

Transformation of Gaseous Technical Mixture of the Alkanes and Alkenes Into Liquid Fraction Over Ni-HZSM-5 Obtained by Ionic Exchange

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Paraffin's and olefins in the cracked naphtha can be transformed into aromatics and iso-paraffins to reduce the olefins content as well to improve the octane number of the gasoline commercial fraction. In this work Ni-HZSM-5 bifunctional catalyst was prepared by ion exchange with Ni(NO₃)₂ aqueous solution. The activity of Ni-HZSM-5 (wt.% 1.34% Ni) catalyst prepared by ion exchange method was investigated in the conversion of light hydrocarbons resulted as by-products of petroleum refining process (mixtures of butenes and (normal + iso) butanes as main components). The obtained Ni-based catalyst has been compare with HZSM-catalyst. The conversion experiments have been performed in a fixed-bed stainless-steel reactor (Twin Reactor System Naky) at 450°C, under 4 atm. (over Ni-HZSM-5) and 8 atm. pressure (over HZSM-5), respectively and at a space velocity (WHSV) of 1h⁻¹. The catalytic activity of (Ni-HZSM-5 catalyst) monitored over 10 catalytic tests (with regeneration of catalyst after each test) using a mixtures butanes-butlenes. The catalytic activity and selectivity towards liquid products - BTX aromatic hydrocarbons and oligo(iC₅-iC₁₀, nC₅-nC₁₀ > C₁₀) - depends on time streaming, composition of butanes-butlenes mixture and pressure. In the first hours of each test the aromatic BTX are the main component of the liquid product (connected with butlenes consume) and after that, the oligo fraction become predominant. The initial aromatization process described as dehydrocyclodimerization of alkanes and alkenes, principally to aromatics BTX and molecular hydrogen, is accompanied by oligomerization, isomerization, cracking and alkylation processes to form finally in the liquid phase product an excessively mixture of iso- and normal - C₅-C₁₀ and > C₁₀ aliphatic hydrocarbons

Keywords: light hydrocarbons, aromatization, dehydrocyclodimerization, HZSM-5, Ni-HZSM-5

Zeolites are widely used in many industrial processes. A large number of ways have been developed to chemically modify these materials of which the incorporation of metal species is the most common one. If a bifunctional metal zeolite material is expected to display desired catalytic properties, its acid sites should be close to the metal sites and the metal sites should be well dispersed thought the zeolite.

Light (-C₂-C₅) alkanes are contained in non-associated natural gas (as compressed natural gas) as well as in associated gas (as petroleum casing-head gas). A considerable amount of C₂-C₄ hydrocarbons (alkanes and alkenes) results from petroleum refining processes, especially from destructive technological processes such as fluid 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 conversion of light alkanes into aromatics is an important catalytic reaction from both industrial and academic points of view.

Indeed light alkanes aromatization leads to the formation of the higher value aromatic hydrocarbons (mainly benzene, toluene and xylenes, BTX) which are valuable intermediates in the chemical and petrochemical industries. This reaction is a highly complex reaction which involves transformation of various hydrocarbons following different reaction steps.

The aromatization of light hydrocarbons over ZSM-5 catalysts can be explained on the bas of a three stage process as below [2-7]:

- Transformation of alkanes into alkenes;
- Interconversion of alkenes into higher alkenes;
- Aromatization of alkenes.

Outstanding aromatization performance have been observed over the HZSM-5 zeolite with the incorporation of some metal species such Pt [8-13], Ga [1, 2, 12, 14-30], Zn [2, 3, 5, 7-17, 20-62]. Ni-HZSM-5 and Ag-HZSM-5 are also active in aromatization process of light hydrocarbons [20, 56, 63-67].

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. Already few commercial processes have been announced based on: HZSM-5 (M2 Forming Process - Mobil Oil [68, 69] and M-Forming Process - Mobil) [70]; Ga/HZSM-5 (Cyclar-BP/UOP [71, 72] and Z-Forming from Mitsubishi Oil and Chiyoda [73]; Zn/HZSM-5 (Alpha process of Asahi Chemical and Petrochemical) [74]; Pt/K(Ba)L (AromaxTM process - Chevron - Phillips Chemical Co. [75]; RZ - Platforming process - UOP [76, 77]; Aroforming from IFP, Salutec based on metal oxides-HZSM-5 [78, 79].

This paper studies the activity and the selectivity of HZSM-5 and HZSM-5 modified with Ni in the conversion of technical fraction C₄/C₄⁼ to liquid fraction rich in C₆-C₈ aromatic hydrocarbons.

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Experimental part

NaZSM-5 zeolite synthesis

NaZSM-5 zeolite ($\text{Si}/\text{Al} = 36.02$; 2.65 wt.% Na_2O), was synthesized in our laboratory by hydrothermal crystallization 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 $\text{kg}\cdot\text{dm}^{-3}$), 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 $\text{kg}\cdot\text{dm}^{-3}$), ethylene glycol (1.1132 $\text{kg}\cdot\text{dm}^{-3}$) 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 chemicals are Romanian technical products and were used as received [80]. The gel was allowed to crystallize in stainless steel autoclave at $180 \pm 5^\circ\text{C}$ for 24h with stirring. The product was then filtered, washed, and dried at 110°C for 6h and calcined at 550°C in air for 6h. The purity and crystallinity of Na-ZSM5 was checked by X-ray diffraction.

Catalysts preparation

The HZSM-5 form was obtained by a triple ion - exchange process with 1M NH_4NO_3 at 80°C for 6h, followed by calcinations in air at 550°C for 6h. Further, zeolite HZSM-5 was converted to Ni-HZSM-5 as well by the triple of ion exchanges process with 0.1 M $\text{Ni}(\text{NO}_3)_2$ aqueous solution (solid:solution = 1 g:5 mL), under stirring conditions at 80°C for 6h each time. The Ni-HZSM-5 sample was filtered, washed, dried at 110°C for 6h and calcined at 450°C in air for 6h. The contained amount of Ni in the sample is 1.34%. The HZSM-5 and Ni-HZSM-5 powders with $\gamma\text{-Al}_2\text{O}_3$ (20%wt.) 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.

Characterization

The type of structure, phase purity and degree of crystallinity for the prepared samples were determined by X-ray powder diffraction on a Philips PW 1830 diffractometer using Ni filtered Cu K radiation at a scanning speed of $0.02^\circ\cdot\text{s}^{-1}$ in the range of $8\text{-}45^\circ$, 2θ . XRD powder pattern of the Na-ZSM-5 sample exhibit only diffraction lines proper to MFI structure high crystallinity. The pattern confirms that the synthesized zeolite has the structure identical to MFI-type zeolite [81-86]. 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 is presented in literature [83-86] revealing the well-defined morphology of crystals indicating highly crystalline material.

The acidity and strength distribution on HZSM-5 and Ni-HZSM-5 were measured using Temperature Programmed Desorption (TPD) technique using ammonia. A known weight of the sample was activated in a dry N_2 flow at 500°C for 4h then cooled to 80°C when ammonia was added. The of ammonia amount desorbed from 100°C to desorbed 800°C (at a heating rate of $10^\circ\text{C}/\text{min}$) was quantitatively monitored by absorption in 1M HCl. The ammonia represents the total acidity (weak and strong) of the sample. The TPD ammonia desorption presents two peaks (not shown here), one at low temperature (LT) and one at high temperature (HT) (table 1). Temperature peak correspond to higher acid strength and is due to ammonia bound to strong structural Bronsted sites ($\text{Si}-\text{O}-\text{Al}$ bridging OH), and possible to strong Lewis sites ($\equiv\text{Al}$ and $\equiv\text{Si}^+$). Low temperature peak correspond to less acidic sites (terminal OH groups, cationic sites M^{z+} , AlO^+). The temperature and the amount of desorbed ammonia give

Table 1
PHYSICO-CHEMICAL CHARACTERISTICS OF THE STUDIED CATALYSTS

Sample	BET surface area, m^2g^{-1}	Acidity, mmol. NH_3/g		Total acidity
		low-peak LT 180°C $80\text{-}300^\circ\text{C}$	high-peak HT 450°C $300\text{-}600^\circ\text{C}$	
HZSM-5	296	0.618	0.282	0.900
Ni-HZSM-5	279	0.669	0.130	0.799

information about strength and number of the acid sites [42, 3, 55, 58, 62, 83-86].

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.

The values of the BET specific surface area and acidity of the HZSM-5 and Ni-HZSM-5 catalysts are presented in table 1.

The BET surface area of the support HZSM-5 is $296.0 \text{ m}^2/\text{g}$ and the area of the Ni-HZSM-5 is $279.0 \text{ m}^2/\text{g}$, the small decrease in surface area after nickel loading may be due to the channel occupation of a small amount of nickel.

The observed enhancement of middle and lower acid sites in the Ni-HZSM-5 catalysts is probably the results of the Lewis acid sites created by nickel. It also found that the strong acid sites (Bronsted probably) decreased that on HZSM-5.

Catalytic performance

The catalytic activity of HZSM-5 and Ni-HZSM-5 for C_4 - C_4 = technical fraction conversion at 450°C and 8 atm. (HZSM-5), and at 4atm. (over Ni-HZSM-5) with WHSV 1 h^{-1} , to aromatics BTX, 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 the 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 [87, 88] and flame ionization detector (FID) for liquid phase and a column (6 m length) with squalane and dimethylsulpholane and a thermal conductivity detector (TCD) for gaseous phase, respectively.

Results and discussions

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

Conversion of mixed butanes-butenes to aromatics over HZSM-5 takes place with low selectivity to BTX, the reactants forming predominantly the cracking products. The operating conditions (temperature 450°C , WHSV 1 h^{-1} and pressure 8 atm.) were in advance selected to obtain the high yield of liquid product during the catalytic tests [25].

The change in the gaseous and liquid products distribution over HZSM-5 with time on-stream (TOS) in the conversion of butanes and butenes are presented in figure 1.

The concentration of butanes ($n\text{-}i\text{-C}_4$) decreased from 56.53 vol.% to 9.16 vol.% in the first 4h of reaction, after that is continuously increasing going beyond the feedstock after 16h. The concentration of butenes ($1\text{-C}_4 =$, $trans\text{-}2\text{-C}_4 =$

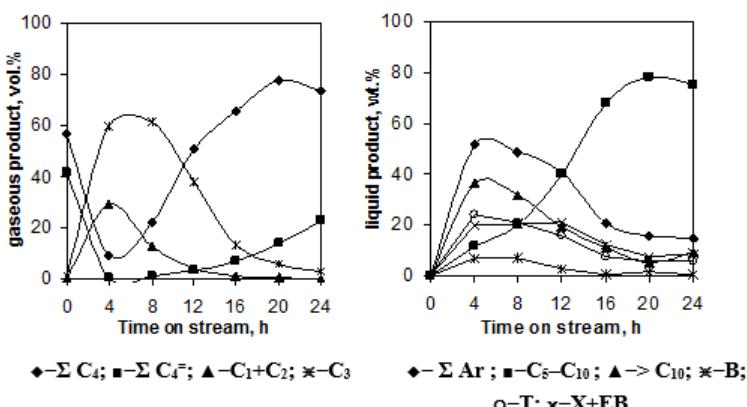


Fig. 1. Gaseous phase composition and liquid phase composition vs. time on stream over HZSM-5 catalyst in butane-butenes conversion; Test No. 3 [25]

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 formation of methane and ethane (C₁ + C₂) reach the maximum value (29.50%) after 4h of reaction while the formation of propane (C₃) occurs after 8h (61.68 vol.%); their production is connected to aromatic hydrocarbons formation. The molecular hydrogen was not detected in the gaseous phase [25].

The catalytic activity and selectivity to aromatic hydrocarbons is maximum for the first 8h run; after that aliphatic C₅-C₁₀ are progressively formed.

HZSM-5 sample was involved in five catalytic tests, after each test; the catalyst being regenerated at 475°C for 8h under nitrogen with 2% oxygen flow [25].

The average output of aromatics BTX over HZSM-5 monofunctional catalyst do not go beyond 35 wt.% in the liquid phase (expectedly catalytic Test No. 3) and the formation of xylenes and toluene is prefer (fig. 2).

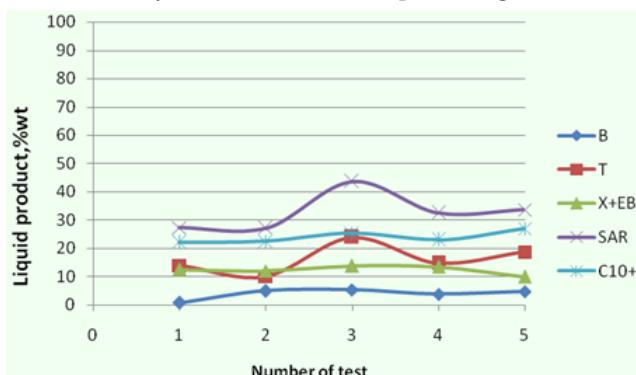


Fig. 2. The aromatics BTX and C10+ fraction average output over HZSM-5 catalyst (450°C, 8 atm., WHSV = 1h⁻¹); (SAR- Aromatics Sum)

It is well known that the surface acidity of the catalyst has decisive effect on its activity. The acidity is influenced by the type of the acid sites, such as the Bronsted (protic acid sites) and Lewis (aprotic acid sites) sites as well as the number and the strength of the acid sites.

Monofunctional HZSM-5 catalyst exhibits preferentially high cracking, isomerization and β -scission reactivity that lead to loss of carbon atoms to undesirable products. Hydrogen rejection from surface occurs by hydrogen transfer to alkanes which limits to aromatic yield that can be obtained on HZSM-5. Formation of aromatic hydrocarbons on HZSM-5 catalyst involving Bronsted-acid centers as active sites. Aromatic molecules were formed from alkenes oligomers by successive deprotonation and hydride transfer to carbenium ions. With this mechanism, the formation of one molecule of aromatic hydrocarbons inevitably accompanies the formation of three molecules of alkanes.

Catalytic performance of Ni-HZSM-5 catalyst in C₄-C₄= hydrocarbons conversion

Aromatization of a mixture containing butanes and butenes over Ni-HZSM-5 takes place with good selectivity to aromatics BTX and with production of molecular hydrogen. The operating conditions (temperature 450°C, WHSV 1 h⁻¹ and 4 atm. pressures) were in advance selected to obtain the high yield of liquid product during the catalytic tests.

Ni-HZSM-5 sample was involved in ten catalytic tests, after each test, the catalyst being regenerated at 475°C for 8h under nitrogen flow containing 2% oxygen.

The changes in the gaseous product distribution over Ni-HZSM-5 with time on-stream (from four to four hours), Test No. 1 and Test No. 10, are shown in figures 3 and 4. The concentration of butenes decreased from ~ 47.237 vol.% to 0.133 vol.% (Test No. 1) respectively from ~ 35.79 vol.% to 0.422 vol.% (test No. 10) after first 4h of reaction and remains at values smaller than 2.0% only after 16h. The concentration of butanes (n+i) decreased from 49.66 vol.% to 15.23 vol.% after 4h of reaction (Test No. 1), respectively from 56.64 vol.% to 11.82 vol.% in firstly 16h, after that is continuously increasing. The hydrogen molecular concentration do not exceeds 12.0 vol.% in all catalytic tests. The thermal treatments and the partial removal of coke deposited can be the reason for this diminution but the Ni is still present in the catalyst. The main gaseous hydrocarbon over Ni-HZSM-5 is propane (over 60 vol.%), in first 40 h of reaction in all catalytic test.

The aromatic hydrocarbon distributions in the liquid phase corresponding to catalytic test on Ni-HZSM-5 catalyst are plotted in figure 5 and 6.

As observed, the mainly resulted aromatic hydrocarbons were toluene (~24.0 wt.%) and xylenes (~22.0 wt.%), while benzene was about 3.5 wt% (the middle value per tests). BTX aromatic hydrocarbons are major components

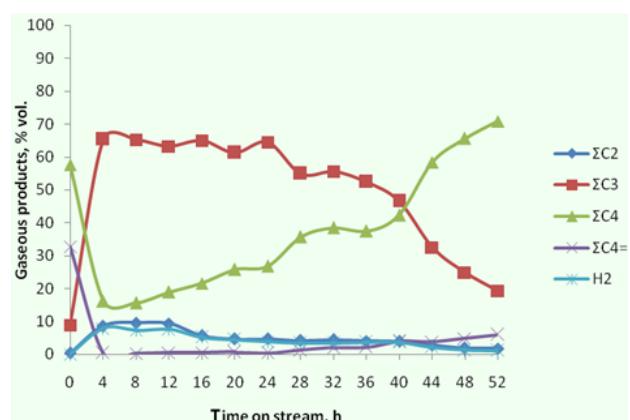


Fig. 3. Gaseous phase composition vs. time on stream over Ni-HZSM-5 catalyst, catalytic Test No.1

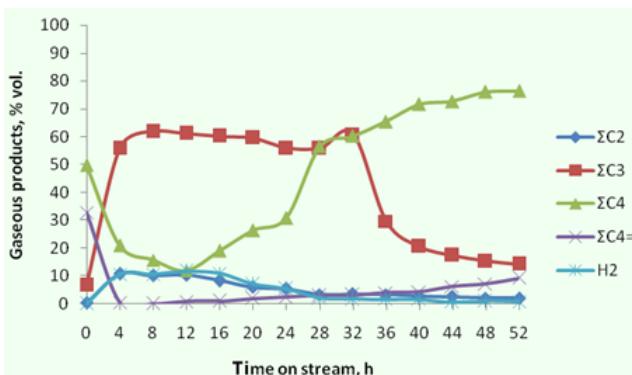


Fig. 4. Gaseous phase composition vs. time on stream over Ni-HZSM-5 catalyst, catalytic Test No.10

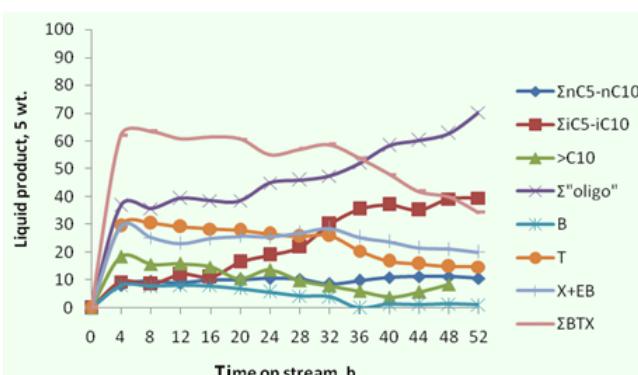


Fig. 5. Liquid composition vs. time on stream over Ni-HZSM-5 catalyst; catalytic Test No. 1

only in first ~ 30h after *your concentration in liquid fraction decrease below 50 wt.%*. The aliphatic hydrocarbons C_5 - C_{10} (normal-alkanes + iso-alkanes) and aliphatic hydrocarbons with more than 10 carbon atoms ($>C_{10}$) (denoted *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.

In figure 7 is presented the average output of aromatics BTX during ten catalytic experiments over Ni-HZSM-5. The average output of aromatic hydrocarbons BTX over Ni-HZSM-5 bifunctional catalyst represent more than 50 wt% in the liquid phase only in three catalytic tests.

In the liquid product resulted on Ni-HZSM-5 the *oligo* fraction which contains mostly alkanes and alkenes in the iso- series together with aromatic hydrocarbons are predominant.

Ni-HZSM-5 catalyzes 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 aromatics hydrocarbons via oligomerization, cracking and isomerization reactions and alkenes hydrogenate to form 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+} cations provide an alternative pathways for the removal of hydrogen atoms in adsorbed

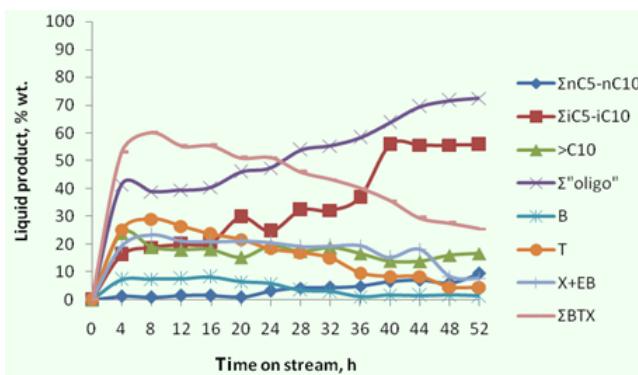


Fig. 6. Liquid composition vs. time on stream over Ni-HZSM-5 catalyst; catalytic Test No. 10

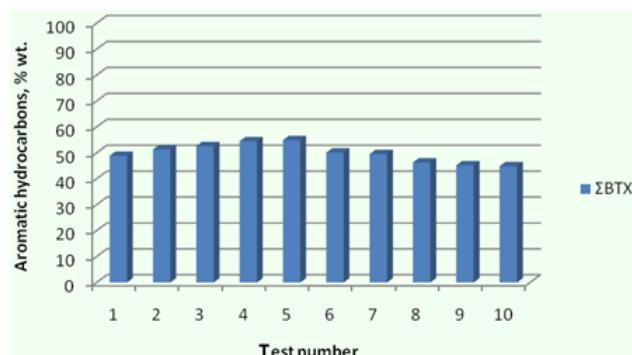
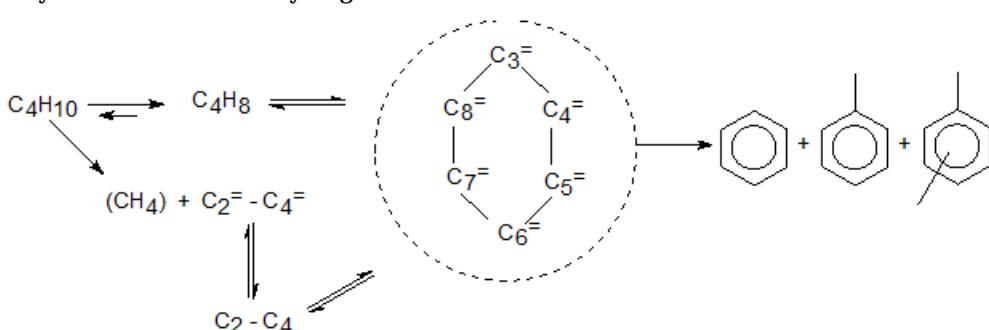


Fig. 7. The aromatics average output over Ni-HZSM-5 catalyst (450°C, 4.atm. pressure, WHSV = 1 h⁻¹)

intermediates as H_2 , Ni^{2+} cations increase the reversibility of hydrogen adsorption-desorption steps. As in the case of zinc and gallium exchanged HZSM-5 zeolites these reactions appear to proceed via bifunctional pathways involving acid OH groups and exchanged metals 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 it has been shown previously also for Zn^{2+} cations [46, 62]. This desorption step is not quasiequilibrated during alkanes reactions on any 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 [25, 26, 43, 46, 53, 54, 60, 62, 82-86].

Butanes-butlenes mixture conversion over HZSM-5 and Ni-HZSM-5 occurs via a complex sequence of cracking, dehydrogenation, oligomerization, isomerization, cyclization, β -scission and H transfer (scheme 1).



Scheme 1

On Ni-HZSM-5 catalyst, butane reaction pathways include primary dehydrogenation steps that form C_4H_8 and $C_2 = C_4$. Secondary products include C_2-C_4 alkanes, and C_6-C_8 aromatic hydrocarbons. Aromatics form via dehydrocyclization reaction of C_6-C_8 alkenes, which form and participate in rapid acid-catalyzed oligomerization-cracking cycles as previously reported on HZSM-5, Zn-HZSM-5 and Ga-HZSM-5 [25, 43, 54, 85, 86].

On HZSM-5 catalyst alkanes (butanes) undergoes initial dehydrogenation to form alkenes (butenes) and hydrogen or cracking to form (CH_4) and $C_2 = C_4$. Alkenes can enter oligomerization cracking cycles where C-C bonds are broken and reformed several times before a stable aromatic molecules via cyclization and dehydrogenation steps. Products exit this cycle either via dehydrogenation steps to forms aromatic hydrocarbons (BTX) and H_2 as via dehydrogenation or cracking steps to form alkanes.

Ni^{2+} cations catalyze the recombinative desorption of hydrogen as H_2 , by providing alternate pathways for kinetically relevant H_2 removal steps. As results Ni^{2+} increase alkanes turnover rates and the rate of formation of dehydrogenated product. This role of Ni^{2+} cations is similar to those ascribed to Zn and Ga in these reactions [25, 43, 54, 85, 86].

Conclusions

Bifunctional catalyst Ni-HZSM-5 exhibits a good selectivity to aromatics BTX in the aromatization process of butanes - butenes mixture (in first ~ 36-40 h), due to dehydrogenation of alkanes to alkenes and dehydrocyclization of alkenic oligomers to naphthenic intermediates on exchanged 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 ~50 wt% only a three tests, and the formation of toluene (~24 wt%) and xylenes (~22 wt%) are prefer. The production of aromatics is explained by the enhanced production of alkenes by the effective dehydrogenating action of nickel on alkanes.

Small selectivity for BTX aromatics of Ni-HZSM-5 compare to Zn-HZSM-5 (nitrate) catalyst in conversion of butanes-butenes technical mixtures is very probably because the hydrogenation reaction of alkenic intermediates to alkanes $C_2 - C_4$ (C_3 hydrocarbons is main component in gaseous fraction of reaction) is faster on Ni-HZSM-5.

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. On the HZSM-5 surface 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 Ni-HZSM-5 catalysts is changing with time on-stream.

The presence of butenes in feed exercise an activation of butanes: it is thought that butenes are protonated forming to carbenium ions from Bronsted acid sites and then activate butanes through hydride abstraction.

The production of hydrogen increased slowly after introduction of Ni^{2+} cations to HZSM-5, indicating that these cations serve as dehydrogenation catalysts.

Ni-HZSM-5 sample exhibits lower $C_4 - C_4$ technical fraction conversion rates and aromatics formation rates

than Zn-HZSM-5 sample very probably because Zn^{2+} cations catalyze recombinative desorption steps more effectively than Ni^{2+} cations.

The catalytic oligo-aromatization reactions over Ni-HZSM-5 catalyst can upgrade the low-value light hydrocarbon byproduct streams from refinery and cracker operations, producing aromatics BTX as octanic components for commercial gasoline (and hydrogen as co-product).

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