

Conversion of Light Hydrocarbons with Butanes and Butenes from Petroleum Refining Processes Over Zn-HZSM-5 and ZnO/HZSM-5 Catalysts

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The conversion of light hydrocarbons resulted as by-product of petroleum refining (mixtures of butenes and (n + i) butanes) over bifunctional Zn-HZSM-5 (wt.% 1.73 ZnO) and 5% ZnO/HZSM-5 (mechanic mixture) catalysts in a fixed-bed stainless-steel reactor (Twin Reactor System Naky) at 450°C, under atmospheric pressure (Zn-HZSM-5) and 4 atm. pressure (ZnO/HZSM-5), and at a space velocity (WHSV) of 1h⁻¹ have been investigated. On Zn-HZSM-5 and ZnO/HZSM-5 catalysts, both Zn cations and protons intervene in alkanes dehydrogenation and further in dehydrocyclodimerization reactions that form C₆-C₈ aromatics. The results indicate that the selectivity to light aromatics – benzene, toluene and xylenes (BTX) and to both the gaseous, H₂ + C₁ and C₂ - C₄ hydrocarbons and liquid (i + n) C₅ - C₁₀ aliphatic hydrocarbons depend of the time on stream of the process. This is a result of coke deposition (polyunsaturated compounds) and catalyst deactivation. Zn-HZSM-5 catalyst exhibits high selectivity to aromatics BTX (mainly compounds in liquid product in all catalytic tests). On the ZnO/HZSM-5 catalyst the aromatics BTX represent 59-60 wt% in the liquid product during the first 24-36 hours time-on-stream and only 20-30 wt% after 40 hours of reaction when the aliphatic hydrocarbon C₅ - C₁₀ (mostly iso) and >C₁₀ (denoted “oligo”) reach to 70–80 wt%. The initial aromatization process described as dehydrocyclodimerization of alkanes and alkenes, principally to aromatics BTX and molecular hydrogen is accompanied by an oligomerization, isomerisation, cracking and alkylation process to form finally in the liquid product an excessively mixture of iso- and normal- C₅ - C₁₀ aliphatic hydrocarbons and > C₁₀.

Keywords: light hydrocarbons, aromatization, ZnO/HZSM-5, Zn-HZSM-5

Light alkanes C₂ - C₅ are contained in non-associated natural gas (as compressed natural gas) and in associated gas (as petroleum casing-head gas). A considerable amount of C₂ - C₄ hydrocarbons (alkanes and alkenes) result from petroleum refining processes, especially from destructive technological processes such as catalytic cracking (FCC). The consumption of light gaseous hydrocarbons as feed materials in petrochemical and other syntheses does not exceed 30% of the overall quantity produced [1].

The most important way to get chemicals with great importance is the direct conversion of lower hydrocarbons (less expensive and abundant) into hydrogen-deficient hydrocarbons (aromatics or alkenes) by catalytic aromatization and oligomerization [2]. The selective transformation of light hydrocarbons C₂ - C₄ (alkanes and alkenes) into more valuable 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) [3].

The main reason for the production of aromatics is the application of their as high octane blending components for gasoline (utilization that will grow less and less due to antipollution legislation and because of carcinogenic nature of benzene, especially), as an excellent solvent and a base chemical in a number of petrochemical (as feedstock for

rubbers and fibers) and chemical (as commodity chemicals) processes [4].

The aromatic hydrocarbons are produced from coal by coking (under pyrolytic conditions) and from crude oil by catalytic reforming or hydroforming of heavy naphtha (reformates up to 60 - 70 vol. %), by naphtha pyrolysis (5 - 60 vol. % BTX) and by catalytic cracking FCC of naphtha gasoline (with about 25 - 35 vol. % BTX) [5-7]. The yield of BTX from catalytic processes controlled by thermodynamics (B: T: X = 32: 36: 32, respectively) does not match the marked demand (55: 11: 43) [8]. The overall alkanes aromatization reaction is endothermic as large amounts of molecular hydrogen must be removed. If the feedstock is a mixture of small alkanes and alkenes in a well-defined proportion it is possible that the reaction system to be almost isothermal.

The activation of light alkanes and alkenes is achieved by using high temperatures (≥450°C) and catalysts with acidic and/or dehydrogenating metal (metallic or ionic) sites. The conversion (dehydrocyclodimerization) of light alkanes into aromatics was first described in 1970 by Csicsery [9] using bifunctional catalysts such as Pt, Cr₂O₃, MnO₂, V₂O₅, WO₃ and MoO₃ on alumina, but with low selectivity towards aromatics, low conversion and at high temperatures (i.e., 18.7% conversion for propane at 560°C on Pt/Al₂O₃). These catalysts were susceptible to coke formed on the catalyst surface resulting in the deactivation.

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The most used heterogeneous catalyst in more than 110 industrial processes employed in petroleum refining and petrochemistry are zeolites [10-14]. Zeolites are considered nanomaterials because of their pore sizes that range from 0.3 to 1.0 nm. Zeolites exhibit unique properties with respect to both activity and selectivity. Activity is mostly determined by the zeolite Brønsted acid sites (hydroxyl donating site associated with a negatively charged framework oxygen's linked with alumina tetrahedral) and by the active metal – phase supported by zeolite; the selectivity is due to the zeolite microspores and/or cavities size and shape. The major role of acid sites is to function as a proton source for alkanes, leading to the formation of carbocations and for interaction with alkenes (π -complex) often resulting in oligomerization. A large number of scientific papers and patents are related to the aromatization of light alkanes and alkenes $C_2 - C_4$, of liquefied petroleum gas (LPG) and of light and heavy naphtha [15-28]. Many types of zeolites structures were tested for the aromatization of lower saturated and unsaturated hydrocarbons: ZSM-5 (MFI) ZSM-11 (MEL), LTL, ZSM-22 (TON), MCM-22 (MWW), BETA (BEA), $AlPO_4-5$; -11 (AFI, AEL) and EU-1 (EUO) [29-79].

The zeolites most frequently used as catalysts in aromatization of alkanes and alkenes are ZSM-5 with pore structure (MFI) in hydrogen - form, HZSM-5 (monofunctional catalyst) or in metal – form, Me/HZSM-5 (bifunctional catalyst). The properties that make ZSM-5 zeolite crucial for industrial applications are its high thermal, hydrothermal and acid stability, unique shape – selectivity, ion exchangeability, pore size and diffusibility, and unusual catalytic activity and coke resistance in many catalytic conversions of hydrocarbons.

ZSM-5 zeolite is a member of the Pentasil family of high – silica zeolites ($Si/Al > 10$) whose structure 3-D is characterized by two dimensionally types of intersecting channels with 10-member ring openings: one type is straight with a near – circular opening (0.53 x 0.56 nm) and the other one is sinusoidal with an elliptical opening (0.51 x 0.55 nm). The two sets of channels intersection creates a supercages cavity with a diameter of about 0.85 – 0.89 nm, the locus of strong – acid sites and of aromatic $C_6 - C_8$ hydrocarbons formation. This 10- member oxygen ring – sized pore system with uniform dimension and the absence of large cages having small windows leads to the resistant of ZSM-5 zeolite to coke formation (no polyaromatics can be formed). Due to the shape – selective properties of the ZSM-5 framework (determined by product shape - selectivity or/and transition – state selectivity due to steric and geometrical spatial constraints) mainly small aromatics (BTX) (monoaromatics and p-dialkylbenzenes) are formed.

Many studies have focused on the ability of the monofunctional acid catalyst HZSM-5 to convert light hydrocarbons to BTX [17, 18, 20, 22, 24, 32, 38, 50, 72-84]. HZSM-5 transforms light alkanes and alkenes to products of very similar composition consisting mainly of $C_6 - C_{10}$ aromatics (with low selectivity, about 12%) and $C_1 - C_4$ aliphatic (especially methane and ethane). This monofunctional acid catalyst offers a preferentially high cracking, isomerization and β -scission-oligomerization (C-C) reactivity, in addition to dehydrogenation, hydrogen transfer, disproportionation and cyclization reactions. Catalytic aromatization of aliphatic hydrocarbons on HZSM-5 catalysts was first described by researchers at Mobil Co. [85, 86] and the production of BTX aromatics as M2-Forming; light alkenes can be converted much faster into aromatics at relatively low temperature (370°C)

whereas light alkanes conversion into alkenes (dehydrogenation) require higher temperature (500 – 550°C). Unfortunately, the unmodified HZSM-5 catalysts are not the best dehydrogenating catalysts because the hydrogen rejection from catalyst occurs by hydrogen transfer to alkenes yielding alkanes which limits the aromatics yield. Aromatization over HZSM-5 is accompanied by substantial cracking that leads to a large selectivity for C_1 and C_4 hydrocarbons, so, has stoichiometric restriction to produce about 3 moles of alkanes per one mole of aromatics. This stoichiometric constraint sets the maximum yield of aromatics.

The selectivity to aromatics and catalytic activity can be increased significantly by incorporation of transition metals of different size and different chemical features or metal oxide on HZSM-5 zeolite. The extra-framework metal active sites make easy the heterolytic cleavage of the C – H bond of the adsorbed alkanes and accelerate the combination of surface hydrogen and removal as molecular hydrogen. With metal / HZSM-5 catalysts aromatization occurs namely through a bifunctional scheme, metal species catalyzing the dehydrogenation of the alkanes and of the naphthenic intermediates and the acid sites catalyzing the oligomerization of alkenes and the cyclization of oligomers to naphthenes.

The catalysts investigated contain as dehydrogenating metal (metallic, ionic, oxide); gallium [1, 17-24, 27, 29-46, 48, 49], zinc [18-22, 27, 30-35, 42-44, 46, 49-80], platinum [20, 24, 27, 30, 83], cobalt [76], molybdenum [54], nickel, iron [75], copper [64], palladium, ruthenium, rhenium, silver, Zn-Ni, Zn-Cu, Zn-Ga, Ga-Pt, Ga-In. The review of studies showed that only the medium pore zeolites ZSM-5 modified with metals as Ga, Pt, Zn and LTL zeolite in K or Ba form modified with Pt or Zn appear to be the most effective catalysts for alkanes/alkenes aromatization reaction [16-27].

The conversion of light hydrocarbons $C_2 - C_4$ (LPG, light naphtha or light alkenes) into aromatics over HZSM-5, metal (Ga or Zn) – HZSM-5 and Pt/K(Ba)L catalysts has been industrially applied using the CYCLAR™ (BP-UOP) process for converting LPG (also called dehydrocyclodimerization, DHCD) using Ga-doped HZSM-5 catalyst (with butane as feed 65% BTX, 5% hydrogen and 30% fuel gas) [81, 82], AROMAX process – Chevron (with C_6 to C_8 alkanes as feed) [83] and RZ – Platforming (BP-UOP) process to reforms naphtha feed using non-acidic Pt / K(Ba)L catalyst [84], M2-Forming to converts light alkanes and M-Forming process using HZSM-5 [85, 86], ALPHA process (Asahi Chemical/Sanyo Petrochemical) to converts olefin-rich hydrocarbons C_2 and C_3 using Zn-doped HZSM-5 catalyst [72], Mitsubishi Z-Forming process (light naphtha on HZSM-5) [87], and AROFORMING (IFP/Salutec) to aromatize LPG or light naphtha [88].

Platinum exhibit great dehydrogenation capacity of light alkanes and catalytic activity but is expensive and is also active in hydrogenolysis to form unreactive alkanes C_1 and C_2 and cyclic compounds, which decrease the selectivity to aromatics [20, 24, 27, 30].

Gallium has the advantage over zinc of the lower volatility under reduced atmosphere at high temperature and of the low activity in hydrogenolysis [70].

Zinc ionic and zinc oxide exhibit good dehydrogenation activity and aromatization selectivity but under severe treatments ($\geq 550^\circ\text{C}$) zinc metallic can be formed and eluted as Zn vapors from the catalyst [62]. The use of a zinc modified HZSM-5 instead gallium might be preferential, especially from the environmental point of view owing to the poisonousness and the high price of gallium. The zinc (ionic, metallic or ZnO)/HZSM-5 catalyst

has been made by aqueous ion exchange, incipient wetness impregnation, wet impregnation, chemical vapours 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. The literature of Zn containing zeolites also shows that the activation of the catalysts and the experiments has been carried out at very different temperatures (420-600°C) and those very different alkanes as model feedstock are used from C_2 up to C_7 alkanes, alkenes and their mixtures. Thus, this fact can lead to the observed controversial conclusions concerning the role of the Zn species in aromatics BTX formation. Moreover at high testing or activation temperatures the loss of zinc by sublimation is pretended from both cationic or non-framework positions [25, 50-65].

The purpose of this study is to test the conversion of light hydrocarbons resulted as byproduct of petroleum refining (C_4 , $C_4^=$) into aromatics over Zn-HZSM-5 made by aqueous ion exchange and physically mixture ZnO/HZSM-5 co-catalyst.

Experimental part

Catalyst preparation

NaZSM-5 zeolite was synthesized by hydrothermal crystallization at $180 \pm 5^\circ\text{C}$ for 24 h from alkaline media containing sodium silicate (29.63 wt.% SiO_2 , 9.55 wt.% Na_2O , 60.82 wt.% H_2O , pycnometric density 1.443 kg dm^{-3}), aluminum sulphate, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (15 wt.% Al_2O_3), sulphuric acid (96 wt.%, 1.835 kg dm^{-3}), ethylene glycol ($1.1132 \text{ kg dm}^{-3}$) as a gel modifier and as a void filler, deionized water and ammonium hydroxide (25 wt.% NH_3) to control the pH of the gel (11.0 – 11.5). All raw materials were used as received.

NaZSM-5 zeolite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 36.02 was crystallized from an aqueous gel with molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3 = 58.93$, $\text{Na}_2\text{O free}/\text{SiO}_2 = 0.11$, ethylene glycol/ $\text{SiO}_2 = 0.47$ and $\text{H}_2\text{O}/\text{SiO}_2 = 33.44$ in a Teflon – lined stainless steel autoclave under static conditions and autogenously pressure at $180 \pm 5^\circ\text{C}$ for 24 h [89]. The white crystals were filtered, washed thoroughly with deionized water, dried at 110°C for 6 h and finally calcined in air at 500°C for 6 h to remove the organic material. The Na^+ form obtained was converted into ammonium form, $\text{NH}_4\text{ZSM-5}$ by three ion-exchanges with a 1M fresh solution of ammonium nitrate under reflux at 80°C for 6h each time ($\text{NaZSM-5 (g)}/\text{solution (mL)} = 1 : 5$). The solid was then filtered, washed with deionized water, dried in air at 110°C for 6h and calcined in flowing air at 550°C for 6 h, when it was converted in the protonic form, HZSM-5.

The HZSM-5 zeolite was converted in the Zn-HZSM-5 form by treating it with 0.1M $\text{Zn}(\text{NO}_3)_2$ aqueous solution (solid : solution = 1g : 5 mL) two times under stirring at 80°C for 6h each time. The Zn-HZSM-5 sample was then filtered, 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 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 Zn-HZSM-5 and ZnO/HZSM-5 powders with 20 % wt, g - Al_2O_3 as binder was extruded and then cut into short cylinders, dried at 110°C for 6h and calcined at 475°C in air for 6 h.

Physicochemical characterization

The structure type, phase purity and degree of crystallinity were determined by X-ray powder diffraction pattern which were obtained on a Philips PW 1830 diffractometer using Ni filtered $\text{Cu K}\alpha$ radiation at a scanning speed of $0.02^\circ \text{ s}^{-1}$ in the range of $6-32^\circ$, 2θ degree.

The morphology and size of the individual crystals were obtained by scanning electron microscopy (SEM) with a Microspec WDX-2A using a 25 kV accelerating potential.

The acidity and strength distribution of HZSM-5, Zn-HZSM-5 and 5% ZnO/HZSM-5 catalysts were evaluated by using temperature programmed of ammonia desorption (TPD) technique. The samples were activated in a flow of dry N_2 at 500°C for 4h and after cooling to 80°C ammonia adsorption were carried out. Physically adsorbed ammonia was removed by degassing in flowing N_2 at 100°C for 3h. The amount of ammonia desorbed from 100 to 800°C (at the rate of $10^\circ\text{C}/\text{min}$) was quantitatively monitored volumetrically (absorption in 1M HCl). The ammonia desorbed represents the total acidity (weak and strong) of the sample.

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

Catalyst evaluation

The performance of the Zn-HZSM-5 and 5% ZnO/HZSM-5 catalysts was tested for light technical hydrocarbons mixtures (alkanes C_4 and alkenes, $C_4^=$) conversion to aromatics BTX in a fixed-bed continuous flow stainless – steel reactor (a commercial Twin Reactor System Naky Metrimplex, Hungary) under atmospheric pressure (Zn-HZSM-5), and 4 atm. total pressure (5% ZnO/HZSM-5) at 450°C and at a weight hourly space velocity (WHSV) of 1 h^{-1} . The catalyst was pretreated with N_2 for 1 h at 450°C to remove the adsorbed impurities and the moisture. After each test regeneration of catalysts was effected at 475°C for 6h in nitrogen flow with 2% oxygen.

The reaction products were separated into liquid and gas fractions through an ice – trap. Composition of products was obtained with two gas chromatographs (GC Carlo Erba, model C and Vega) using a fused silica capillary column (25 m length and 0.32 mm i.d) with SE-52 stationary phase and flame ionization detector (FID) for liquid phase and a column (6 m length) with squalane and dimethyl sulpholane and a thermal conductivity detector (TCD) for gaseous phase, respectively.

Characterization

Structure, morphology, specific surface area and adsorption of ZSM-5 samples have been investigated. Figure 1(a) shows the XRD powder pattern of starting NaZSM-5 sample after calcinations. From the diffractogram, the interplanar distances d_{hkl} and the corresponding relative intensities (I/I_0) were calculated. The calculated d_{hkl} values agree very well with that reported for ZSM-5 (MFI) zeolite. [90].

The NaZSM-5 sample has a high crystallinity derived from the high intensities of the XRD lines in the $6 - 32.2^\circ$ (2θ) range comparatively with a standard ZSM-5 crystallized in presence of tetrapropyl ammonium hydroxide. No other diffraction lines were found in the XRD pattern, which means that only crystalline phase of ZSM-5 zeolite was obtained. The powder-XRD profiles of HZSM-5, Zn-HZSM-5 and of 5 wt. % ZnO/HZSM-5 (not presented) show that the structure of ZSM-5(MFI) was retained with a

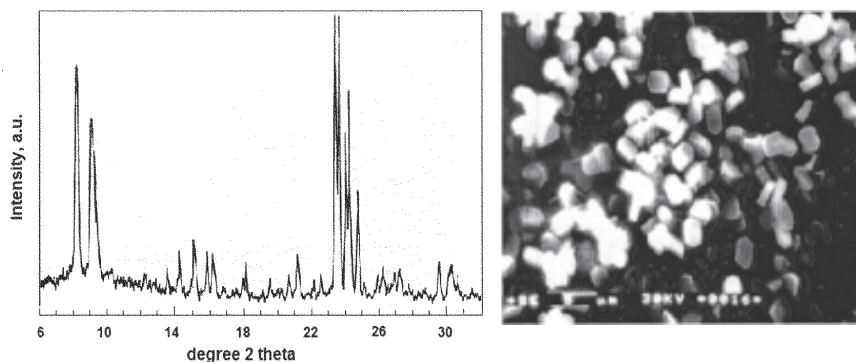


Fig.1. Powder X-ray diffraction pattern (a) and SEM micrograph (b) of calcined NaZSM-5

Sample	SiO ₂ /Al ₂ O ₃ ratio	Zinc loading as ZnO, %	BET surface area, m ² g ⁻¹	Adsorption of n-hexane, %
NaZSM-5 calcined	36.02		314.2	10.42
Zn-HZSM-5	36.02	1.73	275	10.24
ZnO/HZSM-5	36.02	5.0	267.5	10.21

Table 1
PHYSICO-CHEMICAL CHARACTERISTICS
OF THE STUDIED CATALYSTS

slight change in the intensity of the characteristic peaks. The 5 wt.% ZnO/HZSM-5 co-catalyst exhibit diffraction lines at $2\theta = 31.80^\circ$, 34.5° , 36.4° and 56.6° which are characteristic for bulk ZnO but their intensities are decreased during the thermal activation at 500°C indicating a host – guest interaction (solid - state reaction) between Brønsted acid centers of HZSM-5 framework and zinc oxide. SEM image of zeolite NaZSM-5 is shown in figure 1 (b). It reveals the well developed hexagonal – shaped crystals with dimensions of $3.5 - 4.3 \mu\text{m}$ in length and $2.1 - 2.86 \mu\text{m}$ in width. The chemical composition, BET-specific surface area and adsorption properties of NaZSM-5, Zn-HZSM-5 and of ZnO/HZSM-5 co-catalyst are presented in table 1.

Loading of the zinc decreases slightly both the BET surface area, probably due to pore-size reduction and/or pore-mouth blockage.

Acidic properties of Zn-HZSM-5 and 5 wt. % ZnO/HZSM-5

Acidic properties of zeolite catalysts are due to the both types of acidic sites (Brønsted and Lewis) and differ by number ($\text{mmol}\cdot\text{g}^{-1}$), and strength. The total amounts of acid sites calculated from the total amount of NH_3 desorption and the acid strength expressed as the maximum temperature desorption of ammonia are

Catalyst	Total acid sites $\text{mmol}\cdot\text{g}^{-1}$	Acid strength	
		LT 120 – 300°C	HT 300 – 600°C
HZSM-5	1.016	0.785 (200°C)	0.231 (420°C)
Zn-HZSM-5	0.782	0.638 (200°C)	0.144 (420°C)
5% ZnO / HZSM-5	0.862	0.720 (200°C)	0.142 (420°C)

Table 2
TOTAL ACID SITES AND ACID DISTRIBUTION

Feedstock composition (vol. %)	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

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

Table 3
BUTANES-BUTENES FEEDSTOCK
COMPOSITION AND CONDITIONS OF
AROMATIZATION ON Zn-HZSM-5 CATALYSTS

summarized in table 2. The presence of Zn^{2+} and ZnO and the proton of acidic OH groups, by thermal activation at 500°C , caused the decrease of Brønsted acid sites number and corresponding increase of Lewis acid sites number.

The NH_3 -TPD peak at $\sim 200^\circ\text{C}$ (low temperature, LT) is attributed to the desorption of ammonia from weak acid sites – mostly Lewis acid sites (IR band at 3680 cm^{-1}) and the NH_3 -TPD peak at $\sim 420^\circ\text{C}$ (high temperature, HT) to strong acid sites – mostly Brønsted acid sites (IR band at 3610 cm^{-1}) and some Lewis acid sites, related to the presence of extra-framework Al-species and zinc oxide species.

Results and discussions

Catalytic performance of Zn-HZSM-5 catalyst in $\text{C}_4/\text{C}_4^=$ hydrocarbons aromatization

Before the catalytic tests, the catalyst was heated in reactor at 450°C in nitrogen flow for 1 hour.

The Zn-HZSM-5 catalyst was evaluated in ten consecutive tests with intermediary regeneration at 475°C for 6 h in nitrogen with 2% oxygen flow.

The industrially feedstock composition and the conditions of aromatization over ion exchanged Zn-HZSM-5 during ten catalytic tests are given in table 3.

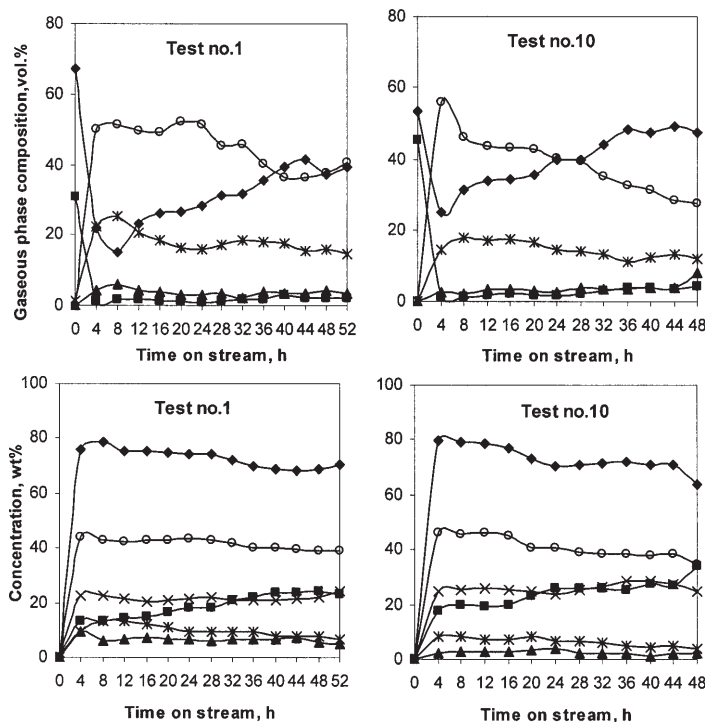


Fig. 2. Gaseous phase composition vs. TOS over Zn-HZSM-5 catalyst: ◆ - ΣC_4 ; ■ - $\Sigma C_4=$; ▲ - $C_2+C_2=$; * - C_3 ; o - $H_2 + C_1$

Fig. 3. Distribution of hydrocarbons in liquid phase: ◆ - ΣAr ■ - C_5-C_{10} ; ▲ - $>C_{10}$; * - B; o - T; x - X+EB

Aromatization of a mixture containing 67.01% 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 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 52h 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°C the catalytic activity and selectivity to aromatics BTX are present. The hydrogen molecular (and C_1) concentration exceeds the butanes concentration during the first 40h 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 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 $C_2-C_2=$. The aromatic hydrocarbon distribution in the liquid phase corresponding to catalytic tests no.1 and no.10 is plotted in figure 3.

The produced aromatic hydrocarbons were mainly toluene (~ 40 wt. %) and xylenes (~ 21 wt%); the benzene

in the aromatics was about 9wt%. 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 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 6wt%. In the liquid product of all catalytic tests is present naphthalene in a concentration below 1.0 wt%.

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 1 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.

Table 4 presents the commercial feedstock composition of each test and operating conditions of aromatization (with intermediate regeneration) on 5 wt. % ZnO / HZSM-5 co-catalyst.

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. The catalytic tests performed over the same sample 5% ZnO/HZSM-5 co-catalyst differ from one to other only by the composition of the feedstock (except tests no. 2 and 6) (table 4). After each test the catalyst was regenerated in nitrogen with 2% oxygen flow at 475°C for 6 h.

Feedstock comp.(vol.%)	Test number							
	1	2,6	3	4	5	7	8	9,10
C ₂	-	0.16	0.67	0.97	0.20	0.12	0.30	0.23
C ₃	0.13	5.36	7.17	8.65	4.16	2.18	2.69	3.81
C ₃ ⁼	0.06	2.03	3.94	5.99	2.64	2.61	2.39	2.08
i-C ₄	14.87	22.70	20.01	20.50	20.75	34.94	20.40	20.74
n-C ₄	24.94	36.58	39.35	31.54	42.45	23.47	39.19	41.86
Σ (n+i)C ₄	39.81	59.28	59.36	52.04	63.20	58.41	59.59	62.60
(1+i)C ₄ ⁼	52.89	23.44	22.89	27.06	25.09	31.44	27.46	26.87
trans-C ₄ ⁼	5.54	6.70	3.95	3.22	3.47	5.03	5.79	3.35
cis-C ₄ ⁼	0.88	2.90	1.80	1.44	1.60	1.50	1.50	0.65
Σ(i+1+tr+cis)C ₄ ⁼	59.31	33.04	28.64	31.72	30.16	36.47	34.75	30.87
1,3-C ₄ ⁼	0.69	0.13	0.18	0.62	0.11	0.21	0.30	0.33

Temperature: 450°C; pressure = 4atm; WHSV=1 h^{-1} ; catalyst; 100 cm^3 ; regeneration of catalyst after each test: 475°C for 6h in nitrogen flow with 2% oxygen

Table 4
BUTANES-BUTENES FEEDSTOCK COMPOSITION AND CONDITIONS OF AROMATIZATION ON ZnO/HZSM-5 CATALYST

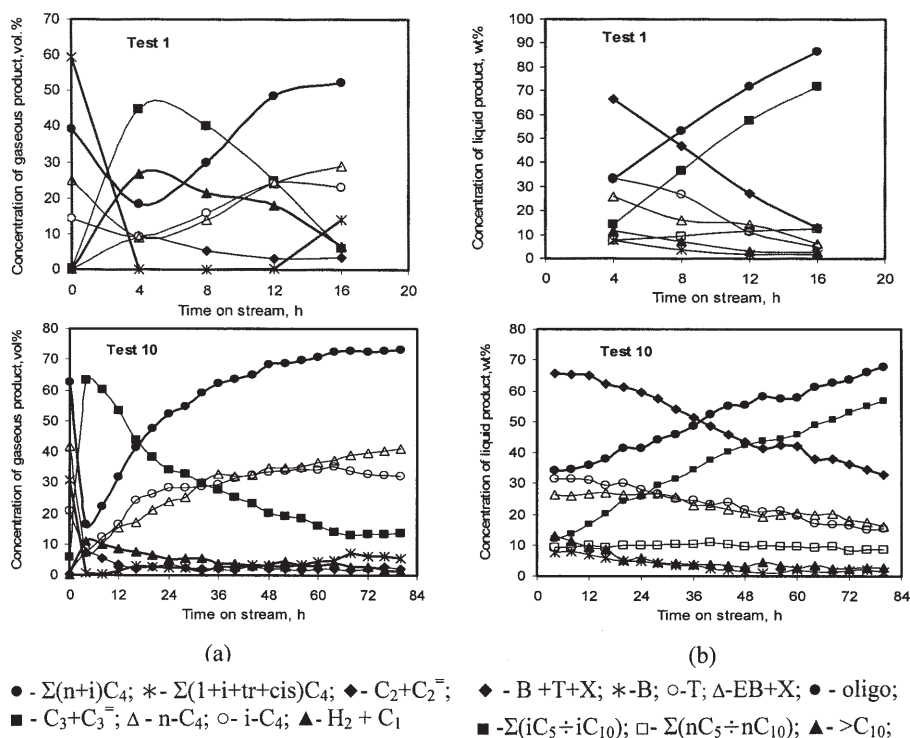


Fig. 4. The gaseous (a) and liquid (b) products distribution resulted from catalytic conversion of commercial feedstock rich in $C_4-C_4=$ hydrocarbons (test number 1, and 10) over 5% ZnO/HZSM-5 co-catalyst vs time-on-stream at 450°C, 4 atm. and WHSV 1h⁻¹

The changes in the composition of gaseous and liquid products resulted over 5 wt% ZnO/HZSM-5 co-catalyst with time on-stream (TOS) are presented in figure 4.

Aromatization of light alkanes and alkenes requires the increase of the chain length up to six carbon atoms and higher as a result of a number of consecutive and parallel reactions including dehydrogenation of alkanes to alkenes, oligomerization of resulted alkenes to dienes, trienes, cyclization of oligomers to naphthenes and dehydrogenation of naphthenes into corresponding aromatic hydrocarbons.

The dehydrogenation of alkanes, C_2-C_4 to alkenes, $C_2=C_4$ take place as a result of C-H bond cleavage with formation of the corresponding alkenes and of hydrogen atom. The existence of C-C bonds in alkanes, with lower bond energy than C-H bond has the possibility to be broken (cracking reaction) with formation of lighter alkanes (C_1, C_2) and alkenes. This cracking reaction is responsible for the decreasing the total selectivity to aromatics.

The resulted alkenes from cracking and dehydrogenating reactions take part in isomerisation, oligomerization to higher alkenes and dienes, cracking (β -scission) and cyclization reactions with particularly formation of naphthenes. The resulted naphthenes are dehydrogenated into respective aromatics and alkanes as a result of hydrogen transfer.

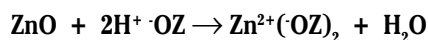
The conversion of light alkanes and alkenes into aromatics is achieved by using high temperature (500-550°C) and catalysts with acidic sites (monofunctional, HZSM-5) or with acidic sites and a dehydrogenated metal (bifunctional, metal ionic, metal oxide/HZSM-5).

Unfortunately, the preferential cracking activity and dehydrogenating via hydrogen transfer of HZSM-5 catalyst, containing predominantly Brönsted strong acid sites, leads to a large selectivity for methane, ethane and propane and of reduced yield of aromatics.

Zn-HZSM-5 catalysts contain 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 tetrahedra ($O-Zn^{2+}-O$) or legated to one internal silanol or

OH group ($\equiv Si-OZn$). In the case of Zn-HZSM-5 catalyst the alkanes dehydrocyclodimerization proceed via bifunctional pathways involving exchanged cations for dehydrogenation of alkanes and dehydrocyclization of alkenes 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, exert strong hydrogen attracting action and promote removal of hydrogen atoms adsorbed as hydrogen molecular, prevents hydrogenation of alkenes required in cyclization and consequently, enhances aromatization.

The co-catalyst contains zinc cations Zn^{2+} and zinc oxide as hydro-dehydrogenating component and molecular sieve ZSM-5 in the hydrogen form as acidic component. Zinc oxide was dispersed on the surface of HZSM-5 by mechanically mixing and heating the mixture at 500°C. Zinc oxide alone is not active of directly dehydrogenating of propane and butanes but is known as a strong hydrogen adsorbent which prevents hydrogenation of alkenes. The behaviour of ZnO/HZSM-5 co-catalyst obtained by physically mixture is different than of ZnO/HZSM-5 obtained by impregnation. During the heat treatment of physically mixture ZnO/HZSM-5 a solid-state reaction between zinc oxide and Brönsted acid sites (strong $\equiv Si-OH-Ala \equiv$ and low silanol $a \equiv Si-OH$) of HZSM-5 yield zinc cations ($Zn^{2+}, ZnOH^+$) incorporated in HZSM-5 structure which are active for aromatization of alkanes and alkenes: [22, 61, 63]



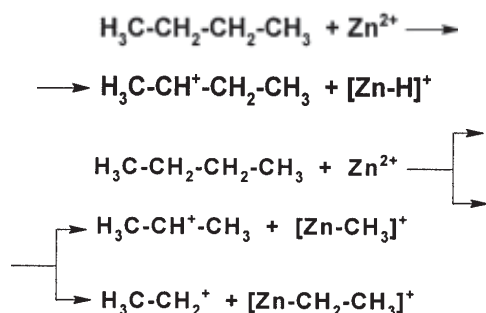
Only a small amount of zinc oxide gets into the pores of the zeolite and reacts with the bridging hydroxyl groups. Thanks to this solid-state reaction the strong Brönsted acid site become a strong Lewis acid site [55-57]. The presence of zinc oxide in the co-catalyst may promote the activation of alkanes molecules by a polarization effect of C-H bonds

and lead to molecular hydrogen formation *via* recombinative desorption of hydrogen atoms in dehydrogenation reactions.

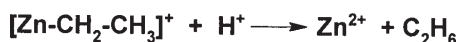
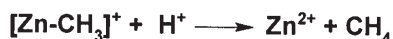
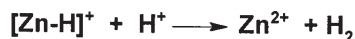
Alkanes are activated by a monomolecular or a bimolecular [91] mechanism depending on the reaction conditions (temperature, surface concentration of reactants and conversion). The dehydrogenation zinc species are efficient in the increase of aromatization selectivity since they activate the C-H bonds and promote the dehydrogenation as well as the migration of hydrogen atom by hydrogen transfer.

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

Zinc cations and ZnO can promote heterolytic cleavage of C-H bonds to give a transition species of the type $[Zn-H]^+$ and to decrease the C-C bond cleavage: [25, 30, 65]



The surface species $[Zn-H]^+$, $[Zn-CH_3]^+$ and $[Zn-CH_2-CH_3]^+$ are immediately scavenged by protons (H^+) of zeolite resulting molecular hydrogen, methane and ethane: [25, 30, 65]



Zinc in cationic exchange positions is stable and remain unreduced during the aromatization of alkanes and alkenes when molecular hydrogen is present [75]. Zinc oxide is possible to gradually be reduced to the zinc metal and to vaporize at the high operating temperatures (500-600°C) which led to an irreversible decline in the aromatization [63, 70]. To avoid the volatilization of zinc we performed experiments at relative high pressure (4 atm.) and at a temperature (450°C) below to melting point of zinc metal.

In accordance with the results plotted in figure 4 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 hours 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. %. In the gaseous product the new hydrocarbons are propane, ethane and methane as a result of cracking and hydrogen transfer.

After that the concentration of (n+i) butanes is growing and after 12 h or reaction become higher than in the feedstock. The aromatization activity of the co-catalyst is reduced because of coke forming.

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. This time, the feedstock contains more alkanes C_3 , C_4 (59.28; 63.20; 62.60 vol. %) than alkenes C_3 , C_4 (33.04; 30.16; 30.87 vol. %). 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. In addition to this is possible to have isomorphic substitution of aluminum with zinc in the network and reaction with free alumina or silica. For this reason the aromatization activity was extended to 24 – 36 h when in the liquid product the BTX represent 59 – 60 wt. % in the average. The dehydrogenation of alkanes and of reaction intermediates 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.

After 24 -36 h the aromatization activity decreased in the favor of oligomerization, isomerization and hydrogen transfer without cyclization. Therefore, the liquid product contain more “oligo” hydrocarbons, a mixture of aliphatic hydrocarbons of the composition C_5-C_{10} , mostly branched (iC_5-iC_{10}), than aromatic BTX (86.97 wt % after 16 h – test no.1 *vs.* 12.98 wt%; 79.05 wt% after 40 h – test no.2 *vs.* 20.41 wt%; 60.71 wt% after 40 h – test no.5 *vs.* 39.05 wt%; 75.59 wt% after 40 h – test no.6 *vs.* 23.58 wt% ; 67.65 wt% after 80 h – test no.10 *vs.* 32.69 wt%).

The yield of aromatic hydrocarbons BTX follows the series:

toluene > xylenes + ethylbenzene >> benzene in the stage of aromatization and:

xylenes + ethylbenzene $\geq$ toluene >> benzene in the stage of oligomerization.

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 alkenes $C_4^=$ are wholly consumed during the first 24 h TOS, after that, especially the concentration of (1+i) $C_4^=$ begin to increase.

The alkanes (n+i) C_4 consumption reach the maximum after first 4 hours (85% for n- C_4 and 65% for i- C_4). Further their concentration is growing up and after 24 – 32 h TOS become higher than in the feedstock, especially of i-butane.

In the gaseous product the main components are propane >> methane + H_2 >> ethane, their concentrations decreasing continuous with TOS. Presence of molecular hydrogen is a result of dehydrogenation and of hydrogen transfer.

The loss of catalytic activity with the reaction progress is a result of the decreasing of the number of active sites upon coke deposition.

The dehydrogenating activity (C-H bond cleavage) of ZnO/HZSM-5 co-catalyst via zinc species in the first 4 h TOS is overcome by the protolytic cracking activity (C-C bond cleavage) when dehydrogenation via acid sites of HZSM-5 involves hydrogen transfer with the formation of low molecular-mass alkanes.

Conclusions

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 product distribution (gaseous and liquid) in the conversion of butanes-butenes mixtures at 450°C and atmospheric pressure over Zn-HZSM-5 catalysts is changing with time on-stream. The 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.

The dispersion and incorporation of ZnO in the HZSM-5 zeolite was successfully carried out by the physical mixing followed by heat treatment when the solid – state ion exchange of zinc oxide and Brønsted acid sites take place and zinc cations are present together with zinc oxide. The preparation method by physical mixture is easy in formulation, safe, lower in cost and environmentally friendly.

Zinc species working synergistically with the Brønsted and Lewis acid sites of the zeolite are responsible for the dehydrogenation of alkanes (C_3 , (n+i) C_4) to alkenes C_2 – C_4 , alkenes oligomers C_4 – C_{10} to dienes C_4 – C_{10} and of cyclonaphthenes C_6 – C_{10} to aromatics C_6 – C_{10} and Brønsted and Lewis acid sites are responsible for the isomerisation of n- C_4 to i- C_4 , oligomerization of C_2 – C_4 to C_4 – C_{10} and cyclization of dienes C_4 – C_{10} to cyclic naphthenes C_6 – C_{10} .

The addition of zinc oxide in HZSM-5 influence the distribution of the acid sites reducing the number of the strong Brønsted acid sites (as proton donors and forming both carbonium and carbenium ions) with medium Lewis acid sites (as electron pair acceptor and forming only carbenium ions).

The aromatization of mixtures of short alkanes (C_3 , C_4) and alkenes (C_3 , C_4) over bifunctional 5 wt% ZnO/HZSM-5 co-catalyst is a complex process, involving a large number of consecutive and parallel reactions. 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.

The dehydrogenation activity of the zinc species in the dehydrogenation of (n+i) butanes reached a maximum during first 4 h TOS and after 24 – 32 h their concentration become higher than in the feedstock and the process is based only on the conversion of alkenes.

In the liquid product the concentration of aliphatic hydrocarbons C_5 – C_{10} (mostly iso) and $> \text{C}_{10}$ (denoted “oligo”) is increasing up to 70 – 80 wt% after 40 h TOS.

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Manuscript received: 10.12.2015