Conversion of Butane-Butylene Mixtures over B(Al)-HZSM-5 Catalyst Prepared by Impregnation and over ZnO/HZSM-5 Co-Catalyst Prepared by Mechanical Mixing

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This paper presents the results of the conversion of light hydrocarbons (mixtures of butanes/butylenes with variable composition) resulted as by-products of the petroleum refining (FCC) over bifunctional B(Al)-HZSM-5 catalyst prepared by impregnation of HZSM-5 zeolite with boric acid and over bifunctional 5% ZnO/HZSM-5 co-catalyst (mechanic mixture) in a fixed-bed stainless-steel reactor (Twin Reactor System Naky) at 450°C, 8 atm. and 4 atm. total pressure and at a space velocity (WHSV) of 1h^{-1}The catalytic activity of the same catalyst were examined during over 10 catalytic tests (with regeneration of catalyst after each test) using mixtures of butanes-butylenes. Catalytic activity and selectivity towards liquid products – BTX aromatic hydrocarbons and oligo (iC_5-iC_{10}, nC_5-nC_{10}, $>C_{10}$) - depend on time on stream, composition of butanes-butylenes mixture and pressure. In the first hours of each test the aromatic BTX are the main component of the liquid product (connected with butylenes consume) and after that, the oligo fraction become predominant.

Keywords: conversion, light hydrocarbons, B- HZSM-5, ZnO/HZM-5

The conversion of light hydrocarbons C_2-C_4 (alkanes and alkenes) into more valuable aromatic-rich liquid hydrocarbons (BTX) and H_2 via nonoxidative route significantly expanded the feedstocks available for synthesis of these valuable products.

The catalysts used in aromatization of light hydrocarbons C_2-C_4 are on the basis of zeolites with medium pores (10-ring aperture), especially ZSM-5 (MFI) in hydrogen form modified with metals (Ga, Zn, Pt) and with large pores (12-ring aperture), especially LTL in K or Ba form modified with Pt or Zn [1-12].

The conversion of light hydrocarbons C_2-C_4 into aromatic hydrocarbons (BTX) over H-ZSM-5 [1, 3, 13-15], Ga-HZSM-5 [1-12, 16-33] and Zn-HZSM-5 [3-7, 12, 15, 34-41] has been studied in detail and industrially applied [9, 42-47].

The HZSM-5 catalyzes the conversion of light alkanes and or /alkenes to aromatics hydrocarbons with low selectivity because of fast β-scission side reactions. Introductions of metals species (Ga, Zn, Pt,) increases the rate and selectivity of aromatization reactions and inhibits β-scission side reactions that led to undesirable product

In the literature, there are three methods for preparation of B-ZSM-5 zeolite,: hydrothermal synthesis (conventional heating, microwave-assisted, ultrasound-assisted) inpresence of different templates (n-propylamine, TPABr, etc) [48-57]; impregnation method (secondary synthesis) – by impregnating HZSM-5 with H_3BO_3, NH_4BF_4, NH_4F [58-61]; vapor phase method or solid-state crystallization reaction when the aluminosilicate gel containing boron is heated in presence of a vapour mixture of EDA, Et_3N and H_2O [62].

The incorporation of boron into the ZSM-5 structure results in the formation of weak Brönsted and Lewis acid sites.. At the present time boron to have results in actual applications for Pentasil (ZSM-5) zeolite materials in Assoreni (methyl tertiobutylether into methanol and isobutene) and Amoco processes (xylenes isomerization and ethyl benzene conversion [63-67].

Zinc ionic and zinc oxide exhibit good dehydrogenation activity and aromatization selectivity but under severe treatments (≥ 550°C) zinc metallic can be formed and eluted as Zn vapours from the catalyst [63]. The zinc (ionic, metallic or ZnO)/HZSM-5 catalyst has been made by aqueous ion exchange, incipient wetness impregnation, wet impregnation, chemical vapour deposition, sublimating volatile compounds onto zeolite, solid state reaction (ion exchange involving thermal treatment), by isomorphic substitution of framework silicon by zinc during the hydrothermal synthesis or by mechanical mixing of ZnO with HZSM-5.

In this paper the catalytic properties of the B(Al)-HZSM-5 prepared by impregnation of HZSM-5 with boric acid at 80°Cfor 10 h and then pre-treated at 400°C, and of the physically mixture ZnO/HZSM-5 co-catalyst, for the transformation of gaseous butanes-butylenes hydrocarbons to liquid hydrocarbons (liquid fuels) were investigated.

Experimental part

Synthesis of NaZSM-5

The NaZSM-5 zeolite was synthesized by hydrothermal crystallization at 180±5°C for 24 h under autogenously pressure from a mixture containing sodium silicate, aluminum sulphate, ethylene glycol (EG), sulphuric acid, ammonia solution and distilled water [68]. The first synthesis of ZSM-5 zeolite using tetrapropylammonium bromide as template belongs to Argauer and Landolt [69]. The crystalline product was filtered, washed with distilled

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water, dried at 110°C for 6 h and calcined at 550°C in air for 6 h to remove the organic material and to obtain sodium form, NaZSM-5.

Zeolite modification

The sodium form of the ZSM-5 (SiO_2/Al_2O_3 = 34.65) was converted into the NH_4-form by ion exchange (three consecutive times) with a solution of 1M NH_4NO_3 at 80°C for 6 h under mild stirring. The solid was then filtered, washed, dried over night at 110°C and calcined in air at 550°C for 6 h when the protonic form HZSM-5 with acid properties was obtained. By treating HZSM-5 sample with 1M solution of H_3BO_3 (0.09 g/g B_2O_3/HZSM-5) at 80°C for 10 h a nonskeletal boron-containing catalyst was prepared. The suspension was dried over night at 110°C and calcined at 400°C for 6 h when nonskeletal and skeletal boron catalyst was prepared. The solid encoded B(Al)-HZSM-5 contain 8.26 wt% as B_2O_3 (2.56 wt% B).

The catalyst ZnO/HZSM-5 used in this study (containing 5 wt.% ZnO) was prepared by mechanically mixing the HZSM-5 powder with ZnO powder (Baker) at room temperature followed by calcinations in air at 500°C for 6h.

The final catalyst was prepared by mechanically mixing the B(Al)-HZSM-5 and ZnO/HZSM-5 co-catalysts powders with 20 wt% γ-Al_2O_3 as binder and a little distilled water until a soft paste was obtained and extruded into pellets. The pellets were dried at 110°C overnight and calcined in air at 450°C for 6 h.

Physical-chemical characterization

X-ray powder diffraction (XRD) patterns were acquired on a PANalytical X'Pert PRO MPD diffractometer using Cu K_α radiation (1.5406 Å), 40 kV, 30 mA in the $5^o \leq 2\theta \leq 31^o$ angular region, with 0.0131° (2θ) step size. Nitrogen adsorption-desorption isotherms at 77 K were obtained with a Sorptomatic Carlo – Erba Series 1800 apparatus. Surface areas were calculated with BET equation.

Scanning electron micrograph (SEM) and elemental analysis (EDX) were collected on a VEGA II LSH (TESCAN) with EDX detector tip Quantax QX2 (Bruker).

The acidity and strength distribution of ZnO/HZSM-5 and B(Al)-HZSM-5 were evaluated by using temperature programmed desorption (TPD) of ammonia technique. The total ammonia desorbed corresponds to number of acid sites and the desorption temperature to the strength of acid sites (weak and strong). Si and Al contents were determined using the ordinary wet chemical methods and the content of Na was measured flamphotometrically at 589 nm.

Catalytic tests

Performances of the B(Al)-HZSM-5 catalyst and ZnO/HZSM-5 co-catalysts for butanes-butylenes technical mixtures conversion were established at 450°C in a fixed bed continuous flow stainless-steel reactor (Twin Reactor System Naky, Metrimpex) at 4 atm. and 8 atm. total pressure, respectively and at a weight hourly space velocity (WHSV) of 1 h^{-1}. Control of temperature, pressure, as well as gaseous feed (60 g butanes-butylenes/h) was done through automatic devices. The reaction products were separated into gaseous and liquid fractions through an ice-trap. The feeding raw material and the gases resulted from catalytic test were analyzed using a Carlo Erba G.C. (Model C, TCD) equipped with a 6 m column filled with squalane and dimethylsulfolane on Chromosorb P. The collected liquid corresponding to each catalytic test was analyzed with a Carlo Erba Vega G.C. (FID) equipped with a 25 m capillary column filled with SE-52 stationary phase.

Results and discussions

Structure, morphology and specific surface area

Figure 1 shows the XRD patterns of parent NaZSM-5 sample after calcinations and of B(Al)-HZSM-5 composite after the heat treatment. The pattern confirms that the synthesized zeolite has the structure identical to MFI-type zeolite [70]. 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 XRD pattern of B(Al)-HZSM-5 composite obtained at 400°C shows that the structure of host ZSM-5 was retained and in addition exhibit reflection at 14.61 and 28.10 (2θ) which are characteristic for the B_2O_3 crystalline particles that cover the external and internal surface of HZSM-5 zeolite. The intensities of these peaks decreased until disappearance during the thermal activation at 400°C for 6 h and after the catalytic tests indicating a host-guest interaction and an isomorphic substitution of tetrahedral aluminium with tetrahedral boron [60].

After 6 h of calcinations at 400°C no more B_2O_3 crystals exist in the B(Al)-HZSM-5 sample. This change might be interpreted by the dispersion of B_2O_3 as a monolayer into the channels of HZSM-5 matrix [71]. Figure 2 presents the SEM images of parent NaZSM-5 and of HZSM-5 and the elemental composition by EDX spectra.

The BET surface area of NaZSM-5, HZSM-5, B(Al)-HZSM-5 and ZnO/HZSM-5 samples were 316.2 m^2/g, 296 m^2/g, 286 m^2/g and 267.5 m^2/g respectively.

Acidity of HZSM-5 and B(Al)-HZSM-5 catalysts

The acid properties of the catalysts determined by means of ammonia temperature programmed desorption (TPD) measurements are presented in table 1.

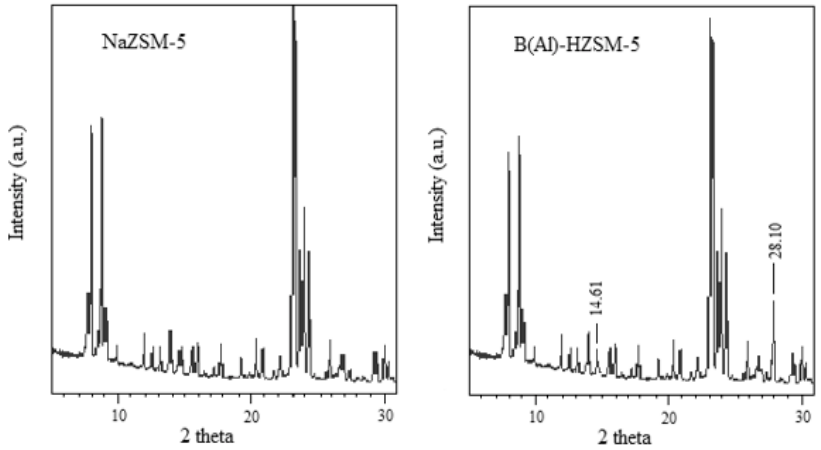
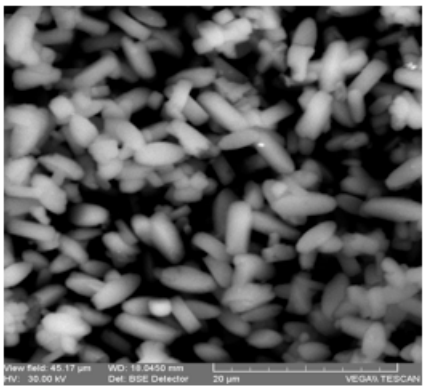
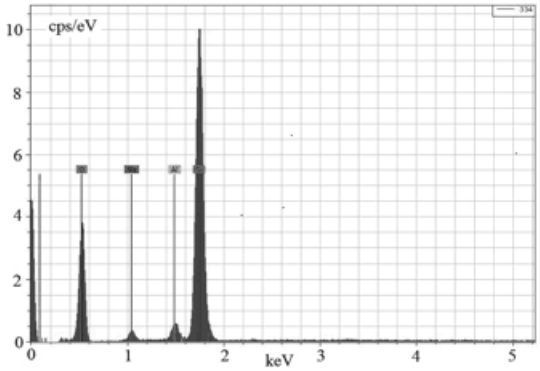


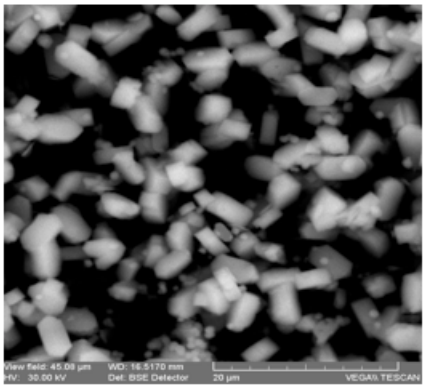
Fig. 1. XRD powder patterns of calcined parent NaZSM-5 and of B(Al)-HZSM-5 composite after the heat treatment at 400°C

NaZSM-5





HZSM-5



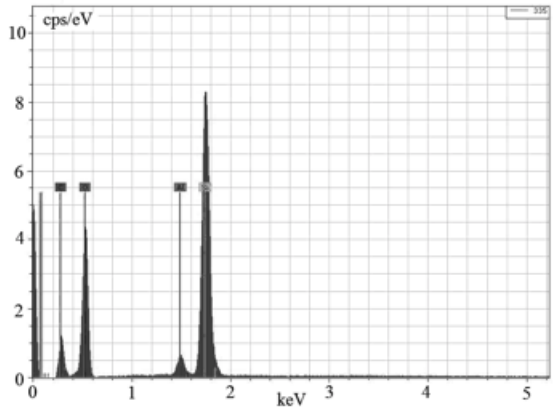


Fig. 2. SEM images of parent NaZSM-5 and HZSM-5 zeolites and their EDX spectra

Catalyst	Total ammonia chemisorbed mmol/g	Acid strength, mmol NH_3/g LT 120 – 300°C	HT 300 – 600°C
HZSM-5	0.916	0.618	0.298
B(Al)-HZSM-5	0.893	0.795	0.098
5% ZnO/HZSM-5	0.862	0.720	0.142

Table 1
TOTAL ACID SITES AND ACID STRENGTH DISTRIBUTION

Performance of B(Al)-HZSM-5 catalyst in conversion of C_4-C_4= mixtures

The catalyst was activated before runs by heating in reactor at 450°C with N_2 for 6 h.

B(Al)-HZSM-5 catalyst was evaluated in 15 consecutive tests with intermediary regeneration at 475°C for 6 h with N_2 + 2 wt% O_2.The operating conditions: temperature 450°C, WHSV 1 h^{-1} 8 atm. and 4 atm. were in advanced selected to obtain the high yield of liquid product during the catalytic test. The changes of the liquid yield, butenes total conversion and BTX concentration with time on-stream (TOS) resulted over B(Al)-HZSM-5 are presented in figures 3 only for the test no.5 at 8 atm and the test no.15 at 4 atm.

During the first 4 h time on-stream the butylenes are completely consumed, after that their concentration is increasing slowly up to 10 vol.% after 40 h TOS (test 5) and after 72 h TOS (test no.15). The liquid yields not exceed over 22% in catalytic test effected at 8 atm., but increased over 30 % in catalytic test No.15 (4 atm.). Aromatic hydrocarbons (BTX) are major compounds in the liquid during the first 24 h TOS (54 wt.%) as a result of aromatization reactions, after that their concentration is diminished up to 10 wt.% for 44 h of reaction (test no.5, 8 atm).

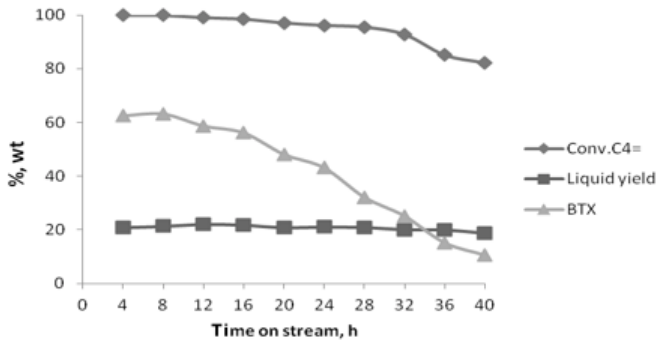


Fig. 3. Variation of the liquid yield, butenes total conversion and BTX concentration with time on-stream (TOS) resulted over B(Al)-HZSM-5 catalyst towards butanes-butylenes mixture: 450°C, 8 atm., WHSV 1 h^{-1} (test No.5)

The content of aromatic hydrocarbons is decreased quickly in the favor of oligomerization reactions with exclusive formation of iC_5 - iC_{10} hydrocarbons (75 wt. %) and nC_5 - nC10 (10 -17 wt. %). The content of hydrocarbons with > C_{10} that arise after the 4 h of reaction (36 wt.%) decreased permanent up to 3.24 wt.% at the end of the test [60]. For a comparison, in the figure 4 is presented the liquid composition resulted from the test no .15 under 4 atm. pressure. The aromatic hydrocarbons (BTX) are the

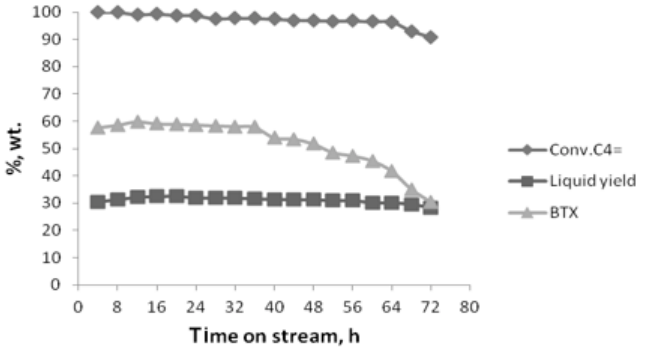


Fig. 4. Variation of the liquid yield, butenes total conversion and BTX concentration with time on-stream (TOS) resulted over B(Al)-HZSM-5 catalyst towards butanes-butylenes mixture: 450°C, 4 atm., WHSV 1 h^{-1} (test No.15)

major compounds of liquid during the first 56 h, after that their content is diminished up to 38 wt.% for 70 hTOS.

These values are dependent on the working pressure. At 8 atm. pressure the cracking reaction of butanes and hydrogen transfer are prevalent and no molecular hydrogen is present in gaseous fraction. The active boron species is considered to be B^{3+} cations. The activity of the boron cations is supposed to be due to strong Lewis acidity. By acting as strong Lewis acidic centers the boron are able to abstract hydride from the adsorbed hydrocarbons molecules, and catalyze the formation of hydrogen gas. This result in increased selectivity to aromatics, as the formation of aromatics no longer requires the coproduction alkanes (figs. 5 and 6).

In accordance with the results plotted in figure 5, the liquid product contain aromatic hydrocarbons (BTX) and alkanes (i+n) C_5-C_{10} and >C_{10} (*oligo*). The *oligo* fraction is major compounds in all catalytic test effected at 8 atm. total pressure. Aromatic hydrocarbons (BTX) are major compounds in the liquid during the firstly hours TOS as a result of aromatization reactions, after that their concentration is diminished. The content of aromatic

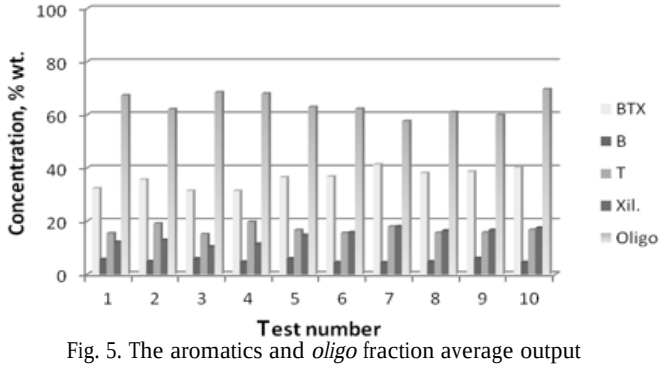


Fig. 5. The aromatics and *oligo* fraction average output over B(Al)-HZSM-5 catalyst: test No.1 – 10 (450°C, 8 atm., WHSV = 1h^{-1})

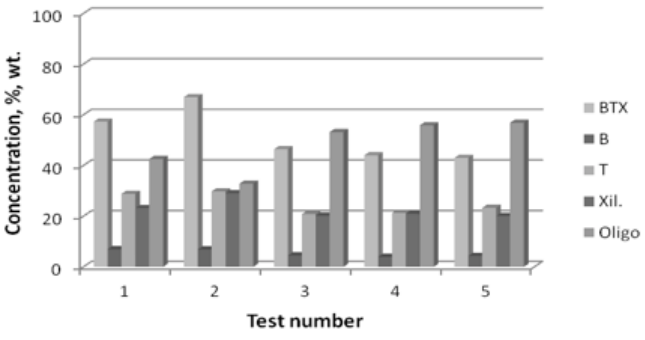


Fig. 6. The aromatics and *oligo* fraction average output over B(Al)-HZSM-5 catalyst: test No.1 – 5 (11-15) (450°C, 4 atm., WHSV = 1h^{-1})

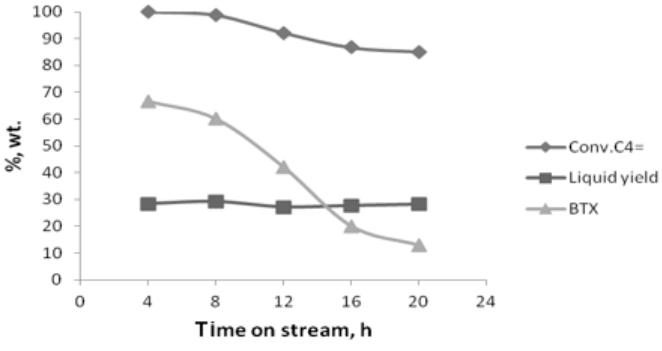


Fig. 7. Variation of the liquid yield, butenes total conversion and BTX concentration (test number 1) over 5% ZnO/HZSM-5 co-catalyst *vs.* time-on-stream at 450°C, 4 atm. and WHSV 1h^{-1}

hydrocarbons is decreased quickly in the favour of oligomerization reactions with exclusive formation of iC_5 - iC_{10} hydrocarbons (75 wt. %) and nC_5 - nC10 (10 -17 wt. %).

For a comparison, in the figure 6 is presented the liquid composition resulted from the tests no .11-15 under 4 atm. pressure. The aromatic hydrocarbons (BTX) are the major compounds of liquid only during tests number 11 and 12 after that their content is diminished to ~ 45 wt.% (tests 13-15). The content of *oligo* fraction is the major compounds in the liquid product.

The catalytic activity of the B(Al)-HSM-5 catalyst was maintained over the 17 tests with regeneration after each test. The modification of catalytic activity of B(Al)-HZSM-5 catalyst is connected with the coke formation. During the reaction, butylenes from the feedstock activate the dehydrogenation of butanes. But after 24 – 56 h TOS the butanes carry out the role of diluents and their concentration exceed the concentration of feedstock.

The weaker Bronsted acid sites in boron-HZSM-5 are attributed to the longer bond distance between the framework boron atom and the framework oxygen atom bound to the hydroxyl proton. Boron exists in the tetrahedral (B^{4+}) coordination in the hydrated state and in the trigonal (B^{3+}) coordination in the dehydration state [50, 72, 73].

Catalytic reactions of light hydrocarbons on 5% ZnO/ HZSM-5

Before the catalytic tests, the catalyst was heated in reactor at 450°C in nitrogen flow for 6 h. The co-catalyst 5 wt. % ZnO/HZSM-5 was evaluated in ten consecutive tests with intermediary regeneration at 475°C for 6 h in nitrogen with 2% oxygen flow. The operating conditions (temperature 450°C, WHSV 1 h^{-1} and pressure 4 atm.) were in advance selected to obtain the high yield of liquid product during the catalytic test. After each test the catalyst was regenerated in nitrogen with 2% oxygen flow at 475°C for 6 h. The changes in the butenes total conversion liquid yield BTX concentration resulted over 5 wt% ZnO/HZSM-5 co-catalyst with time on-stream (TOS) are presented in figures 7 and 8.

In accordance with the results plotted in figure7 and 8 the catalytic activity of the co-catalyst 5wt% ZnO/HZSM-5 in the test no.1 is different from the other one. Although the feedstock contain more alkenes $C_4^=$ (59.31 vol. %) than alkanes (n + i) C_4 (39.81 vol. %) the aromatics formation is maximum at 4 hours TOS (66.65 wt % BTX and 33.35 wt % (i + n) C_5 - C_{10} and > C_{10} in the liquid product) after that decreased quickly in the favor of oligomerization (12.98 wt % BTX and 86.79 wt % (i + n) C_5 – C_{10} and > C_{10}) after 16 h of reaction. During the first 4 h of reaction, the concentration of butenes attain zero and of (n+i) butanes decreased from 39.30 vol. % to 18.26 vol. %.

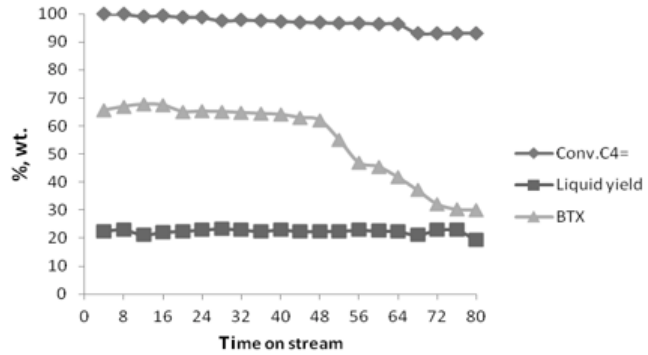


Fig. 8. Variation of the liquid yield, butenes total conversion and BTX concentration (test number 10) over 5% ZnO/HZSM-5 co-catalyst *vs.* time-on-stream at 450°C, 4 atm. and WHSV 1h^{-1}

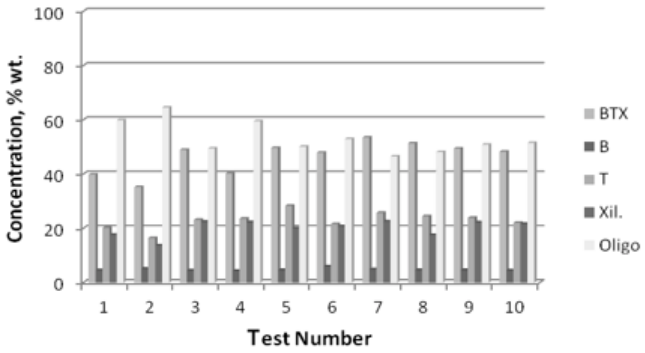


Fig. 9. The aromatics and *oligo* fraction average output over 5% ZnO/HZSM-5 co-catalyst: test No.1 – 10 (450°C, 4 atm., WHSV = 1h^{-1})

B-HZSM-5										
	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
Temp. °C	450	450	450	450	450	450	450	450	450	450
Press., atm.	8	8	8	8	8	8	8	8	8	8
WHSV, h^{-1}	1	1	1	1	1	1	1	1	1	1
Liquid yield, % wt.	18.60	19.93	20.032	26.57	20.89	20.24	30.11	30.67	28.72	26.76
ρ, g/cm^3	0.809	0.926	0.810	0.810	0.805	0.805	0.812	0.798	0.810	0.820
MON	95	97	94	97	98	98	97	97	97	98
B-HZM-5										
	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
Temp. °C	450	450	450	450	450					
Press., atm.	4	4	4	4	4					
WHSV, h^{-1}	1	1	1	1	1					
Liquid yield, % wt.	37.9	34.20	22.67	30.45	30.39					
ρ, g/cm^3	0.833	0.842	0.845	0.820	0.812					
MON	100	99	99	99	98					

Table 2
THE MON AND LIQUID PRODUCTS DENSITY RESULTS ON B(Al)-HZSM-5 CATALYST

ZnO/HZSM-5										
	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
Temp. °C	450	450	450	450	450	450	450	450	450	450
Press., atm.	4	4	4	4	4	4	4	4	4	4
WHSV, h^{-1}	1	1	1	1	1	1	1	1	1	1
Liquid yield, % wt.	28.4	20.75	21.67	22.90	22.48.20.86	22.08	21.69	22.91	22.5	
ρ, g/cm^3	0.796	0.798	0.815	0.802	0.828	0.829	0.824	0.825	0.824	0.813
MON	95	95	97	98	99	100	101	99	101	102

Table 3
THE MON AND LIQUID PRODUCTS DENSITY RESULTS ON 5% ZnO/HZSM-5 CO-CATALYST

The behaviour of the co-catalyst ZnO/HZSM-5 after the first test of reaction and regeneration (in nitrogen with 2 vol. % oxygen flow at 475°C for 6 h) was different from the test no.1. In catalytic test no.10 aromatic hydrocarbons, BTX, are major compounds in fraction liquid during 56 hrs TOS, after As a consequence of the initial heat treatment, of catalytic process (test no.1) and of regeneration, changes take place in the distribution of zinc species because of solid-state reaction between zinc oxide and Brönsted acid sites with changing in strong Lewis acid sites (aprotic strong acid sites) more active in dehydrogenation. This synergistic effect is characteristic of reactions in which the catalytic sites of two components (bifunctional catalysts) participate. Or this reason the aromatization activity was extended to 48 – 56 h when in the liquid product the BTX represent over 60 wt. %. The dehydrogenation of alkanes and of the intermediates reaction in the presence of zinc species which accelerate the combination of surface hydrogen in molecular hydrogen is faster than hydrogen transfer on the acid sites. One the zinc species participating in the aromatization are very probably zinc oxide. An increase of the aromatic yield and the time on stream with the number of reactions / regenerations cycles, this can be explained by a closer intimacy between the two components of the aromatization catalyst HZSM-5 and ZnO (figs. 9).

During the heat treatment of physically mixture ZnO/HZSM-5 a solid – state reaction between zinc oxide and

Bronsted acid sites (strong ≡Si–OH–Al≡ and low silanol ≡Si–OH) of HZSM-5 yield zinc cations (Zn^{2+}, ZnO^{+}) incorporated in HZSM-5 structure which are active for aromatization of alkanes and alkenes: [6, 74 -76]. During the reaction, alkenes from feedstock activate the dehydrogenation of alkanes but after 24 – 36 h TOS the alkanes carry out the role of diluents and their concentration exceed the concentration of feedstock. The average output of the MON (Motor Octane Number) and liquid products density of liquid fractions results on B(Al)-HZSM-5 and on 5% ZnO/HZSM-5 catalysts in conversion of C_4/C_4 = technical fraction is presented in table 2 and 3.

The liquid fraction results and on 5% ZnO/HZSM-5 catalysts can be used as a blending mixture for the octane number enhancing of gasoline because the MON is over 95, on the B(Al)-HZSM-5 and over 98 an on B(Al)-HZSM-5 (4atm) and over 95 on 5% ZnO/HZSM-5 or as raw materials for production of petrochemicals and chemicals intermediate.

Conclusions

H-ZSM-5 zeolite was wet impregnated with boric acid at 80°C and pre-treated at 400°C when B_2O_3 species are dispersed inside the pores and on the surface as a monolayer blocking the most of the Bronsted acid sites (a Si-OH-Al a).

HZSM-5 with boron species proves useful in conversion of butanes-butylenes mixtures (commercial feedstock from FCC unit) to aromatics (BTX) and aliphatic hydrocarbons (iC_5 - iC_{10}, nC_5 – nC_{10}, > C_{10}), a liquid with properties of gasoline. The catalytic activity of B(Al)-HZSM-5 catalyst was checked up during the 15 catalytic tests with regeneration after each test. The best results were obtained at 4 atm pressure.

The preparation method by physical mixture is easy in formulation, safe, lower in cost and environmentally friendly. To avoid the reduction and volatilization of zinc we performed experiments at 4 atm. total pressure, at 450°C and a WHSV of 1 h^{-1}. The catalytic activity is changing with time-on–stream; the aromatics BTX represent 59 – 60 wt% in the liquid product during the first 24 – 36 h TOS after that their concentration is decreased to 20 – 30 wt% at 40 h TOS. In the liquid product the concentration of aliphatic hydrocarbons C_5 – C_{10} (mostly iso) and > C_{10} (denoted *oligo*) is increasing up to 70 – 80 wt% after 40 h TOS.

In the light of discussion above, one can conclude that the conversion of conversion of technical fraction butane-butylenes on B(Al)-HZSM-5 and ZnO/HZSM-5 co-catalyst is a bifunctional process of oligo-aromatization.

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