Synthesis of Ethylbenzene by Benzene Alkylation with Bioethanol on Zeolitic Catalysts

Synthesis and characterization of the catalyst

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The work focuses on the alkylation of benzene with bioethanol on zeolitic catalyst to obtain ethylbenzene. Data for the synthesis of a new zeolitic catalyst (ZMET -La-Zn catalyst). are presented. The reaction and synthesis steps for the obtaining of zeolitic precursor and catalyst are presented together with the structural and textural characterization. Based on the relationship between the synthesis conditions and catalyst structure, a various catalysts with enhanced efficiency and selectivity can be obtained. The new catalyst ZMET was tested for its alkylation activity and some results are presented.

Keywords : ethylbenzene, zeolite catalyst , alkylation, bioethanol

Benzene alkylation with ethanol on zeolite catalysts such as ZSM -5 [1], H-ZSM-5[2], $AlCl_3$ 13X[3] etc. was intensively studied in the laboratory and numerous results were published. In all the cases, the catalyst efficiency depends on its physical and chemical structure, therefore it is important to find the optimal structure for maximum efficiency.

SiO_2/Al_2O_3 ratio, channel dimensions and the presence of metals within zeolite structure influence its catalytic activity [2,4,5].

The yield for different products also depends on the technological conditions: temperature, pressure, feeding flow rates, composition of feeding mixture etc. [4].

In this work the reactions and synthesis steps for the obtaining of zeolitic precursor and catalyst, its modification with La and Zn and structural and textural characterization are presented. The new catalyst ZMET was tested for its alkylation activity of benzene with pure bioethanol and 95% bioethanol aqueous solution and some results are presented. The reaction conditions were chosen, so that optimum results are obtained for the alkylation process of benzene with bioethanol [6].

Experimental part

Materials and methods

Benzene was supplied by Merk Company. Ethanol was obtained by biological processes with two concentrations: pure ethanol and 95% ethanol aqueous solution. Zeolitic catalyst was synthesized in the laboratory with the following characteristics: composition 60% H-ZSM-5 zeolite and 40% γ-Al_2O_3 (as matrix), SiO_2/Al_2O_3 ratio 120-122, chemical modification with metallic salts of La and Zn (as solution 2%).

Synthesis of the catalyst

The synthesis of the catalist consists of the following steps:

-synthesis of ZSM -5 zeolite

- synthesis of zeolite catalyst and chemical modification.

Synthesis of ZSM-5 zeolite

The synthesis of zeolite is performed in hydrothermal conditions and involves a series of elementary steps where a mixture of silica and alumina precursors, alkaline cations and water is transformed into a microporous crystalline aluminosilicate. The crystallization process of a zeolite could be briefly presented as follows:

Reactants —>reaction mixture—>nucleation
—> Crystal growth

Inorganic or organic components from the mixture will influence the crystallization process towards the formation of a specific structure.

The synthesis of zeolite was performed in the presence of hexamethylenediamine (HAD) as structural agent. The raw materials for silica and alumina were sodium silicate and aluminium sulphate.The hydrothermal synthesis was done in the following conditions:

120 g amorphous aluminum silicate, 600 g distilled water and 39 g hexamethylenediamine were mechanically mixed. The aqueous suspension with pH=12…12,2 and molar composition 1Si O_2/0.011 Al_2O_3/0.08 Na_2O/0.24 HDA/ 30 H_2O was introduced into a stainless steel autoclave at 170-175^{0}C, 6-7 bar for 48 h in order to obtain a Na-ZSM-5 zeolite .

The XRD diffractogram (Bruker AXS-XRPD apparatus) for ZSM-5 zeolite synthetised in the presence of HDA shows a single pronounced maximum characteristic for ZSM -5 zeolite (fig 1).

The obtained Na-ZSM-5 (20 g) was transformed into NH_4-ZSM-5 by ionic exchange with 1M NH_4NO_3 solution (100mL at 90^{0}C for 2 h).

After filtration and drying, the product was finally obtained as a dry powder.

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Synthesis of zeolitic catalyst

Formation of zeolitic materials is a key step for the obtaining of a catalyst. For example, in a fixed bed catalyst –type reactor the zeolitic materials are assembled under different shapes: spheres, extrudates, or tablets. The molecular sieves are obtained as fine powders therefore they should by further processed to obtained different shapes. The conventional method for the synthesis of catalyst involves the following steps: mixing the power zeolite with a binder (silica or alumina) followed by a formation process.

Extrusion process is the most economical and the most used method to obtain catalyst and support materials. The first step of the extrusion process implies the preparation of a paste with diluted acidic solution as peptizant for powder material. This process was also used in our experiments with ZSM-5 zeolite.

In order to obtain the catalyst for alkylation of benzene with ethanol, 20 g of NH_4-ZSM-5 zeolite were mixed with 20.5 g alumina (A_2O_3) and $HNO_3$12% solution (0.65-0.8 mL solution/g solid powder). The obtained paste was extruded using an extruder with plunger and a die of 2mm diameter. The extruded product was calcined at 80°C for 8 h and then at 550°C for 6 h. The product, H-ZSM-5 zeolite was modified using metallic salt solutions of La and Zn (2% solutions, La/Zn=1/1 mole/mole) and dried at 80 °C for 2 h.

ZSM-5 and modified catalyst ZMET were characterized by XRD analysis (Bruker AXS –XRPD apparatus) and physical adsorption of gases for solid materials (BET method) (fig. 1-3) (MICROMERITICS, ASAP-2020 apparatus).

Alkylation of benzene with bioethanol on ZMET catalyst

The new catalyst ZMET was tested in an installation for alkylation of benzene with bioethanol [6] and the results are shown in figures 4 - 7. In these figures the chemical compositions of reaction mixture are given as a function of the temperature and ratio benzene/ethanol or ethanol solution 95%. The chemical composition of the reaction mixture was determined by chromatographic analysis (apparatus Varian CP 3800 coupled with Varian MS 4000 detector). The volumetric input of the reactants was 2.5 mL/min , nitrogen input (carrier gas) 2L/h and reactor pressure 2bar. The detailed description of the alkylation installation and reaction conditions is given in our previous work [6].

Results and discussions

Characterization of ZSM –5 zeolite and modified catalyst ZMET

Structural characterization

The XRD analysis (fig1) of the zeolitic material showed a well-crystallized zeolite with the specific MFI lattice. A single pronounced maximum at 2θ~24° is characteristic for crystallized ZSM-5 zeolite.

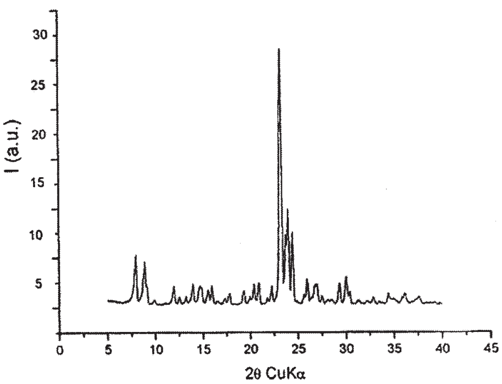

Fig.1. XRD diffractogram for ZSM - 5 zeolite synthesized in the presence of hexamethylenediamine

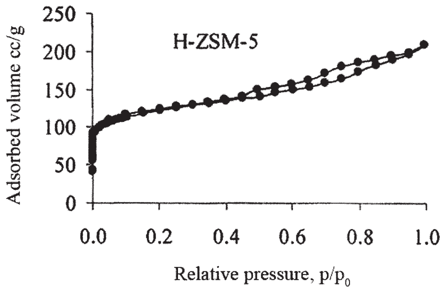

Fig. 2a. Adsorption isotherme / desorption of nitrogen for zeolite H-ZSM-5

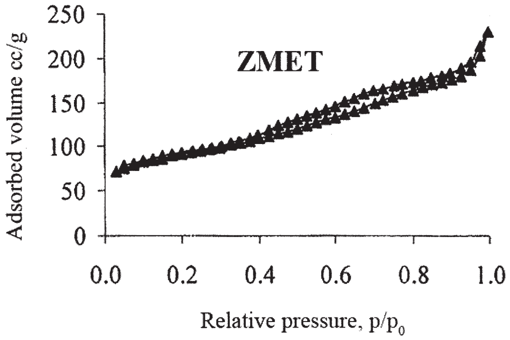

Fig. 2b. Adsorption isotherme / desorption of nitrogen for ZMET catalyst

Textural characterization

Physical adsorption of gases is one of the most used porosimetric method for solid materials. The amount of adsorbed gas onto a solid material is a direct measure of its porosity and structural properties. From these measurements one may obtain valuable data on specific surface, pores volume and distribution for a solid material [7].

Adsorption method is seldom used for the characterization of microporous and mesoporous materials.

Identification of the adsorption isotherm (volume of absorbed gas versus relative gas pressure) is the starting point for textural characterization of a solid material according to IUPAC rules[8].

Measurements for nitrogen adsorption for H-ZSM-5 sample and for the extruded and modified catalyst ZMET were performed at 77 K (-196°C).The experimental isotherms for the analyzed samples are shown in figures 2.a and 2. b

Figure 2.a shows a type -1 isotherm for H-ZSM-5 zeolite (according to IUPAC) typical for solid microporous materials. Nitrogen adsorption at low relative pressure p/p_0 is associated with micropores filling. Adsorption continues without capillary condensation on a broad domain for relative pressure and is associated with the external surface of the zeolite.

Comparison of the curves from the two figures (2a, 2b) reveals the modification of the adsorption/desorption isotherms after zeolite incorporation in the silica matrix, extrusion and modification. Therefore the curve of the extruded catalyst is a type –IV isotherm typical for mesoporous materials with a hysteresis loop of H2 type. This may lead to the modification of the pores geometry during the synthesis of the catalyst. The increase of the adsorbed volume at p/p_0 values close to 1.0 is correlated to gas condensation within the particle spaces.

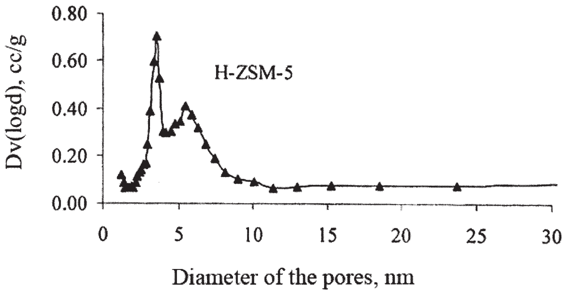

Fig. 3. Pores diameter distribution for H-ZSM-5 catalyst

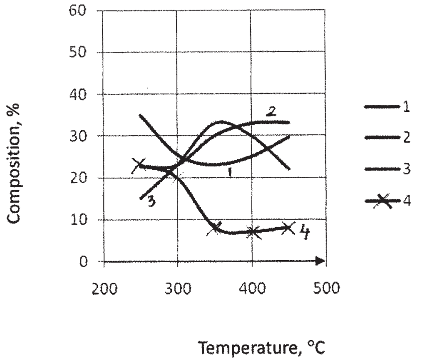

Fig .4.Chemical composition of the alkylation product as a function of the reaction temperature; benzene/ethanol. 2/1(mole/mole). 1-benzene, 2-ethylbenzene, 3-diethylbenzene, 4 -xilene, trimethylbenzene, methylbenzene

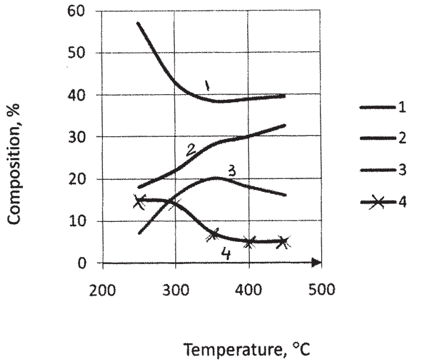

Fig. 5. Chemical composition of the alkylation product as a function of the reaction temperature; benzene/ethanol.3/1(mole/mole). 1-benzene, 2-ethylbenzene, 3-diethylbenzene, 4 -xilene, trimethylbenzene, methylbenzene

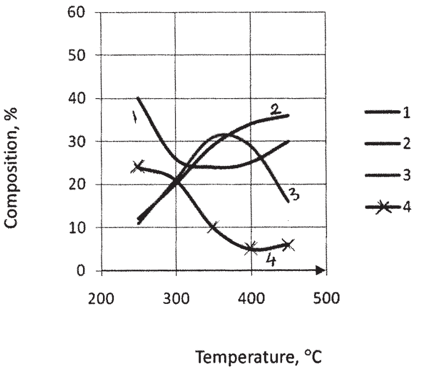

Fig. 6. Chemical composition of the alkylation product as a function of the reaction temperature; benzene/ethanol. solution(95%)=2/1(mole/mole) 1-benzene, 2-ethylbenzene, 3-diethylbenzene, 4 -xilene, trimethylbenzene, methylbenzene

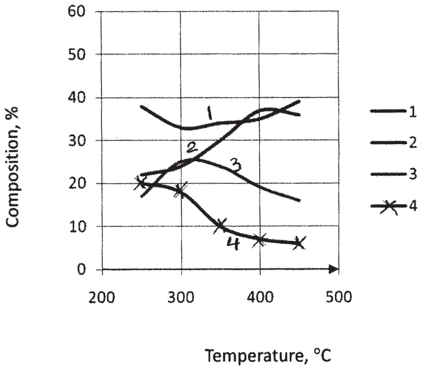

Fig. 7. Chemical composition of the alkylation product as a function of the reaction temperature; benzene/ethanol. solution(95%)=3/1(mole/mole) 1-benzene, 2-ethylbenzene, 3-diethylbenzene, 4 -xilene, trimethylbenzene, methylbenzene

The textural properties of the zeolite and catalyst samples (table 1) were evaluated as follows:

-the specific surface was evaluated by Brunauer Emmett –Teller (BET) method at $p/p_0=0.05-0.2$. The method is applied in the literature for the characterization of the specific surface[8]. The surface and the volume of micropores were determined from adsorption isotherm by t-plot method;

-the total volume of pores was computed from the volume of adsorbed gas at $p/p_0=0.995$;

-the mean diameter of the pores and the pores diameter distribution were computed by Barrett –Joyner-Halenda (BJH) method from desorption isotherm.

Figure 3 shows the curve of the pores diameter distribution. One may see a maximum in the mesopores range at 3.51 nm. A broader maximum is also present but at a low intensity in the mesopores range with higher diameters (5.39 nm).

Textural data from the table 1 reveal a good agreement with the literature data for the values of specific surface and volume of pores for ZMET zeolite [9,10]. The amount of adsorbed nitrogen within the micropores is determined

Table 1
TEXTURAL PROPERTIES OF THE ZEOLITE H-ZSM-5 AND CATALYST ZMET

Sample	**Specific surface (m^2/g)**		**Volume of pores (cm^3/g)**		**Pores diameter BJH,des (nm)**
	BET	**Micropores**	**total**	**Micropores**	
Zeolite H-ZSM-5 (powder)	410	255	0.323	0.103	
ZMET catalyst	280	150	0.349	0.0830	3.60

by the channels size as the dimension (size) of the nitrogen molecule (0.3 nm) is smaller than the pores dimension of the ZSM-5 zeolite (0.55 nm).

Steric and geometric hindrance on the external surface is smaller as compared to the adsorption within the micropores structure. Significant nitrogen adsorption on the external surface of the sample is a clue for low dimension crystals. The lower value of the specific surface for the extruded catalyst as compared to zeolite may be due to the decrease of the micropores surface.

Using the catalyst ZMET in the alkylation process of benzene with bioethanol (fig. 4-7) satisfactory conversions in ethylbenzene were achieved (20-40%) depending on temperature (with a maximum at 400-450^{0}C) and reactants ratio (optimum for benzene/ethanol=2/1 mole/ mole). Catalyst activity and selectivity is not influenced by the concentration of the bioethanol, so it is possible to use a 95% bioethanol solution a cheaper product than pure bioethanol.

Conclusions

Structural and textural characterization of the new catalyst ZMET showed a well crystallized zeolite with the specific MFI lattice.

The experimental isotherms for the analyzed samples show a microporous structure with the pores diameter as the range of 3.60 nm.

ZMET catalyst was tested in laboratory unit with benzene and bioethanol (96 and 100%) as raw materials. Satisfactory conversions in ethylbenzene were achieved (20-45%) depending on temperature, feed flow rate and reactants ratio and the results are comparable with those obtained with catalyst modified with Ni and Ce [6].

Catalyst activity and selectivity do not depend on the conditions of the bioethanol (pure ethanol as 95% aqueous ethanol solution).

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