Investigation of Butane-butylene Technical Mixtures Transformation Over Modified Microporous Materials Prepared by Ion Exchange Method Into Liquid Fraction Rich in Aromatic Hydrocarbons

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The Zn and Ni were introduced into HZSM-5 zeolite by ion exchange method with aqueous solutions of $Zn(NO_3)_2$ and $Ni(NO_3)_2$ to investigate the catalytic activity and selectivity of modified Zn-HZSM-5 and Ni-HZSM-5 catalysts for conversion of butane-butylenes technical mixtures in a fixed-bed stainless-steel reactor (Twin Reactor System Naky) at 450ºC, at atmospheric pressure for Zn-HZSM-5 and at 4 atm. total pressure for Ni-HZSM-5 and at a space velocity (WHSV) of $1h^{-1}$. The catalysts were characterized using XRD, SEM, and NH_3-TPD analysis for their structure, morphology and acidity. 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.

Keywords: conversion, light hydrocarbons, Zn- HZSM-5, Ni-HZM-5, BTX

Light alkanes and alkenes aromatization over zeolite based catalysts is well known. It has been shown that HZSM-5 zeolite can be modified by incorporation of metals and metal oxides in order to obtain catalysts for selective hydrocarbons conversion [1-6].

Activity, selectivity and stability of the zeolite catalysts for those shape selective reactions (e.g. aromatization of light hydrocarbons) depend not only on the porous structure of the zeolite but also on the density of the acid sites and their strength distribution, as well as on metal sites distribution and metal support interaction [7].The catalyst systems prepared in this way operate as bifunctional catalysts. The addition of a catalytic (de)hydrogenating function e.g. Ga, Zn, Ni, Pt, Ag, etc., to HZSM-5 is known to significantly enhance the activity and selectivity to aromatic hydrocarbons BTX (benzene, toluene, xylenes) for the aromatization of light hydrocarbons [7-82]. Among these additives, Ga has been most extensively studied because of its superior selectivity to aromatics and the high stability of Ga-HZSM-5.

The catalytic performance of Zn-HZSM-5 is comparable to that of Ga-HZSM-5, but Zn is less stable due the high vapor pressure of Zn^{2+} [4]. The problem of Zn volatilization can however be alleviated by alloying Zn with Cu, Ni, Ga or Pd [37, 52, 59, 83, 84].

Ni–HZSM-5 (or Ag-HZSM-5) catalysts exhibit a good activity and selectivity towards BTX aromatics in conversion of light alkanes and alkenes [74- 81].

In the present paper, we present the (comparative) results obtained in the conversion of butane-butylenes technical mixtures (in FCC gasses) in a fixed-bed stainless-steel reactor over Zn-HZSM-5 and Ni-HZSM-5 catalysts prepared by ion exchange method with aqueous solutions of $Zn(NO_3)_2$ and $Ni(NO_3)_2$.

Experimental part
Synthesis

The parent Na-ZSM-5 was synthesized with ethylene glycol as the template organic molecule. The starting materials were: sodium silicate solution (29.63 % SiO_2, 9.55 % Na_2O and 60.8 % H_2O), aluminum sulphate $Al_2(SO_4)_3$ ·18 H_2O, concentrated sulphuric acid, and distilled water [86].

Crystallization of the homogeneous gel took place over 24h at autogenously pressure and 180±5°C in steel stainless autoclaves with intermittent stirring. The synthesis product were filtered, washed repeatedly with distilled water, dried at 110°C in air for 6h and calcined at 550°C in air for 6 h in order to remove the organic agent.

The calcined Na-ZSM-5 was converted into H-form by three successive ion exchanges with 1M NH_4NO_3 solution at 80°C for 6h (solid : liquid ratio = 1÷5). Then, the zeolite is separated from the solution by filtering and washing with distillate water. After that, the catalyst is dried over night at 110°C and calcined in air at 550°C for 6h. HZSM-5 sample was converted by ion exchange with 0.1 M aqueous solutions of $ZnNO_3$ in Zn-HZSM-5 with content of metal at 1.39 % wt. and was converted to Ni-HZSM-5 by process of ion exchanges with 0.1 M $Ni(NO_3)_2$ aqueous solution under stirring at 80°C. The Ni-HZSM-5 sample was filtered, washed, dried at 110°C for 6h and calcined at 450°C in air for 6h. The Ni contained in the sample was 1.34 %. The Zn-HZSM-5 and Ni-HZSM-5 powders with 20 % wt., γ - Al_2O_3 as binder was extruded and then cut into short cylinders, dried at 110°C for 6h and calcined at 550°C in air for 6 h.

Catalyst 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 Cu K_α radiation at a scanning speed of $0.02°$ s^{-1} in the range of 6-45, 2θ. XRD powder pattern of the Na-ZSM-5 sample exhibit only diffraction lines proper to MFI structure high crystallinity. The pattern confirmed that the synthesized zeolite has the structure identical to MFI-type zeolite [86]. 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 SEM image of

parent NaZSM-5 revealed the well-defined morphology of crystals indicating highly crystalline material [37,44,49,51,53,58,61,64]. Catalytic tests in a fixed-bed continuous flow stainless - steel reactor (a commercial Twin Reactor System Naky Metrimpex, Hungary) was studied. The reaction products (only aromatic BTX) were on-line analyzed by a gas chromatograph Carlo Erba VEGA equipped with a 25 m capillary column filled with SE-52 and flame ionization detection (FID).

The acidity and strength distribution on HZSM-5, Zn-HZSM-5 and Ni-HZSM-5 catalysts were measured using Temperature Programmed Desorption (TPD) technique using ammonia. A known weight of the sample was activated in a dry N_2 at 500°C for 4h then cooled to 80°C when ammonia was admitted. The amount of ammonia desorbed from 100 to 800°C (at a heating rate of 10°C/min) was quantitatively monitored by absorption in 1M HCl. The desorbed ammonia represents the total acidity (weak and strong) of the sample. The TPD ammonia desorption presents two peaks, one at low temperature (LT) and one at high temperature (HT) (table 1). The peak corresponds to higher acid strength and is done to ammonia bound to strong structural Brönsted sites (Si -O -Al bridging OH), and possible to strong Lewis sites ($\equiv$ Al and $\equiv$ Si$^+$). Low temperature peak correspond to less acidic sites (terminal OH groups, cationic sites M^{n+}, AlO^+). The temperature and the amount of desorbed ammonia give information about strength and number of the acid sites. The observed enhancement of middle and lover acid sites in the Ni-HZSM-5 and Zn-HZSM-5 catalysts is probably the results of the Lewis acid sites created by nickel, and zinc, respectively. It also found that the intensity of strong acid sites (Bronsted probably) decreased compare to parent HZSM-5 [60].

The BET specific surface area was estimated applying the BET equation on sorption isotherms obtained using a Carlo -Erba Sorptomatic Series 1800 instrument at -469K and at sub-atmospheric pressure with nitrogen as the analysis gas. The values of the BET specific surface area and acidity of the Ni-HZSM-5 and Zn-HZSM-5 catalysts are presented in table 1.

Temperature programmed desorption spectra of NH_3 revealed that the acid strength of HZSM-5 was considerably reduced by introducing Zn^{2+} and Ni^{2+} cations. It was indicated from the results that the acid sites distribution of the Zn-HZSM-5 or Ni-HZSM-5 changed after the metal incorporation in HZSM-5 (the incorporation of the Zn^{2+} and Ni^{2+} ions into cationic positions), the medium and strong acid sites, in the catalysts weakened due the effect of Zn and Ni.

It was found that the intensity of the strong acid sites (Brönsted probably) in the modified zeolite samples decreased compare to HZSM-5.

Catalytic performance

The catalytic activity of Zn-HZSM-5 and Ni-HZSM-5 for C_4-$C_4^=$ technical fraction conversion to aromatics BTX, at 450°C and atmospheric pressure (Zn-HZSM-5), and at 4atm. (over Ni-HZSM-5) with WHSV 1h^{-1}, in a fixed-bed continuous flow stainless -steel reactor (a commercial Twin Reactor System Naky Metrimpex, Hungary) was studied. The catalysts were pre-treated with N_2 for 6h at 450°C to remove the adsorbed impurities and the moisture.

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 (6m length) with squalane and dimethylsulpholane and a thermal conductivity detector (TCD) for gaseous phase, respectively.

Results and discussions
Catalytic reactions of technical fraction $C_4/C_4^=$ on Zn-HZSM-5 catalyst

Before the catalytic tests, the catalyst was heated in reactor at 450°C in nitrogen flow for 6 h. The Zn-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 1h^{-1} and atmospheric pressure) were in advance selected to obtain the high yield of liquid product during the catalytic test. The changes of the liquid yield, butenes total conversion and aromatics hydrocarbon BTX concentration over Zn-HZSM-5 catalyst with time on-stream (from four to four hours), are presented in figure 1.

Sample	BET surface area, m²/g	Acidity, mmol. NH₃/g		Total acidity
		low-peak LT 353-573K	high-peak HT 573-873K	
HZSM-5	302.46	0.618	0.282	0.900
Zn-HZSM-5	286	0.738	0.144	0.882
Ni-HZSM-5	289	0.669	0.130	0.799

Table 1
PHYSICO-CHEMICAL CHARACTERISTICS OF THE STUDIED CATALYSTS: Ni-HZSM-5 and Zn-HZSM-5 IN COMPARISON WITH HZSM-5
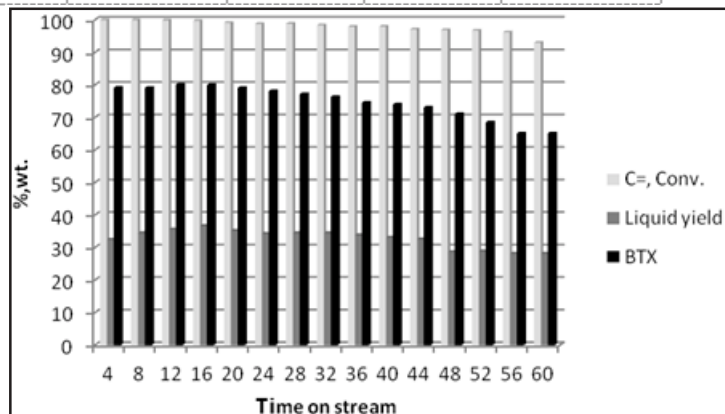

Fig.1. Variation of BTX concentration, butenes conversion, and liquid yield vs. time on stream over Zn-HZSM-5 catalyst at 450°C, atmospheric pressure and WHSV 1h^{-1}(Test No.5)

Butenes are consumed almost in totality during first 44 h on stream. Butanes are consumed during first 20 h of reaction after their become mainly components in reaction gases. C_3 and C_2 hydrocarbons were obtained in more quantity in first 24 h of reaction. The liquid product yield went up to 32% and the aromatic hydrocarbons BTX represent over 75%wt. after 40h, and finally, 65 %wt. after 60h of the time spent test.

Zn presence modifies the acid properties of the HZSM-5 catalyst decreasing the strong acid sites (Bronsted) number and creates new acid sites associated to Zn (Lewis). This element exhibits a strong attraction to hydrogen, preventing thus the hydrogenation of alkenes, and consequently, enhancing aromatization process. Zn presence promotes actualy the formation of aromatics via dehydrogenation of oligomerized and cyclized alkenes (naphtenes).

Due to the dehydrogenating activity of zinc, the hydrogen appears in the gaseous fraction (up to 42 % vol., after 24h) and the aromatic hydrocarbons become mainly components of the liquid fraction results in the reaction mixture (fig. 2).
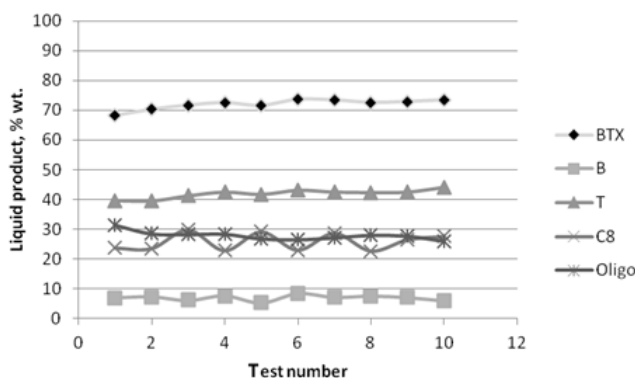

Fig.2.The aromatics and C_5+ fraction (Oligo) average output over Zn-HZSM-5 catalyst (450ºC, atmospheric pressure and WHSV = 1h⁻¹); (C8 – Xylenes + ethyl benzene, T - toluene, B - benzene, BTX - benzene, toluene, xylenes)

The yield of BTX hydrocarbons follows the series:
Toluene >Aromatics hydrocarbons C_8 >> benzene

In the liquid product the aromatic hydrocarbons, BTX, are predominant over 71%wt in all ten catalytic tests performed over Zn-HZSM-5 catalyst, toluene being the main aromatic hydrocarbon.

Zn cations distributed in HZSM-5 zeolite structure were involved in all dehydrogenation steps required for the alkane's aromatization, but only by catalyzing the recombinative desorption of H-atoms as H_2, while all other steps occurred on acid sites.
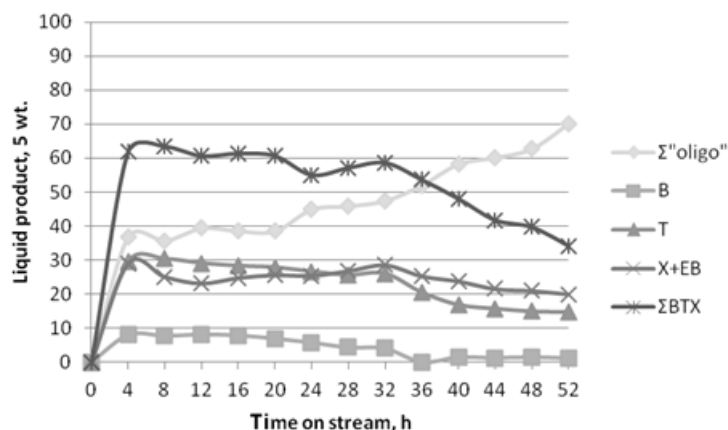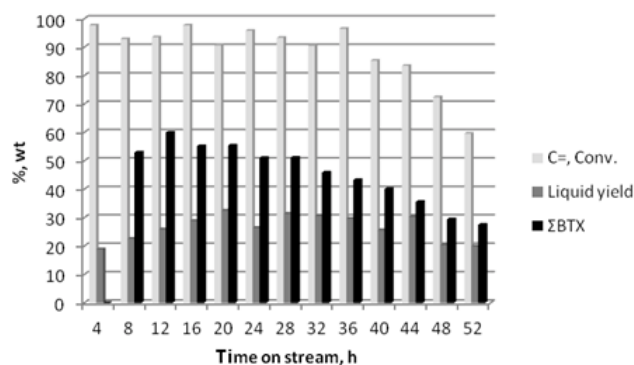

Fig.3. Variation of butenes conversion, liquid yield and BTX concentration, vs. time on stream over Ni-HZSM-5 catalyst (Test No.5)

Alkanes dehydrogenation and naphtenes dehydrogenation steps occur on the Zn^{2+} cations, and all required steps occur as well on the Bronsted /Lewis acid sites within zeolite pores. The study suggested a synergy between acid sites and exchanged cations where alkanes activation and initial C-H cleavage can occur, but hydrogen atoms must be preferentially removed via hydrogen transfer to hydrocarbon species to form C_2 - C_4 or via recombinative desorption on cation sites to form H_2 [3-5].

Catalytic reactions of technical fraction $C_4/C_4^=$ on Ni- HZSM-5 catalyst

Before the catalytic tests, the catalyst was heated up in reactor at 450ºC in nitrogen flow for 6 hour. The catalytic activity of Ni-HZSM-5 was evaluated in ten consecutive tests with intermediary regeneration at 475ºC for 6 h in nitrogen with 2% oxygen flow.

The operating conditions (temperature 450ºC, WHSV 1 h⁻¹ and 4 atm. pressures) were selected in advance to obtain the high yield of liquid product during the catalytic test. The changes of the liquid yield, butenes total conversion and aromatics hydrocarbon BTX concentration over Zn-HZSM-5 catalyst with time on-stream (from four to four hours), are presented in figure 3.

Butylenes are consumed in first 40h on stream but in small quantities with respect to Zn-HZSM-5. Liquid yield do not exceed over 30% wt. during the whole reaction time. Aromatics hydrocarbons, BTX, are obtained in higher quantities (over 50% wt. in liquid product but not exceed over 60% wt.) only in first 28h of reaction time. The hydrogen molecular concentration do not exceed 12.0 vol. % in all catalytic tests. Butanes are consumed in significant quantities only in the first 16h time on stream, over his becomes main components of gaseous fraction results in reaction and with C_2 and C_3 hydrocarbons.

Fig.4.The aromatics hydrocarbons, BTX and C_5+ fraction (Oligo) average output over Ni-HZSM-5 catalyst (450ºC, 4 atm. pressure and WHSV = 1h⁻¹)
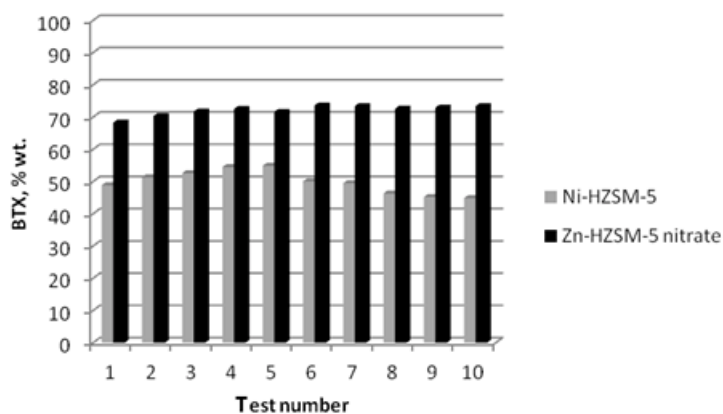
Fig.5. Variation of BTX aromatic hydrocarbons concentration, middle values per tests, in the liquid products resulted during the conversion of butanes /butenes technical fraction over Zn-HZSM-5 and Ni-HZSM-5 catalysts.

Ni cations exhibit a strong attraction to hydrogen, thus preventing the hydrogenation of alkenes, and consequently, enhancing the aromatization process (only in the first hours of the reaction). Nickel presence promotes actually the formation of aromatics via dehydrogenation of oligomerized and cyclized alkenes (naphtenes).

Due to the dehydrogenating activity of Ni, the hydrogen appears in the gaseous fraction and the aromatic hydrocarbons are the main components of liquid fraction results in reaction (but in small quantities compare to Zn-HZSM-5) (fig. 4).

Toluene ≈Aromatics hydrocarbons C_8 (xylenes + ethyl benzene) >> benzene.

Aromatic hydrocarbons were mainly toluene (of ~24.0 wt %) and xylenes (of ~22.0 wt %), benzene being about 3.5 wt% (middle value per tests). BTX aromatic hydrocarbons are the major components only in the first ~ 30h of the reaction, when the concentration in liquid fraction decreases below 50%. wt. The aliphatic hydrocarbons C_5-C_{10} (n-+i-alkanes) and aliphatic hydrocarbons with more than 10 carbon atoms ($> C_{10}$) (denoted as $\Sigma oligo$) are the main components in the liquid fraction after about 24-30 h of reaction in all ten catalytic tests performed on Ni-HZSM-5, as the figure 4 reveals.

A comparison of the aromatic hydrocarbons BTX concentration in the liquid fraction resulted on Zn-HZSM-5 and Ni-HZSM-5 (middle values for the test) in ten catalytic tests of aromatization of butanes-butylenes $C_4/C_4^=$ technical fraction is presented in the figure 5.

On Zn-HZSM-5 (nitrate) the average BTX concentration is over 72% wt. in liquid products and on Zn-HZSM-5 (acetate) not exceed of 55 % wt (middle values per tests).

Zn-HZSM-5 and Ni-HZSM-5 catalyze alkane's dehydrogenation and aromatization reactions. Alkanes undergo two primary reactions: dehydrogenation to alkenes and H_2 and cracking to light alkanes and alkenes. Alkenes then form aromatic hydrocarbons via oligomerization, cracking and isomerization reactions and alkenes hydrogenate to form the light alkanes C_2 - C_4 respectively, via both hydrogen transfer from co-adsorbed intermediates and dissociative adsorption of H_2. The reaction pathways resemble those occurring on HZSM-5, but Ni^{2+} and Zn^{2+} cations provide alternative pathways for the removal of hydrogen atoms in adsorbed intermediates as H_2. Zn^{2+} and Ni^{2+} cations increase the reversibility of hydrogen adsorption-desorption steps. As in the case of gallium exchanged HZSM-5 zeolites these reactions appear to proceed via bifunctional pathways involving acid $^-$OH groups and exchanged metal cations [25, 26, 43, 53, 54, 60, 82].

Ni-HZSM-5 shows higher yields for aromatic hydrocarbons and H_2 than HZSM-5 because Ni^{2+} cations catalyze the recombinative desorption of hydrogen atoms as H_2, as shows previously also for Zn^{2+} cations. This desorption step is not quasiecquilibrated during alkanes reactions on any

Zn-HZSM-5 (nitrate)										
	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
Temp. °C	450	450	450	450	450	450	450	450	450	450
Press., atm.	1	1	1	1	1	1	1	1	1	1
WHSV, h⁻¹	1	1	1	1	1	1	1	1	1	1
Liquid yield, % wt.	30,93	34.39	34.91	32.33	32.46	33.10	34.5	35.11	33.52	33.93
ρ, g/cm³	0.833	0.846	0.843	0.839	0.827	0.829	0.836	0.825	0.837	0.847
RON	105	107	102	108	109	103	103	104	105	103

Table 2
THE RON AND LIQUID PRODUCTS DENSITY RESULTS ON Zn-HZSM.5 CATALYST

Ni-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
WHSV, h⁻¹	1	1	1	1	1	1	1	1	1	1
Liquid yield, % wt.	23.93	25.28	24.21	22.83	25,15	24,18	20,5	21.11	24,32	23.97
ρ, g/cm³	0.777	0.769	0.743	0.779	0.781	0.779	0.766	0.759	0.7367	0.770
RON	99	98	100	99	100	98	99	99	99	98

Table 3
THE RON AND LIQUID PRODUCTS DENSITY RESULTS ON Ni-HZSM.5 CATALYST

these materials (HZSM-5, Ni-HZSM-5, Zn-HZSM-5) and catalytic sites provided by these cations remove the kinetic bottlenecks that limit the rate and selectivity of alkanes aromatization reactions [82]. Ni-HZSM-5 exhibits lower alkanes conversion rates and aromatics formation rates than Zn-HZSM-5, because Zn^{2+} cations catalyze recombinative desorption steps more effectively than Ni^{2+} cations [6,49,52,53,58-62,66].

The average output of the RON (Research Octane Number) and liquid products density of liquid fractions results on Zn-HZSM-5 and Ni-HZSM-5 catalysts in conversion of the butanes /butylenes, $C_4/C_4^=$ technical fraction are presented in table 2 and 3.

The liquid fraction resulted on Zn-HZSM-5 and Ni-HZSM-5 catalysts can be used as a blending mixture for the octane number enhancing of gasoline because the RON is over 98, or as raw materials for the production of petro-chemicals and chemical intermediates, especially of the liquid fraction obtained over the Zn-HZSM-5 catalyst.

Conclusions

Bifunctional catalysts, Zn-HZSM-5 and Ni-HZSM-5, exhibit high selectivity to aromatics BTX (especially Zn-HZSM-5) in the aromatization process of butanes-butenes mixture, due to dehydrogenation of alkanes to alkenes and dehydrocyclization of alkenic oligomers to naphthenic intermediates on exchanged Zn^{2+} and Ni^{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 55 wt.% during the first 32 hours' time on stream on Ni-HZSM-5, and more than 75 wt.% during the same time interval on stream on Zn-HZSM-5. The significant production of aromatics is explained by the enhanced production of alkenes by the effective dehydrogenating action of zinc and nickel on alkanes and naphtenes intermediates.

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

The presence of butenes in the butanes feed exercises the activation of butanes: it is thought that butenes are the result of the protonation to carbenium ions from a Bronsted acid site and then activate butanes through hydride abstraction.

The catalytic activity of HZSM-5 catalyst in the aromatization process of butenes / butenes technical fraction can greatly be improved by the introduction of Zn^{2+} and or Ni^{2+} cations by ion exchange.

Zinc and nickel species affect the Brönsted acidity of the zeolite; the supplementary Lewis sites associated with the extra-framework of zinc and /or nickel species are provided, sites that are able to subtract hydride from the adsorbed hydrocarbons molecules and catalyze the formation of hydrogen gas.

The role of Zn is most favorably attributed to the removal of hydrogen atoms from the zeolite surface through a *reverse hydrogen spillover* effect where Zn acts as active site for the recombination of hydrogen atoms to hydrogen molecules, in order to be desorbed to gas phase.

The acidic sites of zeolite would catalyze the oligomerization of light alkanes and the cyclization of C_6-C_8 alkenes or dienes.

In the presence of Zn^{2+} and Ni^{2+} cations, the aromatization of butanes /butenes technical mixture is changed from the cracking and the subsequent aromatization mechanism to the direct aromatization by dehydrogenation pathway.

The loss of catalytic activity of Zn-HZSM-5 and Ni-HZSM-5 catalysts with the reaction progress is a result of decreasing for the number of active sites upon coke deposition.

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

Small selectivity for BTX aromatics of Ni-HZSM-5 (compare with Zn-HZSM-5 catalyst in conversion of butanes-butenes technical mixtures is very probably because Zn^{2+} cations catalyze recombinative desorption steps more effectively than Ni^{2+} cations

Zinc and Ni species working synergistically with the Brönsted 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 cyclonaphtenes C_6 -C_{10} to aromatics C_6- C_{10} and Bronsted 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 naphtenes C_6 - C_{10}.

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