Alkylation of Benzene with Technical Fraction Propylene - Propane Over Modified B-(Al)-HZSM-5 Catalysts

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Benzene alkylation with propylene - propane technical mixture over B-(Al)-HZSM-5 zeolite, as solid acid catalyst has been studied. It was found that isopropylbenzene (IPB) formation associate with a low level of byproducts, e.g., n-propylbenzene (NPB) and di-isopropylbenzenes (DIPB) as result of the inherent multiple competing reactions. Under the specific conditions in the alkylation of benzene with propylene - propane mixture, the maxim yields of IPB (% wt.) and the IPB selectivity based on benzene reaction (wt.%) were 86, 87 and 87.0 %.

Keywords: alkylation, benzene, isopropylbenzene, B-(Al)-HZSM-5

In the last decades, the pentasil - type zeolites, containing B, Ga, Zn, Fe, Ti, etc., were found very active catalysts in many reactions: aromatization, alkylation, oxidation, etc. Ga-HZSM-5 and /or pentasil-type gallosilicates, and Zn-HZSM-5 proved to be very active catalysts for the aromatization of light hydrocarbons (alkanes and alkenes) [1-33].

The MFI-titanosilicates are industrial catalyst for the oxidation of alkenes or aromatics hydrocarbons with hydrogen peroxide as oxidant [34].

B-HZSM-5 and borosilicates MFI-type are preferred in selective production of p-disubstitute dialkylbenzenes by alkylation, isomerization and disproportionation reactions [35,36]. The Fe-MFI zeolites found their best application in the selective alkylation [37, 38].

The conventional catalysts for benzene alkylation with alkenes (C2=, C3=) are supported phosphoric acid in a fixed bed reactor with reactants in liquid phase (UOP) or Friedel-Crafts AlCl3 (Monsanto). Environment protection, process safety and avoidance of corrosion risk for replacing these catalysts by regenerable solid acids.

Benzene and toluene alkylation with olefins was effected on Y or X zeolite and mordenite [39-42]. These catalysts present good activities but short time of reaction because of catalysts deactivation by coking. The application of a Y type zeolite operating in the liquid phase, alkylation of benzene with ethylene was industrially performed and commercialized since 1989 by Lummus/Unocal/UOP [43]. The MFI zeolite is a very good catalyst for benzene alkylation (Mobil-Badger) in commercial use since 1976, and toluene alkylation with ethylene operating in gas phase [44-46]. Benzene alkylation with propylene in liquid phase was studied on, mordenite, MCM-22, ZSM-5, USY, ZSM-12 and zeolite ß [47-59].

In this work we are presenting our results on alkylation of benzene with C3/H3 technical fraction on the B-HZSM-5 catalyst.

Experimental part
Synthesis of Na-ZSM-5

The NaZSM-5 zeolite was synthesized by hydrothermal crystallization at 180±5°C for 24 h under autogenously pressure from a mixture containing sodium silicate, aluminum sulphate, ethylene glycol (EG), sulphuric acid, ammonia solution and distilled water. The procedure of synthesizing NaZSM-5 in our laboratory from the amorphous hydrogel with molar ratio SiO2/Al2O3 = 58.92, HO available/SiO2 = 0.22, Na+ total/SiO2 = 0.72, EG/SiO2 = 0.40 and H2O/SiO2 = 31.10 and pH = 11.50 is based on method described in [60]. The first synthesis of ZSM-5 zeolite using tetrpropylammonium bromide as template belongs to Argauer and Landolt [61]. The crystalline product was filtered, washed with distilled water, dried at 110°C for 6 hours and calcined at 550°C for 6 h to remove the organic material and to obtain sodium form, Na-ZSM-5.

Zeolite modification

The sodium form of the Na-ZSM-5 (SiO2/Al2O3 = 34.65) was converted into the NH4+ form by ion exchange (three consecutive times) with a solution of 1M NH4NO3 (ratio solid: liquid = 1: 5) at 80°C for 6 h under mild stirring. The solid was then filtered, washed, dried over night at 110°C and calcined in air at 550°C for 6 h when the protonic form HZSM-5 with acid properties was obtained.

By treating HZSM-5 sample with 1M solution of H3BO3 (0.09 g/g B2O3/HZSM-5) at 80°C for 10 h a nonskeletal boron-containing catalyst was prepared. The suspension was dried over night at 110°C and calcined at 400°C for 6 h when non-skeletal and skeletal boron catalyst was prepared. The solid encoded B-(Al)-HZSM-5 contain 8.26 wt% as B2O3 (2.56 wt% B).

The final catalyst was prepared by mechanically mixing the B-(Al)-HZSM-5 powders with 20 wt% γ-Al2O3 as binder and a little distilled water until a soft paste was obtained and extruded into pellets. The pellets were dried at 110°C overnight and activated in N2 at 450°C for 6 h.

Physico-chemical characterization

X-ray powder diffraction (XRD) patterns were acquired on a PANalyticalX Pert PRO MPD diffractometer using CuKα radiation (1.5406 Å), 40 kV, 30 mA in the 5° ≤ 2θ ≤ 30° angular region, with 0.0131° (2θ) step size. Nitrogen adsorption-desorption isotherms at 77 K were obtained with a Sorptionatic Carlo - Erba Series 1800 apparatus. Surface area was determined by BET method using nitrogen gas at liquid nitrogen temperature (77 K) and was calculated, taking N2 as the adsorbing gas. TGA/DTA thermograms were recorded in air on a Setaram simultaneous DTA/TG apparatus in the temperature range 30-800°C at a heating rate of 10°C/min.

In this work, we present our results on alkylation of benzene with C3/H3 technical fraction on the B-HZSM-5 catalyst.

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areas were calculated with BET equation. Scanning electron micrograph (SEM) and elemental analysis (EDX) were collected on a VEGA II LSH (TESCAN) with EDX detector tip Quantax QX2 (Bruker).

The acidity and strength distribution of H-ZSM-5 and B-(Al)-HZSM-5 were evaluated by using temperature programmed desorption (TPD) of ammonia technique. The samples were activated in a flow of dry N₂ at 500°C for 4 h and after cooling to 80°C ammonia adsorption take places. Physically adsorbed ammonia was removed by degassing in flowing N₂ at 100°C for 3 h. The amount of ammonia desorbed from 100 to 800°C (at the rate of 10°C/min) was quantitatively monitored volumetrically (absorption in 1 M HCl). The total ammonia desorbed corresponds to number of acid sites and the desorption temperature to the strength of acid sites (weak and strong). Si and Al contents were determined using the ordinary wet chemical methods and the content of Na was measured flammotopically at 589 nm.

Catalytic tests

Performances of the B-Al-HZSM-5 catalyst for benzene alkylation with C₆=C₃ technical fraction were established in temperature at 250°C, under 40 atm. pressure, WHSV = 2.35 h⁻¹ and benzene : propylene molar ratio of 7:1, in a fixed bed continuous flow stainless-steel reactor (Twin Reactor System Naky, Metrimpex). The operating conditions (temperature, WHSV, pressure and benzene: propylene molar ratio) were in advance selected to obtain the high yield of IPB during the catalytic tests. Control of temperature, pressure, as well as gaseous feed was done through automatic devices. The reaction products were separated into gaseous and liquid fractions through an ice-trap. 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-HZSM-5 composite after the heat treatment. The pattern confirms that the synthesized zeolite has the structure identical to MFI-type zeolite [62]. 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

![Fig.1. XRD powder patterns of calcined parent NaZSM-5 and of B-(Al)-HZSM-5 composite after the heat treatment at 400°C [63]](image1)

![Fig. 2. SEM images of parent NaZSM-5 and HZSM-5 zeolites and their EDX spectra [63]](image2)
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 samples. This change might be interpreted by the dispersion of B2O3 as a monolayer into the channels of HZSM-5 matrix. [64-66]

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 narrows the pore openings and plugs 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 1.

| Catalyst          | Total ammonia chemisorbed (mmol/g) | Acid strength, mmol NH3/g | LT       | HT       |
|-------------------|-------------------------------------|---------------------------|----------|----------|
|                   |                                     |                           | 120-300°C | 300-600°C|
| HZSM-5            | 0.916                               |                           | 0.618    | 0.298    |
| B(Al)-HZSM-5      | 0.891                               |                           | 0.705    | 0.098    |

HZSM-5 modified by impregnation with boric acid and pre-treated 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. 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 [53-57].

Performance of B-(Al)-HZSM-5 catalyst in benzene alkylation with C3/C3 technical fraction

Six catalytic of approximately 48 h working tests with regeneration after each one were performed on B-(Al)-HZSM-5 at 250°C, under 40 atm. pressure, WHSV = 2.35 h-1 and benzene: propylene molar ratio of 7:1. Variation of the propylene concentration and the corresponding liquid product after each 3 working hours during a 54h test is present in figure 3 and 4. During the 36 h the propylene are consumed after he concentration in reaction gases increased off because the catalyst inactivation by progressive cocking. Among propylbenzenes compounds, cumene (IPB) is the main product, representing approx. 84 wt. % in this.

n-Propylbenzene, an undesirably by-product is obtained in a small quantity, his concentration in liquid product exceed of 2.0 wt.% only in firstly hours, and diisopropylbenzenes (1,3 and 1,4-DIPB) is obtained very probably by direct cumene alkylation with propylene and his concentration is up 2.0 wt.% in liquid product. Propylbenzenes distribution and IPB, and DIPB selectivity (middle values per test) over the six catalytic working tests of benzene alkylation with C3/C3 technical fraction over B-(Al)-HZSM-5 are presented in table 2 and figure 5.

IPB selectivity vs. of benzene consumed is up 83 wt. % and IPB selectivity vs. of propylene is up 76 wt. %. The IPB concentration (middle values per test) is up 84 wt.% in HZSM-5 modified by impregnation with boric acid and pre-treated 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. 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 [53-57].

Fig. 3. Variation of the propylene concentration in reaction gases vs. time on stream in benzene alkylation with technical fraction C3/C3 at 250°C and 40 atm

Fig. 4. Variation of the propylbenzenes concentration vs. time on stream in benzene alkylation with technical fraction C3/C3 at 250°C and 40 atm

Fig. 5. Variation of liquid components concentration over six catalytic working tests of benzene alkylation with C3/C3 technical fraction over B-(Al)-HZSM-5 liquid products, the n-PB concentration not exceed of 2.5 wt.% and the DIPB concentration increased at 1.910 wt.% in the first test at 6.28 wt.% (fig. 5).

Propylbenzenes (PB) selectivity was calculated as:

\[ \text{PB selectivity} = \frac{\text{quantity of benzene (B) or propylene (C\textsubscript{3}) consumed for PB obtained}}{\text{total quantity of reactant consumed in reaction}} \times 100 \]

The reaction scheme for benzene alkylation with propylene by zeolite catalyst can be illustrated by the following typical equations:
| Parameter          | Test number |
|-------------------|-------------|
|                  | 1 | 2 | 3 | 4 | 5 | 6 |
| Temp, °C         | 250 | 250 | 250 | 250 | 250 | 250 |
| P, atm           | 40 | 40 | 40 | 40 | 40 | 40 |
| E/C, %           | 7/1 | 7/1 | 7/1 | 7/1 | 7/1 | 7/1 |
| Time, h          | 39 | 87 | 51 | 54 | 39 | 33 |
| WHSV, h⁻¹        | 2.33 | 2.33 | 2.33 | 2.33 | 2.33 | 2.33 |
| C₂₉₆ nm, %        | 87.19 | 89.16 | 91.18 | 88.84 | 89.38 | 89.76 |
| CIPB, %          | 83.59 | 84.13 | 84.41 | 85.72 | 86.78 | 84.11 |
| SBIPB, %         | 86.89 | 83.11 | 85.97 | 86.85 | 87.69 | 85.91 |
| S₁⁻IPB, %        | 77.90 | 80.78 | 76.25 | 79.02 | 76.60 | 72.69 |
| S⁻₂IPB, %        | 1.59 | 4.26 | 3.10 | 4.47 | 2.4 | 3.05 |
| S⁻³IPB, %        | 2.85 | 8.29 | 5.51 | 8.43 | 4.67 | 5.10 |

The formation of NPB during the alkylation catalyzed by zeolites has been reported as isomerization of IPB by intramolecular and by intermolecular transalkylation with benzene [44, 46]:

\[
\begin{align*}
CH_2\!\!\!\!\!=\!\!\!\!\!=CH\!\!\!\!\!\!\!=CH_3 + H^+\text{-Zeolite} & \rightarrow CH_3\!\!\!\!\!=\!\!\!\!=CH\!\!\!\!\!\!\!=CH_3 + \text{Zeolite}^- \\
\text{alkylation} & \\
CH_2\!\!\!\!\!=\!\!\!\!=CH_3 + & \rightarrow \text{IPB} + H^+\text{-Zeolite} \\
\text{dialkylation} & \\
3HC\!\!\!\!\!=\!\!\!\!=CH\!\!\!\!\!\!\!\!\!=CH_3 & \rightarrow \text{DIPB} \\
\text{transalkylation} & \\
3HC\!\!\!\!\!=\!\!\!\!=CH\!\!\!\!\!\!\!\!\!=CH_3 + & \rightarrow \text{IPB} \\
\text{isomerization: monomolecular} & \\
3HC\!\!\!\!\!=\!\!\!\!=CH_2\!\!\!\!\!\!\!\!\!=CH_3 & \rightarrow \text{n-PB} \\
\text{or bimolecular} & \\
3HC\!\!\!\!\!=\!\!\!\!=CH_2\!\!\!\!\!\!\!\!\!=CH_3 + & \rightarrow \text{n-PB} + \text{n-PB}
\end{align*}
\]
Acid-catalysed alkylation's reactions of benzene with propylene are commonly considered to take place via carbenium-ion type mechanism. Propylene is first protonated on Bronsted acid site forming the active carbocations (secondary propenium ions). By the electrophilic attack on secondary propenium ions on the benzene ring cumene (isopropylbenzene, IPB) is formed. Primary IPB can be dialkylated to o-, p-, and m-DIPB.

Depending on reaction conditions and catalysts, the DIPB isomers can by transalkylate with benzene to form technical fraction. IPB selectivity vs. benzene and propylene consumed in reaction is upper 83 wt. %, in all effectuated tests.

The n-PB, an undesirable by-product, is obtained in small quantity. The di-isopropylbenzenes (1,3- and 1,4-DIPB) are the important by-products because they are separated in the liquid product and by transalkylation reaction with benzene in excess producing a supplementary quantity of cumene. Benzene alkylation with propane-propylene mixture on the B-(Al)-HZSM-5 catalyst has been demonstrated to be prospective routes for synthesis of isopropylbenzene.

The unique advantages of zeolites as replacements for conventional acids and bases catalysts will serve as driving force to continue the expansion of practical uses of zeolites.

Conclusions
B-(Al)-HZSM-5 catalyst presented good activities and selectivity's in reaction of benzene alkylation with primary fraction. IPB selectivity vs. benzene and propylene consumed in reaction is upper 83 wt. %, in all effectuated tests.

The n-PB, an undesirable by-product, is obtained in small quantity. The di-isopropylbenzenes (1,3- and 1,4-DIPB) are the important by-products because they are separated in the liquid product and by transalkylation reaction with benzene in excess producing a supplementary quantity of cumene. Benzene alkylation with propane-propylene mixture on the B-(Al)-HZSM-5 catalyst has been demonstrated to be prospective routes for synthesis of isopropylbenzene.

The unique advantages of zeolites as replacements for conventional acids and bases catalysts will serve as driving force to continue the expansion of practical uses of zeolites.

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