

Conversion of Butanes and Butenes from Industrial Feedstock over Zn-HZSM-5(acetate) Catalyst

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The activity and selectivity of Zn/HZSM-5 (wt% 0, 77 ZnO) catalyst prepared by ion exchange with solution of zinc acetate in the aromatization of C₄/C₄= hydrocarbons was investigated. The experimental results showed that the conversion of C₄/C₄= hydrocarbons on the bifunctional Zn-HZSM-5 (acetate) catalyst and the selectivity to aromatics BTX are higher than that on monofunctional HZSM-5, but lower than on Zn/HZSM-5 (nitrate). On HZSM-5, protons (Bronsted acid sites) and on Zn-HZSM-5, both Zn cations and protons are responsible to alkanes dehydrogenation and further in dehydrocycloaromatization reactions that form C₆-C₈ aromatics. In the liquid product, on HZSM-5 catalyst at 450°C and 8 atm., after 24h time on stream the aromatics represented an average of 30 wt%, with more xylenes and toluene. On Zn/HZSM-5 (acetate) catalyst, at 450°C and 4 atm., after 176h time on stream, the aromatics represented more than 46 wt% with more toluene and aromatics C₈. The aromatization process is accompanied by the oligomerization of C₄/C₄= hydrocarbons (more C₉-C₁₀ and >C₁₀ aliphatic hydrocarbons) especially on HZSM-5 catalyst.

Keywords: aromatization, butanes, butenes, HZSM-5, Zn/HZSM-5 (acetate).

The transformation of light hydrocarbons C₂-C₄ (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 a base chemical in a number of petrochemical and chemical processes [2].

The aromatization of light alkanes contained in non-associated natural gas, in associated gas (as petroleum casing-head gas) and from petroleum refining processes (as liquefied petroleum gas, LPG) represent a new attractive way of producing BTX aromatics. The conversion of light alkanes into aromatics (with low selectivity to BTX) was first described in 1970 by Csicsery, [3, 4] 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 [5 – 19]. Activity of catalyst is mostly determined by the zeolite Bronsted acid sites and by the active metal-phase supported by zeolite and selectivity is due to the zeolite micropores and/or cavities size and shape. The structure 3-D of ZSM-5 zeolite is characterized by two dimensional types of intersecting channels (2-D pore system) with 10-member ring (MR) openings: one type is sinusoidal (zig-zag) with a near-circular (0.53x0.56nm) openings and the other one is linear with an elliptical (0.51x0.55nm) openings. The channel intersections have a diameter of 0.89 nm and are the locus of strong acid sites and of aromatic C₆-C₈ hydrocarbons formation [20, 21].

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 the coke deposition is relatively slow, because no appreciable amounts of polyaromatics can be formed [22].

Already a few commercial processes [23] have been announced based on: HZSM-5 (M2 Forming process – Mobil Oil [24] and M-Forming process – Mobil) [24]; Ga/HZSM-5 (Cyclar-BP/UOP [25-29] and Z-Forming from Mitsubishi Oil and Chiyoda) [30]; Zn/HZSM-5 (Alpha process of Asahi Chemical and Petrochemical) [31]; Pt/K(Ba)L (Aromax™ process – Chevron – Phillips Chemical Co. [32] and RZ-Platforming process – UOP [33,34] and Aroforming from IFP and Salutec based on metal oxides-HZSM-5 [35, 36].

ZSM-5 (MFI) zeolite was discovered in the late 1965's by Mobil researchers and was patented in 1972 [37]. Many studies have focused on the ability of the monofunctional acid catalyst (HZSM-5) to convert light hydrocarbons to BTX [6-9, 13-15, 18, 19, 24, 25, 39, 40, 43-46]. HZSM-5 catalysts are not the best dehydrogenating catalysts because the hydrogen rejection from catalyst occurs by hydrogen transfer to olefins which limits the aromatics selectivity. Aromatization over HZSM-5 is accompanied by substantial cracking of C – C bond of alkanes with a production of 3 moles of small alkanes per one mole of aromatics.

The enhancement of light alkane's conversion to aromatics has been demonstrated by using metal-containing HZSM-5 catalysts. The catalytically active species (metal, metal ion, metal oxide) facilitate the heterolytic cleavage of the C-H bond of the adsorbed alkanes (dehydrogenation of alkanes) and accelerate the combination of surface hydrogen atoms formed via the dehydrogenation and dehydrocyclization process and their removal as molecular hydrogen.

Particular attention was directed to the utilization of Pt, Ga and Zn for the aromatization of light alkanes, in combination with HZSM-5 [20-50]. The poisonousness and the high price of gallium salt have a limiting role. The utilization Zn-based HZSM-5 catalyst instead of Ga-based HZSM-5 catalyst might be preferential from the environmental point of view (is a low-waste catalyst), from

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technological (profitable) and economical (cheaper) aspects.

In this study, we report, the catalytic performances of the fresh and reactivated zinc ion exchanged HZSM-5 zeolite catalyst prepared by ion exchange with zinc acetate, in comparison with HZSM-5 on butanes-butenes mixture aromatization under fixed-bed down-flow conditions, 8atm. and 4atm. at 450°C and at a space velocity of 1h⁻¹.

Experimental part

NaZSM-5 zeolite synthesis

The chemicals used in hydrothermal synthesis were sodium silicate solution (29.63wt% SiO₂, 9.55wt% Na₂O, 60.82wt% H₂O), aluminum sulphate, Al₂(SO₄)₃·18H₂O (15wt% Al₂O₃), sulphuric acid (96 wt% H₂SO₄), ammonium hydroxide solution (25wt% NH₃), ethylene glycol, and demineralized water.

NaZSM-5 has been synthesized according to procedure described previously [41]. The zeolite having SiO₂/Al₂O₃ molar ratio of 36.02 was crystallized from a hydrogel with molar composition: 6.49 Na₂O-Al₂O₃-58.92 SiO₂-29.43 EG-1832 H₂O having a molar ratio HO⁻_{free}/SiO₂ = 0.21. The synthesis has been carried out at 180 ± 5°C for 24h in a Teflon-lined stainless steel autoclave under intermittent stirring and autogenously pressure. The solid material was filtered, washed with demineralized water, dried at 110°C for 6h and heated in air at 550°C for 6h.

The calcined sample has been characterized by X-ray diffraction (XRD) to identify the zeolite structure type, phase purity, degree of crystallinity and crystallite size. The XRD measurement was performed using a Philips PW 1830 computerized-diffractometer with CuK_α radiation and Ni filter with a scan rate of 0.02° . s⁻¹ in the 2θ range of 4-30°. The surface morphology and the size of the crystals of calcined NaZSM-5 zeolite was studied by SEM (Microspec WDX-2A) using a 30kV accelerating potential. The chemical composition of the calcined NaZSM-5 sample was analyzed by wet method after dissolving in HF solution: aluminum concentration (Al₂O₃) was determined by the chelatometric titration using EDTA and Zn standard solution, sodium concentration (Na₂O) by flame photometry using a Karl Zeiss Jena Phlamenphotometer and SiO₂ by difference between the calcined weight of sample at 950°C and weight of calcined residuum at 950°C after the treatment with HF solution.

Catalyst Zn/HZSM-5 (acetate) preparation

First, the ammonium form, NH₄ZSM-5 has been obtained by ion exchange of NaZSM-5 zeolite, three times, with 1M NH₄NO₃ solution (solid (g) : solution (mL) ratio of 1:5) at 80°C for 3h each time. The NH₄ZSM-5 was filtered, washed, dried at 110°C for 6h and calcined in air at 550°C for 6h to get protonic HZSM-5 zeolite. The HZSM-5 zeolite was

converted in the Zn/HZSM-5 form by treating it with 0.1M Zn(CH₃COO)₂ aqueous solution (solid:solution = 1g/5mL) two times under stirring at 80°C for 6h each time. The Zn/HZSM-5 (acetate) sample was washed, dried at 110°C for 6h and calcined in air at 450°C for 6h.

The zinc contained in the sample was 0.77wt% as ZnO. The structure of HZSM-5 and Zn/HZSM-5 (acetate) samples was checked up by X-ray diffraction, the specific surface area was determined applying the BET method using a Carlo-Erba Sorptomatic Series 1800 instrument at -196°C and the total acidity (Bronsted and Lewis) of HZSM-5 and Zn/HZSM-5 (acetate) catalysts have been carried out by ammonia TPD method.

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

Catalytic experiments

The catalytic experiments were carried out in a continuous flow fixed-bed stainless-steel reactor (Twin Reactors System Naki) (with 25mm internal diameter) at 8atm. (over HZSM-5) and at 4atm. (over Zn/HZSM-5 (acetate)) at 450°C and a space velocity (WHSV) of 1h⁻¹ without recirculation of resulted gaseous products. The volume of catalyst was 100 cm³ and the time on stream (middle values) was 24 h for HZSM-5 (five tests) and 176h for Zn/HZSM-5 (test no. 5). The effluents from the reactor were cooled in a condenser and the liquid and the gaseous fractions collected after each 4h were analyzed gas chromatographic: a GC Carlo Erba Mega using a fused silica capillary column (25 length 0.32mm i.d.) with SEE 52 stationary phase and FID for liquid phase, and a GC Carlo Erba Model C, using a column (6m length) with squalane and dimethyl sulpholane for gaseous phase. After each test, the catalyst was regenerated at 475°C for 8h in nitrogen with 2% oxygen flow.

Results and discussions

X-ray diffraction analysis

The diffraction pattern of the starting pentasil NaZSM-5 with SiO₂/Al₂O₃ = 36.02 is presented in figure 1. From the diffractogram, the positions of diffraction lines (2θ_{hkl}), the calculated d_{hkl} values (λ = 2dsinθ) and the corresponding relative intensities (I/I₀) agree very well with the reported values for ZSM-5 (MFI) zeolite [19, 20, 42].

The zeolite have a high degree of crystallinity (99.6%) derived from the high intensities of the XRD lines in the region 22.5 – 25°2θ, based on a standard ZSM-5 crystallized in presence of tetrapropylammonium hydroxide.

No other diffraction peaks were found in this range (4-30° 2θ), which means that the pure ZSM-5 was obtained.

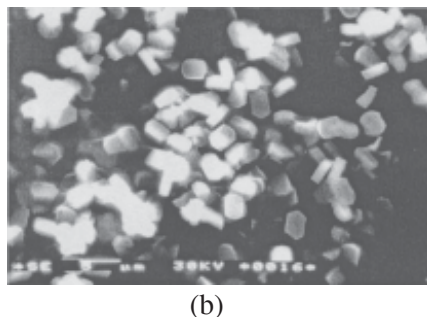
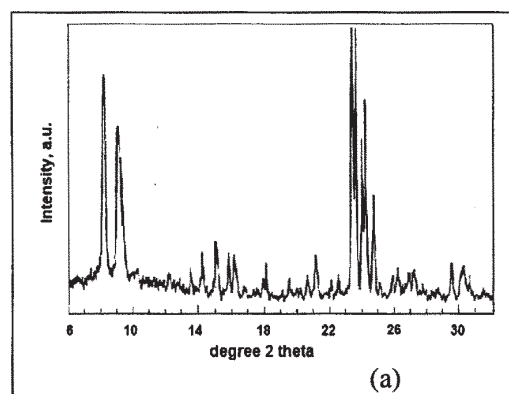


Fig.1. Powder X-ray diffraction pattern (a) and SEM micrograph (b) of calcined NaZSM-5

Composition, wt%	SiO ₂	Al ₂ O ₃	Na ₂ O	SiO ₂ / Al ₂ O ₃	ZnO
	NaZSM-5	92.92	4.38	2.70	36.02
Zn/HZSM-5			-	36.02	0.77
S _{BET} , m ² g ⁻¹	NaZSM-5		HZSM-5		Zn/HZSM-5
	302.5		291.0		260.0

Table 1
CHEMICAL COMPOSITION OF
CALCINED Na-ZSM-5 AND OF Zn-
HZSM-5 (ACETATE)

The XRD patterns of HZSM-5 and of zinc-exchanged HZSM-5 (not presented) are similar to NaZSM-5; the ion exchange process and thermal treatment not producing any damage to the zeolite network. The Zn/HZSM-5 sample exhibits no diffraction peaks at $2\theta = 31.60, 34.2, 36.1$ and 56.6° which are characteristic for ZnO indicating that the zinc is present as Zn²⁺ highly dispersed in the zeolite matrix.

Morphology of the NaZSM-5 sample

The scanning electron micrograph of the NaZSM-5 sample is shown in figure 1 (b). It can be seen the well developed hexagonal-shaped crystals with size of 3.5 - 4.3µm in length and 2.1 - 2.86µm in width.

Elemental analysis and specific surface area

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

Acidity and strength distribution

The acidity of the HZSM-5 and Zn/HZSM-5 (acetate) catalysts has been evaluated by using temperature programmed desorption (TPD) of ammonia technique TPD (amount of ammonia desorbed, mmol/g, vs. temperature of desorption, °C). The total amount of acid sites (Bronsted protic and Lewis aprotic acid sites) and the acid strength (expressed as the maximum temperature of ammonia desorption) are summarized in table 2.

Both catalysts give two humps one at low temperature (LT) ($T < 300^\circ\text{C}$) and the other one at high temperature (HT) ($T > 300^\circ\text{C}$). The low region with $T_{\text{max}} = 200 - 220^\circ\text{C}$ corresponds to the low strength of Lewis and weak Bronsted acid sites and consists of the physisorbed ammonia (ammonia coordinative bonded to the terminal silanol groups).

The high region with $T_{\text{max}} = 420^\circ\text{C}$ correspond to the moderate and high strength of Bronsted acid sites and consists of the chemisorbed ammonia (ammonia forms ammonium ions hydrogen-bonded to oxygen's of the framework). Incorporation of zinc by ion exchange into cationic positions of HZSM-5 zeolite modify the acid strength with formation of new Lewis acid sites responsible for aromatization

Catalytic activity and selectivity of Zn-HZSM-5(acetate) during C₄/C₄=hydrocarbons aromatization

Aromatization of a mixture containing butanes and butenes over Zn/HZSM-5 (acetate) takes place with good selectivity to aromatics BTX and with production of molecular hydrogen.

The same catalyst Zn/HZSM-5 (acetate) has been used in five tests with regeneration after each test.

The changes in the gaseous product distribution over Zn/HZSM-5 (acetate) with time on-stream (from four to four hours), test no.1, and test 5 are shown in figures 2 and 4. The concentration of butenes decreased from 27.47vol. % to 1.20vol. % after first 4h of reaction and remains at values smaller than 2.5% after ~ 96h of reaction. The concentration of butanes (n+i) decreased from 67.25vol.% to 35.03vol.% after 8h of reaction, after that is continuously increasing without to rise above the initial concentration. The hydrogen molecular concentration exceeds the butanes concentration during the first 43h of reaction in test no.1 but does not exceed in test no.5. 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 (acetate) is propane (~30vol. %), less than over HZSM-5 (about 60vol. %).

The aromatic hydrocarbon distribution in the liquid phase corresponding to catalytic tests no.1 and no.5 is plotted in figure 3 and 5.

Aromatic hydrocarbons were mainly toluene (~25wt %) and xylenes (~25wt %), benzene being about 5 wt%. The aliphatic hydrocarbons C₅-C₁₀ content is increasing from ~ 20 wt% after 4h of reaction to ~ 40 wt% after 96h of reaction and is based on C₉ and C₁₀ hydrocarbons. The formation of aliphatic hydrocarbons with more than 10 carbon atoms (> C₁₀) is limited to about ~ 7 wt%. In the liquid product of all catalytic tests naphthalene is present in a concentration below 1.0 wt%. Zn/HZSM-5 (acetate) is less active and selective than Zn-HZSM-5 (nitrate) (1.37% wt as ZnO) obtained by ion exchange. The catalytic tests were carried at atmospheric pressure, 450°C and WHSV of 1h⁻¹. On Zn-HZSM-5 were carried ten tests. After each tests, the catalyst was regenerated at 475°C for 8h in nitrogen with 2% oxygen flow [51, 52].

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

Catalyst	Desorbed ammonia, mmol/g			T _{max} , °C	
	1 st peak (LT)	2 nd peak (HT)	Total acidity	1 st peak	2 nd peak
HZSM-5	0.618	0.282	0.900	220	420
Zn-HZSM-5	0.630	0.141	0.771	200	420

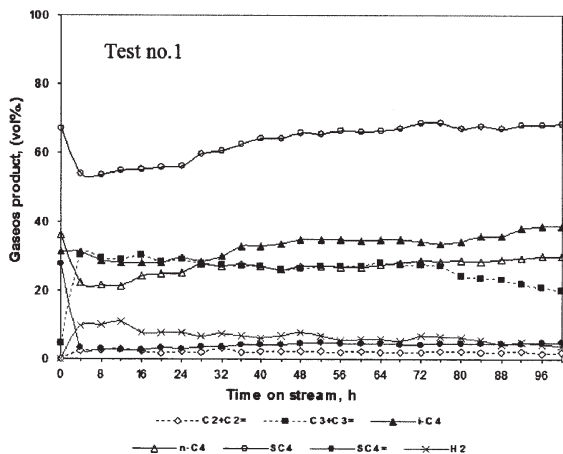


Fig. 2. Gaseous phase composition vs. time on stream over Zn-HZSM-5 (acetate) catalyst

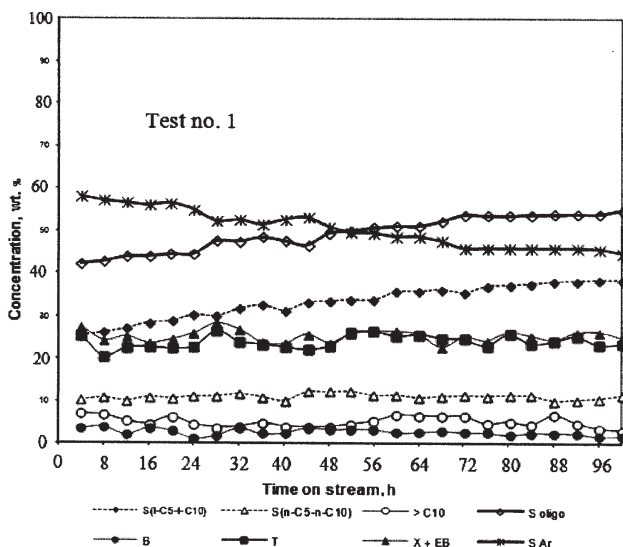


Fig. 3. Liquid composition vs. time on stream over Zn-HZSM-5 (acetate) catalyst

Aromatization of a mixture containing butanes and butenes over Zn-HZSM-5 (nitrate) takes place with high selectivity to aromatics BTX and with production of molecular hydrogen.

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

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

The change of the gaseous composition (vol.%) and of liquid phase composition (wt%) with time on-stream over HZSM-5 catalyst in the transformation of a mixture of (n+i) butanes and butenes are presented in figures 6 and 7.

The concentration of butanes (n+i) decreased from 56.53 vol.% to 9.16 vol.% in the first 4h of reaction, after that there is a continuously increasing going beyond the feedstock after 16h. The concentration of butenes (1-C₄, trans-2-C₄ and cis-2-C₄) decreased from 41.63 vol.% to 0.84 vol.% in the first 4h, and to 3.32 vol.% after 12h of reaction.

The forming of methane and ethane (C₁ + C₂) reach the maximum value (29.50 vol.%) after 4h of reaction and the forming of propane (C₃) after 8h of reaction (61.68 vol.%); their content is connected to aromatic hydrocarbons

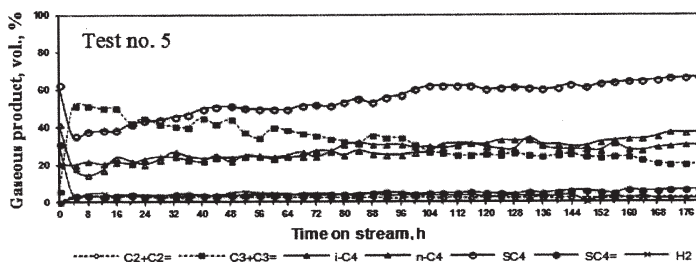


Fig. 4. Gaseous phase composition vs. time on stream over Zn/HZSM-5 (acetate) catalyst

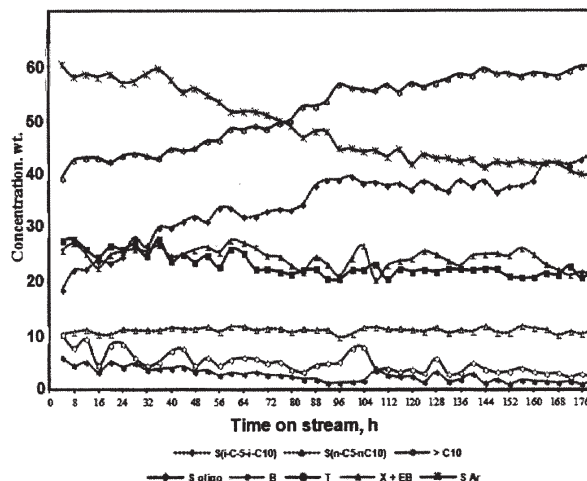


Fig.5. Liquid composition vs. time on stream over Zn/HZSM-5 (acetate) catalyst

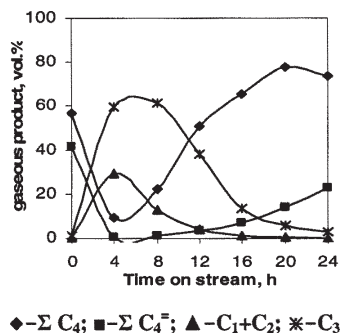


Fig.6. Gaseous phase composition vs. time on stream over HZSM-5 catalyst in butane/butenes conversion

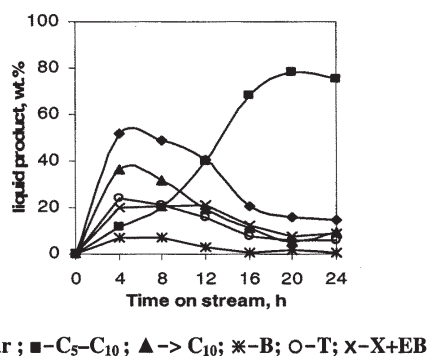


Fig.7. Liquid phase composition vs. time stream over HZSM-5 catalyst in butane / butenes conversion

formation. The molecular hydrogen was not detected in the gaseous phase.

The catalytic activity and selectivity to aromatic hydrocarbons are visible for first 12h run after that aliphatic C₅ - C₁₀ are formed.

Aromatization of a multicomponent feedstock is complex, involving a large number of heterogeneous reactions.

It is generally agreed that the aromatization of low molecular weight alkanes can be represented as a three stage process: 1) alkanes conversion into small alkenes, $C_2=C_4$; 2) alkenes oligomerization and cracking, and 3) aromatization of small alkenes into C_6-C_{10} aromatic hydrocarbons.

The relevant reactions consist of: 1) alkanes C-H bond activation through a pentavalent carbonium ion and of alkenes 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 dienes to cyclic alkenes; 8) dehydrogenation of cyclic alkenes to cyclic dialkenes and finally to aromatics, C_6-C_{10} [14, 40,46,47, 53].

Conclusions

Bifunctional catalyst Zn/HZSM-5 (acetate) exhibits a good selectivity to aromatics BTX in the aromatization of butanes- butenes mixture (in first ~ 50 h), 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 ~50 wt% and the formation of toluene (~25 wt%) and xylenes (~25 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.

Small selectivity for BTX aromatics of Zn/HZSM-5 (acetate) comparative with Zn-HZSM-5 (nitrate) catalyst in conversion of butanes-butenes technical mixtures is very probable because of the organic macromolecular species that results after calcinations of Zn/HZSM-5 (acetate) fresh catalyst (and/or Zn content). This macromolecular species blocked (partially) access of the reactants molecule on the active catalytic centers (Brønsted and Lewis acid centers and Zn centers).

The high Bronsted acidity of HZSM-5 catalyst is responsible for the high percentage of C_5-C_{10} aliphatic hydrocarbons (~80 wt% after 24h TOS), in comparison with Zn/HZSM-5 (acetate) catalyst (~25 wt% after 96h TOS).

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

The product distribution (gaseous and liquid) in the conversion of butanes-butenes mixtures at 450°C and 8 atm. pressure over HZSM-5 and 4 atm. pressure over Zn/HZSM-5 (acetate) catalysts is changing with time on-stream. The HZSM-5 catalyst deactivates fast and Zn/HZSM-5 (acetate) catalyst is able to sustain activity and selectivity for a longer period.

The presence of butenes in feed exercise an activation of butanes: it is thought that butenes are protonate to

carbenium ions from Bronsted acid sites and then activate butanes through hydride abstraction.

The production of hydrogen increased sharply after introduction of zinc cations to HZSM-5, indicating that these cations serve as dehydrogenation catalysts. The zinc species work as a dehydrogenation centre. In presence of cations zinc alkenes may undergo direct abstraction of a hydrogen atoms (or ions) to form allylic species. Aromatic hydrocarbons may be formed by the successive abstraction of hydrogen atoms from higher alkenes or direct coupling of two allylic species with simultaneous production of hydrogen molecules.

On HZSM-5 the formation of aromatic hydrocarbons involves Brønsted acid centers active sites. The aromatic molecules were formed from alkenes oligomers by successive deprotonation and hydride transfer to carbenium ions [38, 47, 53].

The catalytic aromatization reactions over Zn/HZSM-5 (acetate) 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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Manuscript received: 10.10.2013