Conversion of Butane-Butylene Mixtures over B(Al)-HZSM-5 Catalyst Prepared by Impregnation Technique

IULIAN V. ASAFTEI, NICOLAE BILBA, ION SANDU*, GHEORGHE IOFCEA
1 "Al. I. Cuza" University of Iasi, Faculty of Chemistry, Laboratory of Materials Chemistry, 11 Carol I Blv, 700506, Iasi, Romania
2 ARHEOINVEST Interdisciplinary Platform, "Al. I. Cuza" University of Iasi, 22 Carol I Blv, 700506, Iasi, Romania
3 S.C."Oltplast" S.A., Onesti, Romania

This paper presents the results of the conversion of light hydrocarbons (mixtures of butanes/butylenes with variable composition) resulted as by-products of the petroleum refining (FCC) over bifunctional B(Al)-HZSM-5 catalyst prepared by impregnation of HZSM-5 zeolite with boric acid. The catalyst was characterized using XRD, SEM, EDX and NH3-TPD for their structure, morphology and acidity. The catalytic activity of the same catalyst was examined during 17 catalytic tests (with regeneration of catalyst after each test) using mixtures of butanes-butenyes. The catalytic tests were carried out in a continuous fixed bed flow stainless-steel reactor (Twin Reactor System Naky) fed at a WHSV = 1 h⁻¹ at a temperature of 450°C and a pressure of 8 atm (tests no. 1-11) and 4 atm (tests no. 12-17), respectively. Catalytic activity and selectivity towards liquid products - BTX aromatic hydrocarbons and “oligo” (iC₅-iC₁₀, nC₅-nC₁₀, >C₁₀) - depend on time on stream, composition of butanes-butenyes mixture and pressure. In the first hours of each test the aromatic BTX are the main component of the liquid product (connected with butylenes consume) and after that, the “oligo” fraction become predominant. The yield of liquid product, density and Motor Octanic Number alter between 18.60 wt% - 37.9 wt%, 0.760 – 0.852 g/cm³ and 97 – 109, respectively. The yield of liquid product (>30 wt %) and MON higher than 100 was obtained working at 4 atm pressure.

Keywords: conversion, light hydrocarbons, higher hydrocarbons, boron, HZSM-5

The selective conversion of light hydrocarbons C₂-C₄ (alkanes and alkenes) into more valuable aromatic-rich liquid hydrocarbons (BTX) and H₂ by direct catalytic nonoxidative route is until now an area of academic interest and of great industrial relevance.

The activation of light alkanes and alkenes is achieved by using high temperatures (≥ 450°C) and catalysts with acidic sites (monofunctional catalysts) or with acidic and dehydrogenating metal sites (bifunctional catalysts). The catalysts used in aromatization of light hydrocarbons C₂-C₄ are on the basis of zeolites with medium pores (10-ring aperture), especially ZSM-5 (MFI) in hydrogen form or with large pores (12-ring aperture), especially LTL in K or Ba form modified with Pt or Zn [1-12].

The conversion of light hydrocarbons C₂-C₄ into aromatic hydrocarbons (BTX) over H-ZSM-5 [1, 3, f3-15], Ga-HZSM-5 [1-12, 16-33] and Zn-HZSM-5 [3-7, 12, 15, 34-43] has been studied in detail and industrially applied [9, 44-49]. Processes such as Cyclar, have been used for the conversion of light alkanes into aromatic compounds, mainly BTX.

The aromatization reaction of light hydrocarbons C₂-C₄ includes the successive steps [8, 18]:
- dehydrogenation of alkanes to alkenes and hydrogen (by cracking and by hydrogen transfer – dehydrogenation);
- oligomerization of the alkenes to increase the hydrocarbon chain length up to six carbon atoms and higher;
- cyclization of oligomers to napthenes;
- dehydrogenation of napthenes into corresponding aromatics.

In the case of Metal-HZSM-5 catalysts, the metal species catalyse the dehydrogenation of the alkanes and of the napthenic intermediates and the acid sites (Brønsted and Lewis) catalyse the oligomerization of alkenes to diene, triene and the cyclization of the oligomers to napthenes.

Side reactions such as catalytic cracking (C-C bond) over strong acid sites (Brønsted acid sites), hydroisomerization in presence of excess hydrogen, alkylisation, isomerization, disproportionation and hydrogenolysis also occur with various yields over monofunctional and bifunctional catalysts.

The alkanes adsorbed on zeolite surface are protonated by Brønsted acid sites with formation of carbonium ions (five-coordinated carbon atom) and alkenes adsorbed with formation of carbenium ions (tri-coordinated carbon atom). The carbonium ions may undergo cracking (C-C bond breaking) to yield a lower alkane (C₄, C₃) and alkene or to dehydrogenation (C-H bond breaking) to yield molecular hydrogen and an alkoxide specie which is desorbed as alkene corresponding to alkane or may take part in hydride transfer between alkane molecule with formation of an lower alkane and a new alkoxide which can participate to isomerization and/or β-scission.

The carbenium ions adsorbed on the surface of zeolite may add a new alkene molecule existing in the feedstock and resulted from alkane cracking and dehydrogenation with formation of a large new carbenium ion which by loosing the proton (H⁺) to zeolite form a dimmer. Strong Brønsted acid sites (proton donating) generated by tetrahedrally coordinated Al atoms forming =Al-O(H)-Si= bridges are responsible for substantial cracking instead of aromatization and for the hydrogen transfer to alkenes with yielding of new alkanes. At temperatures above 500°C the Brønsted acid sites are converted (by dehydroxylation and by dealumination) in Lewis acid sites (electron donating...
rearrangement of cyclohexanone, oxime to isomerization of linear alkenes, the Beckmann boronaluminosilicate is enough to catalyze the double-bond sites. The lower acid strength of boralite and results in the formation of weak Brönsted and Lewis acid.

5 prepared by impregnation of HZSM-5 with boric acid at ethanol alkylation [65-69].

methanol to hydrocarbons, methane conversion, toluene-lactame, hexane cracking, ethylbenzene dealkylation, 80oC for 10 h and then pretreated at 400 oC for the heated in presence of a vapour mixture of EDA, Et3N and

amorphous hydrogel with molar ratio SiO2/Al2O3 = 58.92, aluminum sulphate, ethylene glycol (EG), sulphuric acid, pressure from a mixture containing sodium silicate, crystallization at 180±5 oC for 24 h under autogeneous

Synthesis of NaZSM-5

Catalyst preparation

Experimental part

In this paper the catalytic properties of the B(Al)-HZSM-5 were investigated.

Zeolite modification

The incorporation of boron into the ZSM-5 structure results in the formation of weak Brönsted and Lewis acid sites. The lower acid strength of boron and boronolaminosilicate is enough to catalyze the double-bond isomerization of linear alkenes, the Beckmann rearrangement of cyclohexanone, oxime to ε-caprolactame, hexane cracking, ethylene glycol dehydration, methanol to hydrocarbons, methane conversion, toluene-acetamide, 80oC for 10 h and then pretreated at 400 oC for the transformation of gaseous butanes-butylenes hydrocarbons to liquid hydrocarbons (liquid fuels) were investigated.

Table 1

<table>
<thead>
<tr>
<th>Components</th>
<th>Test number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butanes: ΣC4</td>
<td>51.89</td>
<td>56.53</td>
<td>52.21</td>
<td>54.95</td>
<td>60.74</td>
<td>60.74</td>
<td>60.74</td>
<td>39.92</td>
<td>38.49</td>
<td>31.30</td>
</tr>
<tr>
<td>Butenes: ΣC5</td>
<td>39.05</td>
<td>42.19</td>
<td>46.40</td>
<td>40.44</td>
<td>38.20</td>
<td>59.37</td>
<td>59.91</td>
<td>67.77</td>
<td>53.13</td>
<td>8.10</td>
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<tr>
<td>C3-C5</td>
<td>1.00</td>
<td>1.20</td>
<td>1.30</td>
<td>4.12</td>
<td>0.92</td>
<td>0.50</td>
<td>1.30</td>
<td>0.72</td>
<td>8.10</td>
<td></td>
</tr>
</tbody>
</table>

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No. 10

resulted from gas fractionation

components of feedstock

unit of a FCC unit

Table 1

| Components | Test number | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |
|------------|-------------|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Butanes: ΣC4 | 48.45 | 35.35 | 38.82 | 51.63 | 62.44 | 62.45 | 57.45 | 94.31 |
| Butenes: ΣC5 | 43.13 | 62.68 | 60.70 | 42.85 | 37.20 | 37.19 | 32.25 | 5.20 |
| C3-C5 | 8.12 | 1.75 | 0.32 | 5.3 | 0.22 | 0.21 | 10.10 | 0.28 |

ΣC4 = n-C4 + i-C4; ΣC5 = 1-C5 + isom-C5 + cis-2-C5 + trans-2-C5
Catalytic tests

Performances of the B(Al)-HZSM-5 catalyst for butanes-butylenes mixtures conversion were established at 450°C in a fixed bed continuous flow stainless-steel reactor (Twin Reactor System Naky, Metrimpex) at 8 and 4 atm total pressure, respectively and at a weight hourly space velocity (WHSV) of 1 h⁻¹. Control of temperature, pressure, as well as gaseous feed (60 g butanes-butylenes / h) was done through automatic devices. The reaction products were separated into gaseous and liquid fractions through an ice-trap. The feeding raw material having the composition given in table 1 for the 17 catalytic tests and the gases resulted from catalytic test were analyzed using a Carlo Erba G.C. (Model C, TCD) equipped with a 6 m column filled with squalane and dimethylsulfolane on Chromosorb P. The collected liquid corresponding to each catalytic test was analyzed with a Carlo Erba Vega G.C. (FID) equipped with a 25 m capillary column filled with SE-52 stationary phase.

Results and discussions
Structure, morphology and specific surface area

Figure 1 shows the XRD patterns of parent NaZSM-5 sample after calcinations and of B(Al)-HZSM-5 composite after the heat treatment. The pattern confirms that the synthesized zeolite has the structure identical to MFI-type zeolite [72]. The parent NaZSM-5 has a high crystallinity derived from the high intensities of the XRD reflections in the range of 22.5°–25° (2θ). No other diffraction lines were found in the XRD pattern. The XRD pattern of B(Al)-HZSM-5 composite obtained at 400°C shows that the structure of host ZSM-5 was retained and in addition exhibit reflection at 14.61 and 28.10 (2θ) which are characteristic for the B₂O₃ crystalline particles that cover the external and internal surface of HZSM-5 zeolite. The intensities of these peaks decreased until disappearance during the thermal activation at 400°C for 6 h and after the catalytic tests indicating a host-guest interaction and an isomorphic substitution of tetrahedral aluminium with tetrahedral boron.

After 6 h of calcinations at 400°C no more B₂O₃ crystals exist in the B(Al)-HZSM-5 sample. This change might be interpreted by the dispersion of B₂O₃ as a monolayer into the channels of HZSM-5 matrix [73].

Figure 2 presents the SEM images of parent NaZSM-5 and of HZSM-5 and the elemental composition by EDX spectra. It reveals the well-defined morphology of crystals.
indicating highly crystalline material. The EDX spectrum of HZSM-5 zeolite proves the absence of Na+ ions after the ammonium exchange of NaZSM-5 zeolite.

The chemical oxidic composition of the calcined NaZSM-5 sample corresponds to values: 92.70 wt% SiO2, 4.54 wt% Al2O3 and 2.76 wt% Na2O; SiO2/Al2O3 = 34.65, Na2O/Al2O3 = 1.001.

The BET surface area of NaZSM-5, HZSM-5 and B(Al)-HZSM-5 samples were 316.2 m²/g, 296 m²/g and 286 m²/g respectively. The boric acid impregnation of HZSM-5 zeolite may narrow the pore openings and plug the channels, so the specific surface area is decreased.

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

The acid properties of the catalysts determined by means of ammonia temperature programmed desorption (TPD) measurements are presented in table 2. HZSM-5 modified by impregnation with boric acid and pretreated at high temperature (400°C) (B(Al)-HZSM-5 catalyst) contain nonskeletal boron (B2O3) and skeletal tetrahedral and trigonal boron (≡Si-O(H)B≡) as a result of partially dealumination of ZSM-5 matrix [68]. The hydroxyl groups associated with skeletal B3+ led to weak Bronsted acid sites and in consequence different catalytic properties in comparison with the parent HZSM-5 catalyst.

Performance of B(Al)-HZSM-5 catalyst in conversion of C4=C5 mixtures

The catalyst was activated before runs by heating in reactor at 450°C with N2 for 6 h.

B(Al)-HZSM-5 catalyst was evaluated in 17 consecutive tests with intermediary regeneration at 450°C for 8 h with N2 + 2 wt% O2. The commercial feedstock composition utilized in each test is specified in table 1.

The operating conditions (temperature 450°C, WHSV 1 h⁻¹ and pressure 8 atm (1 – 11 tests) and 4 atm (12-17 tests) were in advance selected to obtain the high yield of liquid product during the catalytic test.

The changes in the composition of gaseous phase with time on-stream (TOS) resulted over B(Al)-HZSM-5 catalyst are presented in figure 3 only for the test no.1 at 8 atm and the test no.12 at 4 atm.

The feedstock in catalytic test no.1 contains more butanes (51.89 vol.%) and in test no.2 more butylenes (60.70 vol.%). During the first 4 h time on-stream the butylenes are completely consumed, after that their concentration is increasing slowly up to 10 vol.% after 40 h TOS (test no.1) and after 104 h TOS (test no.12) (fig.4).

Butanes conversion is the maximum in the first 4 h TOS when the concentrations of propane-propylene and ethane-ethylene fractions are at higher level (about 60 vol.% and 28 vol.% in test no.1 and 52 vol.% and 20 vol.% in test no.12, respectively). These values are dependent on the working pressure. At 8 atm pressure the cracking reaction of butanes and hydrogen transfer are prevalent and no molecular hydrogen is present in gaseous fraction. At 4 atm pressure the dehydrogenation takes place in addition to cracking and molecular hydrogen is present in gaseous fraction.
The composition of the corresponding liquid products obtained during the tests no. 1 and no. 12 is represented in figure 5.

In accordance with the results plotted in figure 5, the liquid product contain aromatic hydrocarbons (BTX) and alkanes (i+n) C5-C10 and >C10 ("oligo").

Aromatic hydrocarbons (BTX) are major compounds in the liquid during the first 24 h TOS (54 wt.%) as a result of aromatization reactions, after that their concentration is diminished up to 10 wt.% for 44 h of reaction (test no.1, 8 atm). The yield of aromatic hydrocarbons follows the series: toluene > xylenes + ethylbenzene >> benzene.

The content of aromatic hydrocarbons is decreased quickly in the favour of oligomerization reactions with exclusive formation of iC5 - iC10 hydrocarbons (75 wt.%); nC5 - nC10 (10-17 wt.%). The content of hydrocarbons with > C10 that arise after the 4 h of reaction (36 wt.%), decreased permanent up to 3.24 wt.% at the end of the test.

For a comparison, in the figure 5 is presented the liquid composition resulted from the test no. 12 under 4 atm pressure. The aromatic hydrocarbons (BTX) are the major compounds of liquid during the first 56 h, after that their content is diminished up to 46 wt.% for 104 h TOS. The yield of BTX hydrocarbons follows the same series: toluene > xylene + ethylbenzene >> benzene. The aromatization reactions begin by the formation of small alkenes by dehydrogenation and by cracking of small alkanes (n-i C4). The formed alkenes and those existing in the feedstock undergo oligomerization and disproportionation to form mixture of higher alkenes that cyclize to napthenes which by dehydrogenation and hydrogen transfer with alkenes gives aromatics. In this case the molecular hydrogen is present in gaseous product.

The content of "oligo" fraction in the liquid product increased from 32 wt.% in the first 4 h of reaction to 64 wt.% after 104 h TOS. The iso-alkanes iC5 - iC10 are formed continuously during the reaction, their content being 12 wt.% after 4 h TOS and 50 wt.% after 104 h TOS. The content of n-alkanes nC5 - nC10 changes between 5 wt% and 12 wt.%. Hydrocarbons with more than 10 C atoms (> C10) are formed in a small quantity, 14 wt % after first 4h TOS and 3 wt.% at the end of the test.

The evidence of iC5 - iC10 aliphatic hydrocarbons formation during the catalytic tests no.1 and no.12 is represented in figure 6 and of nC5 - nC10 in figure 7.
The catalytic activity of the B(Al)-HSM-5 catalyst was maintained over the 17 tests with regeneration after each test. The modification of catalytic activity of B(Al)-HZSM-5 catalyst is connected with the coke formation. The yield of liquid, density and MON of liquid hydrocarbons during the 17 catalytic tests is presented in table 3.

The composition of the corresponding liquid products obtained during the tests no.1 and no.12 is represented in figure 5.

During the reaction, butylenes from the feedstock activate the dehydrogenation of butanes. But after 24 – 56 h TOS the butanes carry out the role of diluents and their concentration exceed the concentration of feedstock.

The weaker Brönsted acid sites in boron-HZSM-5 are attributed to the longer bond distance between the framework boron atom and the framework oxygen atom bound to the hydroxyl proton. Boron exists in the tetrahedral (B(4+)) coordination in the hydrated state and in the trigonal (B(3+)) coordination in the dehydration state [52, 74, 75]. Both kinds of boron can occur in boron-HZSM-5, depending on the hydration state and can be characterized by 11B MAS NMR and IR spectroscopy [56, 60, 62]. Boric acid impregnated HZSM-5 has different species of boron depending on the pre-treatment conditions: in the non-pretreated sample boron exist as H3BO3; in the pretreated sample at 0.1 mPa and 400 °C boron exist as a \( \equiv \text{Si}-\text{OH-Al} \equiv \) species as a result of condensation of H3BO3 with the Brönsted sites. If boron is present in excess, the most B2O3 exist as amorphous [60]. At 400 °C the dispersion of B2O3 takes place inside the pores and on the surface of HZSM-5 with formation of a monolayer of B 2O3. The presence of B2O3 changes the diffusivity of hydrocarbons by reducing the number of accessible active sites. The changes of both diffusivity and acidity enhance the shape selectivity.

Butanes-butylenes mixtures conversion over B(Al)-HZSM-5 occurs via a complex sequence of cracking, dehydrogenation, oligomerization, isomerization, cyclization, \( \beta \)-scission and H transfer (scheme 1).

**Table 3**

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Test number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield of liquid, wt%</td>
<td>1</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>0.809</td>
</tr>
<tr>
<td>MON</td>
<td>98</td>
</tr>
</tbody>
</table>

**Scheme 1**

H-ZSM-5 zeolite was wet impregnated with boric acid at 80°C and pretreated at 400°C when B2O3 species are dispersed inside the pores and on the surface as a monolayer blocking the most of the Brönsted acid sites \( \equiv \text{Si}-\text{OH-Al} \equiv \). Some quantities of H3BO3 react with the Brönsted acid sites forming \( \equiv \text{Si}-\text{O}-\text{B(OH)}_2 \) species in the framework.

Presence of boron species in HZSM-5 matrix reduce the Brönsted strong acid sites, the catalyst having much Lewis medium and low acid sites.

HZSM-5 with boron species proves useful in conversion of butanes-butylenes mixtures (commercial feedstock from FCC unit) to aromatics (BTX) and aliphatic hydrocarbons (iC5 - iC10, nC5 – nC 10, > C 10), a liquid with properties of gasoline.

The catalytic activity of B(Al)-HZSM-5 catalyst was checked up during the 17 catalytic tests with regeneration after each test. The best results were obtained at 4 atm pressure; at 8 atm the coks' formation is intensified and at atmospheric pressure the butanes are not converted at all.

Butanes are consumed during the first 4 h TOS after the content is raising. Butylenes are consumed in totality until the coks is constant. The yield of liquid product varies between 18.93 wt. % to 37.40 wt. % and the MON between 97 and 109.

**References**
