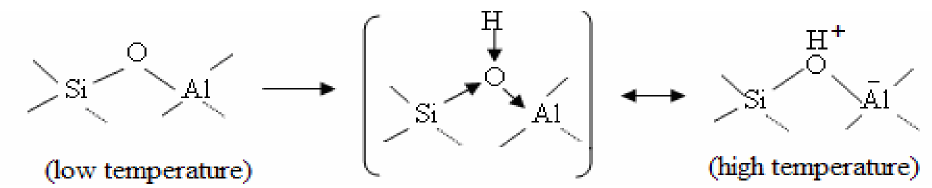
The acidity of the HZSM-5 and Zn/HZSM-5 catalysts was evaluated by using temperature programmated desorption (TPD) of ammonia technique and the NH_3-spectra TPD (amount of ammonia desorbed, mmol/g, *vs* temperature of desorption, ºC). Being a small molecule, ammonia (kinetic diameter 2.62 Å) can reach all the acid sites in a zeolite. The total amount of acid sites (Brönsted protic and Lewis aprotic acid sites) and the acid strength (expressed as the maximum temperature of ammonia desorption) are summarized in Table 2.

Table 2. Quantitative results of ammonia desorbed (total acidity) and the maximum temperature of desorption (acid strength).

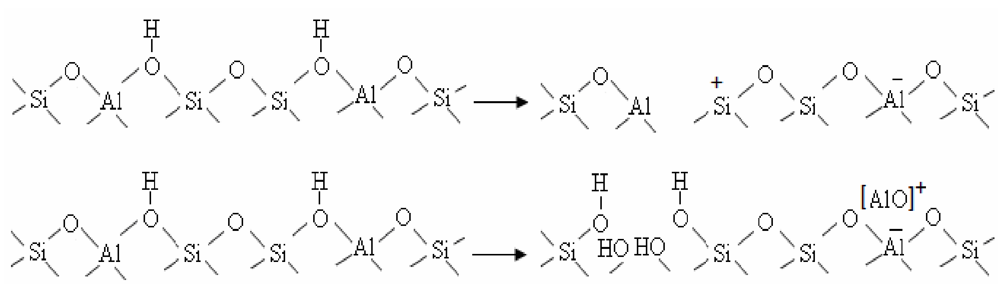
Catalyst	Desorbed ammonia, mmol/g			T_{max}, ºC	
	1st peak (LT)	2nd peak (HT)	Total acidity	1st peak	2nd peak
HZSM-5	0.618	0.282	0.900	220	420
Zn/HZSM-5	0.638	0.144	0.782	200	420

Both catalysts give two humps (peaks), one at low temperature (LT) (T < 300 ºC) and the other one at high temperature (HT) (T > 300 ºC). The low region with T_{max} = 200 – 220 ºC corresponds to the low strength of Lewis and weak Brönsted acid sites and consists of the physisorbed ammonia (ammonia is coordinatively bonded to the terminal silanol groups). The high region with T_{max} = 420 ºC corresponds to the moderate and high strength of Brönsted acid sites and consists of the chemisorbed ammonia (ammonia forms ammonium ions hydrogen-bonded to oxygen of the framework).

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



Cation exchange of HZSM-5 with multivalent cations or transition metal ions (Zn^{2+}) 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 ºC, 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 Brönsted 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 (Lovenstein's rule). The catalytic activity of zeolite catalyst takes into consideration the total number of acid sites, the ratio of Brönsted to Lewis sites and the acid strength distribution of each types of site.

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

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

Table 3. The butanes-butenes feedstock composition and conditions of aromatization on HZSM-5 catalyst.

Feedstock composition %(vol)	Test number 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
Time on stream, h	30	24	20	24	28

Temperature, ºC	415	450	450	450	450
WHSV, h^{-1}	1	1	1.2	1	1
Pressure, atm	8	8	8	8	8
Catalyst, cm^3	100	100	100	100	100

The performances of the HZSM-5 catalyst during the test no.4 corresponding to each 4 h time on stream are presented in Table 4 and Table 5.

Table 4. Gaseous hydrocarbons (HC) distribution over HZSM-5 catalyst.

HC (vol.%)	Time on stream, h					
	4	8	12	16	20	24
$C_1 + C_2$	29.50	12.71	4.21	1.14	0.46	0.13
$C_2^=$	0.14	0.07	0.32	0.55	0.61	0.24
C_3 (1.11)	59.68	61.68	37.73	13.61	5.72	2.98
i-C_4 (23.84)	3.77	10.39	23.83	35.28	32.21	27.56
n-C_4 (32.69)	5.39	12.05	27.07	39.97	45.46	46.00
i-C_5	0.53	1.56	2.58	1.61	0.97	0.35
1-$C_4^=$ (22.33)	0.11	0.09	0.25	2.03	3.41	6.76
i-$C_4^=$ (0.07)	0.46	0.89	2.23	3.05	3.99	2.83
tr 2-$C_4^=$ (12.66)	0.14	0.14	0.51	1.25	3.76	5.57
cis-2-$C_4^=$ (6.57)	0.13	0.11	0.33	0.92	2.64	7.45
1,3-$C_4^{==}$ (0.33)	0.02	0.08	0.31	0.11	0.28	0.20

In parenthesis: concentration in feedstock no.4

Table 5. Liquid hydrocarbons (HC) distribution over HZSM-5 catalyst

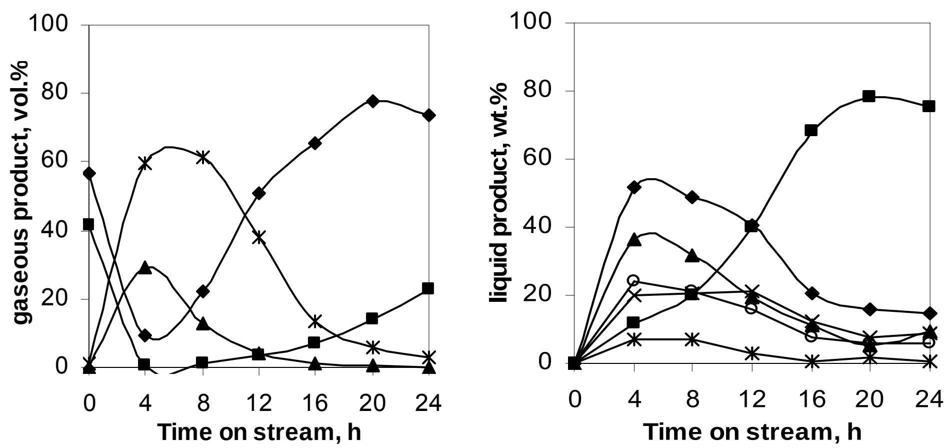
HC (vol.%)	Time on stream, h					
	4	8	12	16	20	24
i-C_5	2.02	5.61	12.08	16.15	16.10	11.78
n-C_5	0.19	0.93	2.77	1.62	1.08	0.92
i-C_6	-	0.66	3.43	8.05	10.47	6.94
n-C_6	0.10	0.26	0.84	0.64	1.33	0.66
i-C_7	0.08	0.62	5.04	13.42	14.10	9.42
B	7.29	7.08	2.84	0.76	1.95	0.45
n-C_8	-	0.23	0.76	1.22	1.42	0.91
n-C_7	-	0.10	1.14	5.11	7.00	5.53
i-C_8	-	0.21	1.66	4.94	7.73	10.94
T	24.00	20.92	16.16	7.36	5.83	5.68

i-C_9	-	0.26	1.33	7.39	12.39	21.34
EB	0.14	0.07	0.09	0.90	1.46	1.84
X	20.08	20.29	21.00	10.84	5.84	5.44
n-C_9	5.30	4.48	3.71	3.05	2.41	2.51
IPB	-	0.23	0.01	0.52	0.53	1.27
i-C_{10}	0.09	-	0.30	1.27	1.62	1.93
n-C_{10}	4.18	6.47	7.23	5.48	2.86	2.70
$> C_{10}$	36.28	31.59	19.29	11.04	5.54	9.45
Σ Ar	51.51	48.36	40.09	19.86	15.60	14.98
$C_5 - C_{10}$	11.96	19.74	39.98	68.35	78.42	75.28

B–Benzene; **T**–Toluene; **X**-Xylene, **EB**–Ethyl Benzene; **IPB**–iso propyl benzene

Conversion of mixed butanes/butenes feedstock no.4 to aromatics over HZSM-5 takes place with low selectivity to BTX, the reactants forming predominantly the cracking products.

The changes 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.



◆–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**

Figure 2. Gaseous phase composition and liquid phase composition *vs* time on stream over HZSM-5 catalyst in butane/butenes conversion.

The concentration of butanes (n+i) decreased from 56.53% to 9.16% in the first 4 h of reaction, after that is continuously increasing going beyond the feedstock after 16 h. The concentration of butenes (1-$C_4^=$, *trans*-2-$C_4^=$ and *cis*-2-$C_4^=$) decreased from 41.63% to 0.84% in the first 4 h, and to 3.32% after 12 h of reaction. The forming of methane and ethane (C_1 + C_2) reach the maximum value (29.50%) after 4 h of reaction and the forming of propane (C_3) after 8 h of reaction (61.68%); 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 12 h 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 ion exchanged Zn/HZSM-5 during of ten catalytic tests are given in Table 6.

Table 6. The butanes-butenes feedstock composition and conditions of aromatization on Zn/HZSM-5 catalyst.

Feedstock composition (vol.%)	Test number									
	1	2	3	4	5	6	7	8	9	10
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-C_4	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
tr.-2-$C_4^=$	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

TOS : 52 h; temperature: 450 ºC; atmospheric pressure; WHSV=1 h^{-1}; catalyst; 100 cm^3; regeneration of catalyst after each test: 475 ºC for 6h in nitrogen flow with 2% oxygen.

The performances of the Zn/HZSM-5 catalyst during the catalytic test no.1 are presented in Table 7 and 8.

Table 7. Gaseous hydrocarbons (HC) distribution over Zn/HZSM-5 catalyst.

HC	Time on-stream, h												
vol. %	4	8	12	16	20	24	28	32	36	40	44	48	52
C_2	2.38	4.81	2.98	2.37	1.62	1.87	1.99	1.25	2.47	1.94	1.86	2.24	1.37
$C_2^=$	1.87	1.05	1.41	1.58	1.24	1.16	1.22	0.69	1.46	1.49	1.41	1.93	1.85
C_3	22.36	25.21	20.48	20.26	16.20	15.73	17.25	23.21	21.76	17.49	15.01	18.00	12.68
i-C_4	14.5	8.03	15.2	18.07	18.91	19.83	22.48	21.69	25.39	27.33	28.53	25.52	28.84
n-C_4	7.24	7.0	8.03	8.16	7.59	8.22	8.96	10.0	10.1	11.9	12.87	11.68	10.43
i-C_5	0.67	0.49	0.46	0.66	0.68	0.61	0.78	0.76	0.71	0.98	1.04	0.89	0.80
1-$C_4^=$	0.16	0.26	0.23	0.18	0.16	0.11	0.13	0.15	0.17	0.29	0.16	0.21	0.21
i-$C_4^=$	0.62	0.80	0.73	0.78	0.73	0.61	0.78	0.77	0.78	1.83	1.25	1.16	1.10
tr-2-$C_4^=$	0.25	0.27	0.31	0.27	0.24	0.24	0.26	0.27	0.33	0.44	0.50	0.45	0.38
*cis*2-$C_4^=$	0.19	0.23	0.25	0.20	0.30	0.01	0.19	0.20	0.24	0.28	0.36	0.25	0.30
H_2	50.0	51.43	49.52	47.14	52.09	51.47	45.50	40.95	36.20	36.36	36.57	37.75	42.45

Table 8. Liquid hydrocarbons (HC) distribution over Zn/HZSM-5.

HC	Time on-stream, h												
vol.%	4	8	12	16	20	24	28	32	36	40	44	48	52
i-C_5	1.18	2.34	5.36	3.00	4.57	5.07	5.81	6.88	7.65	7.57	8.0	7.16	6.93
i-C_6	0.14	0.11	0.29	0.50	0.62	0.48	0.51	0.42	0.55	1.58	1.67	1.69	1.51
i-C_7	0.07	0.05	0.01	0.24	0.31	0.38	0.37	0.71	1.08	1.50	1.37	1.29	1.16
B	9.53	13.0	12.48	11.93	10.99	9.42	9.22	9.19	9.31	7.89	7.67	7.55	6.80
i-C_8	-	0.02	0.06	0.06	0.07	0.05	0.05	0.09	0.16	0.20	0.33	0.32	0.30
T	43.71	43.03	41.36	42.89	42.75	43.26	43.06	41.59	40.02	39.84	39.50	39.18	39.24
X+EB	22.77	22.37	21.43	20.24	20.89	21.41	22.13	21.10	20.72	20.88	21.21	22.13	24.31
n-C_9	7.24	6.59	6.64	6.27	6.20	7.14	6.52	6.61	6.65	6.52	5.63	6.47	6.30
IPB	0.16	0.20	0.22	0.43	0.41	0.24	0.32	0.20	0.21	0.39	0.33	0.20	0.21
n-C_{10}	4.43	4.25	4.74	4.50	4.52	5.09	4.94	5.54	5.33	5.55	5.75	6.80	6.25
i-C_{10}	0.20	0.01	0.21	0.30	0.24	0.14	0.14	0.63	0.67	0.81	0.67	0.63	0.76

> C_{10}	9.09	6.22	5.54	6.90	6.66	6.75	6.28	6.44	6.43	6.48	6.91	5.55	4.92
N	1.34	1.64	1.17	2.29	2.10	0.06	-	-	-	-	-	0.22	0.19
Σ Ar	76.01	78.40	75.27	75.06	74.63	74.09	74.41	71.88	70.05	68.61	68.38	68.86	70.35
C_5-C_{10}	13.26	13.37	17.31	14.87	16.53	18.35	18.34	20.88	22.09	23.73	23.42	24.36	23.31

B–Benzene; **T**–Toluene; **X**-Xylene, **EB**–Ethyl Benzene; **N-** Naphtalene

Aromatization of a mixture containing 57.41% butanes and 30.87% 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-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.

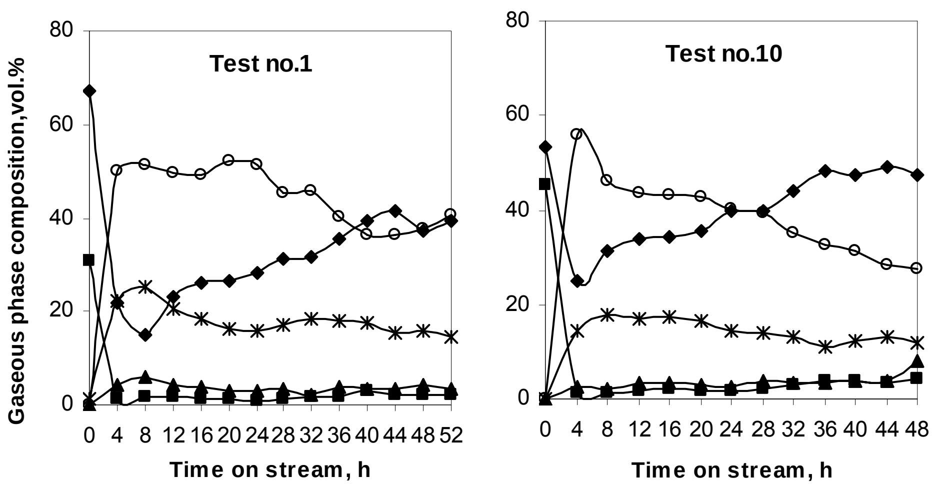


Figure 3. Gaseous phase composition *vs.* TOS over Zn/HZSM-5 catalyst:

◆-Σ C_4; ■-Σ $C_4^{=}$; ▲-C_2+$C_2^{=}$; ⋇-C_3 ; ○-H_2

The concentration of butenes decreased from 30.87 vol.% to 1.22 vol.% after first 4 h of reaction and remains at values smaller than 2.0% after 52 h of reaction. The concentration of butanes (n+i) decreased from 67.01% to 15.03% after 8 h of reaction, after that is continuously increasing without to rise above the initial concentration. It is evident that after about 470 h of catalytic reaction and nine regeneration steps at 475 ºC the catalytic activity and selectivity to aromatics BTX are present. The hydrogen molecular concentration exceeds the butanes concentration during the first 40 h of reaction in test no.1 and after 24 h of reaction in test no.10. The thermal treatments and the partial removal of coke deposited could 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%) near by C_2-$C_2^{=}$, more 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.

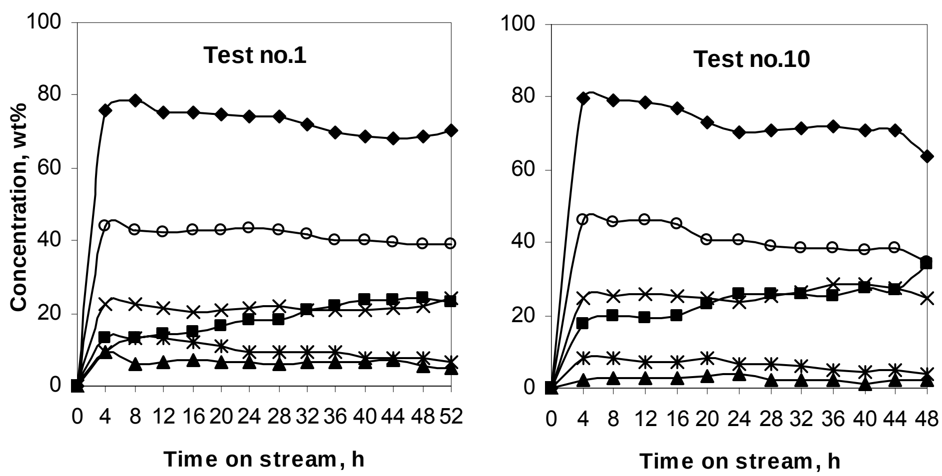


Figure 4. Distribution of hydrocarbons in liquid phase:

◆– Σ Ar ; ■–C_5–C_{10} ; ▲–> C_{10}; ⁎–B; ○–T; x–X+EB

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 4 h of reaction to ~ 23 wt% after 52 h 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 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.

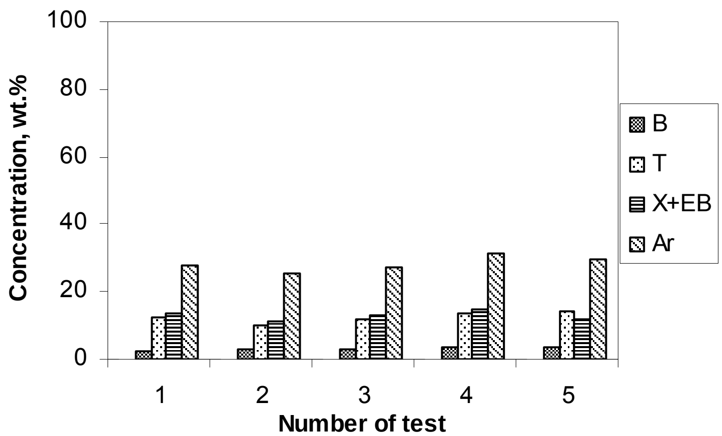


Figure 5. The aromatics average output over HZSM-5 catalyst (450^0C, 8 atm., WHSV=1 h^{-1}).

The average output of aromatics BTX over HZSM-5 monofunctional catalyst does 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.

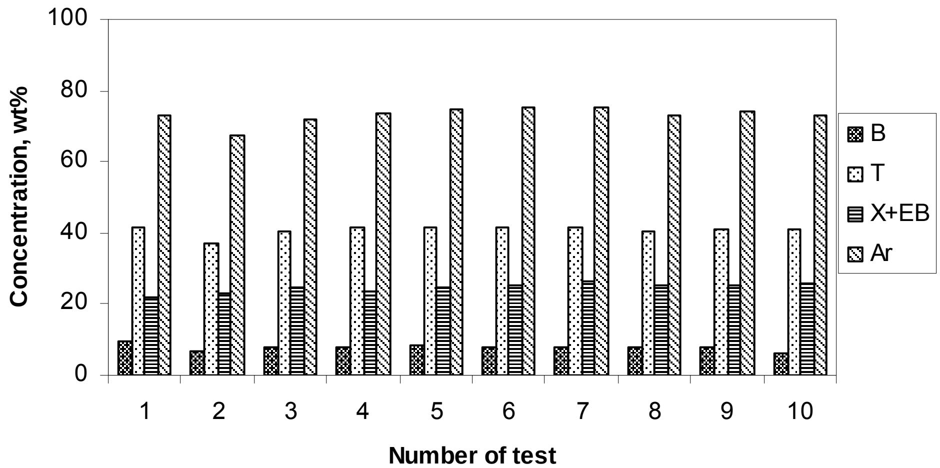


Figure 6. The aromatics average output over Zn/HZSM-5 catalyst (450^0C, atm. pressure, WHSV =1 h^{-1}).

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) alkene oligomerization and cracking, and 3) aromatization of small alkenes into C_6-C_{10} aromatic hydrocarbons.

The relevant reactions consist of: 1) alkane C-H bond activation through a pentavalent carbonium ion and of alkene C-H through a trivalent carbenium ion (through protonation); 2) dehydrogenation of carbonium ion to carbenium ion and finally to small alkenes, $C_2^{=}$- $C_4^{=}$; 3) oligomerization of small alkenes to higher alkenes, C_6- $C_{10;}$ 4) rapid isomerization, 5) β-scission; 6) dehydrogenation of higher alkenes to dienes; 7) cyclization of diene to cyclic alkenes; 8) dehydrogenation of cyclic alkenes to cyclic dialkenes and finally to aromatics, C_6- C_{10}.[15,41,47,48,76]

In the presence of HZSM-5 catalyst, the first stage of alkane transformation proceeds via two routes: **protolytic cracking route** of C-C and C-H bonds in the alkane molecules on strong acid sites to very unstable carbonium ion that collapses to give alkanes (or H_2) and adsorbed carbenium ions, and **hydrogen transfer route** (dehydrogenation) between the alkane 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, alkene interconversion, includes alkene isomerization, oligomerization and cracking steps. The third stage, alkene 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 Brönsted (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 $(AlO_4)^-$ and non-framework position. The total amount of acid sites (Brönsted 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. Brönsted sites can form both carbenium and carbonium ion intermediates whereas Lewis sites produce only carbenium ions.

The HZSM-5 catalyst contains predominantly Brönsted strong acid sites related to aluminum located in the framework and Brönsted weak acid sites related to some silanol groups and Lewis acid sites related to the extra-framework aluminum (AlO^+ species) or distorted aluminum in framework. The HZSM-5 catalyst is a solid Brönsted superacid, which at high temperature (~ 500 ºC) can even protonate alkanes. The acid strength of HZSM-5 catalyst is enhanced by the presence of extra-framework aluminum which is easily generated during the synthesis of ZSM-5 by non-template method. The total acidity of HZSM-5 catalyst determined by ammonia-TPD method has the value of 0.900 mmol/g and the high strength (mostly Brönsted acid sites) to the region with T_{max}= 420 ºC (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 ºC is only 0.144 mmol/g. After the zinc incorporation by ion exchange method the concentration of Brönsted 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. The 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 tetrahedra ($^-O\text{-}Zn^{2+}\text{-}O^-$) or legated to one internal silanol or OH group (≡ Si-OZn).[53,74] In the case of Zn/HZSM-5 catalyst the alkanes dehydrocyclodimerization proceeds via bifunctional pathways involving exchanged cations for dehydrogenation of alkane and dehydrocyclization of alkenic oligomers and acidic OH groups for alkene interconversion and aromatic formation. Zinc cations as Lewis acid sites promote alkane dehydrogenation (heterolytic cleavage of the C-H bond) to alkene (dehydrogenation function) and oligomers dehydrogenation to oligomers with one or more double bonds, decreases the β-scission rates and the residence time of alkenes within oligomerization/ β-scission cycles,[16] exerts strong hydrogen attracting action and promotes 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 Zn^{2+} cations in Zn/HZSM-5 do not reduce to zerovalent species (Zn^0).[14,52]

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 Brönsted 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 naphtenic intermediates on exchanged Zn^{2+} cations (Lewis strong acid sites), and of alkene interconversion and aromatic formation on acid OH groups (Brönsted strong acid sites). The average output of aromatics BTX in the liquid phase represents 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 Brönsted acidity of HZSM-5 catalyst is responsible for the high percentage of C_5-C_{10} aliphatic hydrocarbons (~80 wt% after 24 h TOS), compared 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 ºC 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 exercises the activation of butanes: it is thought that butenes are protonated to carbenium ions from a Brönsted 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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