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## RESEARCH ARTICLE

### ALKYLATION OF BENZENE WITH BIOETHANOL USING A ZSM-5 CATALYST MODIFIED WITH ND.

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#### ABSTRACT

Alkylation of benzene over modified ZSM-5 catalysts with Nd and Pd has been done in a laboratory tubular reactor using a new modified zeolitic catalyst. The alkylation experiments have been done at different reaction temperatures, pressures and benzene (ethylbenzene)/bioethanol molar ratio in order to establish their influence on the final composition of the reaction product, selectivity and conversion. The feed and products are analyzed by XR-Fluorescence Spectrometer and phase purity and phase purity were confirmed by X-ray diffraction (XRD apparatus X'Pest PRO-MPD).

#### INTRODUCTION

The alkylation of benzene (B) with ethylene over ZSM-5 zeolite is an industrial process (Mobil Badger Process) for the synthesis of ethylbenzene (EB), an important raw material in manufacturing of polystyrene and other copolymers of styrene (Dwyer et al., 1976). The use of ethanol (E) instead of ethylene for benzene or toluene alkylation has been reported in other paper (Jun-Jun, 2006; Jun-Jun, 2004; Dandekor et al., 2003; Bhat et al., 1995). For industrial scale is very important to replace ethylene or ethanol obtained from petrochemical processes with „bioethanol” derived from biomass, a renewable raw material. The catalytic conversion of benzene to ethylbenzene or other chemicals with bioethanol over different types of zeolites or modified zeolite catalysts has been reported earlier (Sridevi et al., 2001; Walendziewski, 1996; Sabu et al., 1994; Loredano et al., 2012). Some interesting results with high selectivity for ethylbenzene in alkylation of benzene with ethanol using a zeolite catalyst modified with lanthanum were recently reported (Li et al., 2012). In this work, the results of the alkylation of benzene with bioethanol (96% aqueous ethanol solution obtained from biomass) over a modified ZSM-5 zeolite with Nd cations as catalyst, were reported. We studied the influence of the catalyst, composition of the reaction mixture and alkylation process temperature, on the benzene conversion to ethylbenzene, diethylbenzene and other chemicals. Also, we compared the results obtained using the modified catalyst with Nd and the unmodified zeolite catalyst.

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#### Experimental part

##### Materials

All used chemicals were commercial (Merck, Aldrich) were of high purity reagents. Aqueous ethanol solution with 96% purity („bioethanol” in our work) was separated by distillation from aqueous mixture obtained by fermentation of carbohydrates. The catalysts used in benzene alkylation with „bioethanol” were synthesized in the following steps (Anca Gabriela Parciulea et al., 2013; Anca Gabriela Parciulea et al., 2014; Biosint EB-SRL ).

##### Synthesis of ZSM-5 zeolite

The mixture of silice and alumina precursors with the molar composition 1.0 SiO<sub>2</sub>/0.01 Al<sub>2</sub>O<sub>3</sub>/1.2Na<sub>2</sub>O/0.22 HDA/ (hexamethylene-diamine) was transformed into a microporous crystalline aluminosilicate in the presence of the binding agent (HDA). The hydrothermal synthesis was done in a stainless steel autoclave at 70-175°C, pH=12 for 48 hours and under continuous stirring. The product, Na-ZSM-5 was transformed into NH<sub>4</sub>-ZSM-5 by ionic exchange with 1M NH<sub>4</sub>NO<sub>3</sub> solution and finally a zeolite as dry powder obtained (Z).

##### Synthesis of zeolitic catalyst

The powder zeolite NH<sub>4</sub>-ZSM-5(60%), alumina (40%) as a binder and nitric acid (as 10% aqueous solution) were mixed to obtain a paste. This paste was transformed into cylinders ( =2 mm, L=5 mm) using a plunger-type extruder and the catalyst was dried (80°C, 8 hours) and calcined (550°C, 6 hours, 2°C/min) to obtain the final form of H-ZSM-5(ZC).

The chemical modification of the catalyst (ZC) was achieved by impregnation with 0.1M NdCl<sub>3</sub> aqueous solution, dried at 80°C and calcined at 500°C to obtain ZC-Nd catalyst

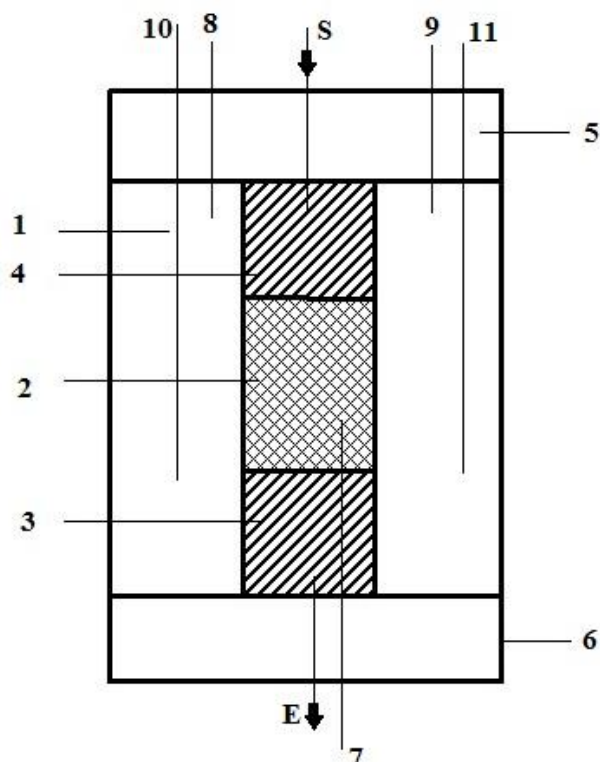
### Characterization of Z, ZC, and ZC-Nd catalysts

Chemical composition of H-ZSM-5 was established using an XR-Fluorescence Spectrometer –S8-Tiger. Crystallinity and phase purity were confirmed by X-ray diffraction (XRD apparatus X'Pest PRO-MPD, PANalytical). Nitrogen adsorption isotherms were measured at 77<sup>0</sup>K on a Micrometrics ASAP 2010 volumetric adsorption analyzer. The specific surface area was calculated by the BET method and for diameter of the pores was used the BJM method. The acidity of the catalyst was determined by temperature programmed desorption

(TPD) of diethylamine (DEA) Thermogravimetric analysis (TGA) was performed with a Du Pont Instrument device., Thermal Analyst 2000/2100"coupled to a module 951 Thermogravimetric Analyzer. Desorption of the DEA was carried out by heating the sample from 20<sup>0</sup>C to 600<sup>0</sup>C in nitrogen atmosphere with 10<sup>0</sup>C/min.

### Alkylation reaction

The alkylation reaction was performed in a metallic reactor (see Fig.1)



**Fig. 1. Alkylation Reactor 1. Reactor Body, 2. Catalyst zone, 3-4 Inert zones, 5-6 Flanges, 7-11 thermocouples, S – reaction mixture supply, E – exit of reaction products**

Details about the reactor have been reported earlier (11,13).The experiments were done at 250-450<sup>0</sup>C with different molar ratio B/E ( 1/1, 2/1 and 3/1) at 2 bar pressure and at feeding flow rate of 2.5 mL/min. The nitrogen was used as carrier gas (30mL/min).

The reaction mixture was analyzed by gas chromatography to establish its chemical composition (Varian CP3800 apparatus coupled with MS Varian 4000).

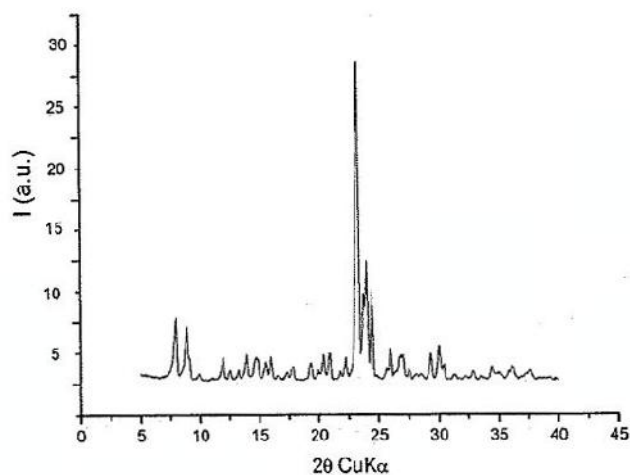
## RESULTS AND DISCUSSION

The properties of H-ZSM-5 zeolite powder (Z), H-ZSM-5/Al<sub>2</sub>O<sub>3</sub> (ZC) and, H-ZSM-5/Al<sub>2</sub>O<sub>3</sub> modified with Nd ( ZC-Nd) materials are presented in the Table 1.

**Table 1. Properties of the catalysts: Z, ZC and ZC-Nd**

Properties	Z	ZC	ZC-Nd
SiO <sub>2</sub> , mole %	8.6		
Al <sub>2</sub> O <sub>3</sub> , mole%	1.03		
Na <sub>2</sub> O, mole%	0.37		
SiO <sub>2</sub> / Al <sub>2</sub> O <sub>3</sub> ,mole/mole	96		
Pores diameter, nm		3.51	3.40
BET surface area, m <sup>2</sup> /g	410	300	291
Micropores surface area, m <sup>2</sup> /g	255	170	
Total volume pores, cm <sup>3</sup> /g	0.323	0.103	0.100
Micropores volume, cm <sup>3</sup> /g	0.357	0.089	
Nd content,%			3.01
Acidity (loss of DEA) (mEqDEA/g)/(%)			
Total		0.486/100	0.685/100
Weak		0.206/42.5	0.378/55.2
Medium		0.164/33.7	0.165/24.1
Strong		0.116/23.8	0.142/20.7

We selected a H-ZSM-5 with the ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 100 according to the results presented in the literature (3).This type of catalyst gives a high selectivity for EB in alkylation process of benzene with ethanol. For ZC catalyst BET surface area and pores volume are smaller than for Z zeolite because Al<sub>2</sub>O<sub>3</sub> used as binder is a mesoporous material. There are not important modifications when ZC is transformed into ZC-Nd catalyst (Table 1). The XRD analysis of zeolitic material (Z) showed (Fig.2) a well crystallized material with specific MFI lattice. (14).



**Fig. 2. XRD diffractogram for ZSM-5 zeolite synthesized in the presence of hexamethylenediamine**

The values of acid strength (the loss with temperature of DEA in mEq/g catalyst) for ZC and ZC-Nd catalysts are presented in table 1 and on the Fig 3 and 4. There are three delimited zones (A,B,C) on the graphs which are assigned to the weak, medium and strong acidity. The presence of the Nd cations reduces the total acidity (increased loss of DEA) and will influence its activity in alkylation process. The chemical composition (%) of the reaction mixtures (benzene, ethylbenzene, diethylbenzene-DEB, xylene-X,

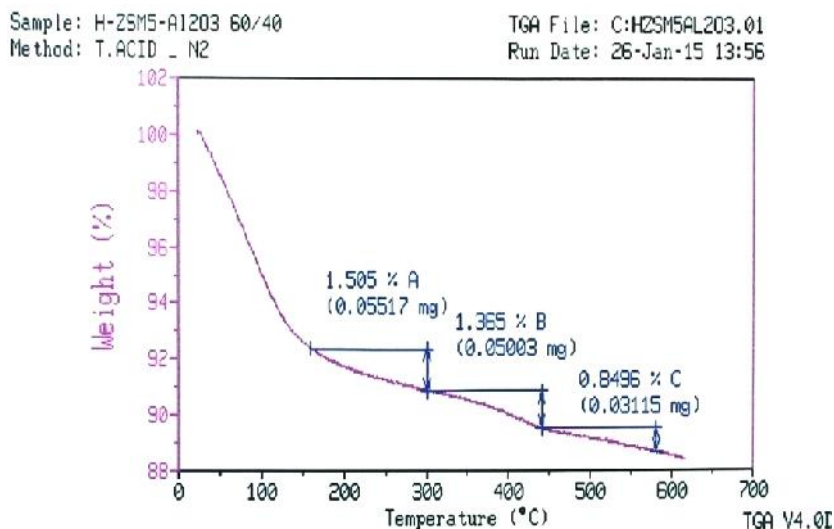


Fig. 3. The loss of DEA with temperature for ZC catalyst

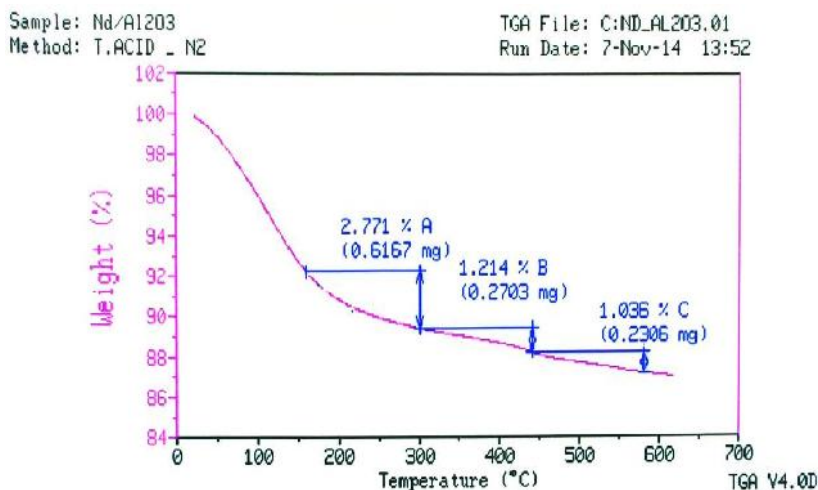


Fig. 4 The loss of DEA with temperature for ZC-Nd catalyst

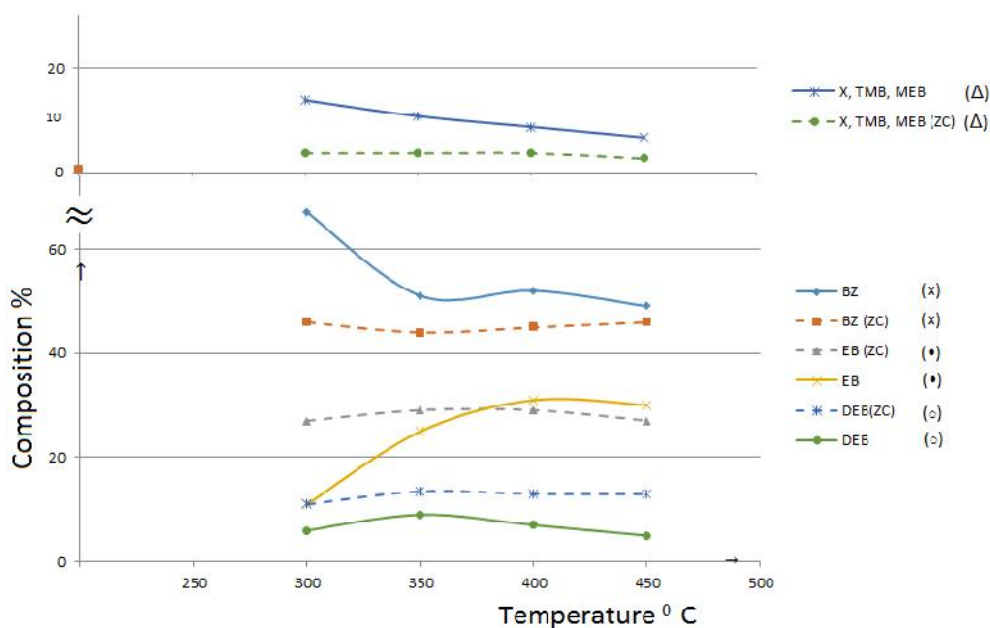


Fig. 5. Concentration of the components in reaction mixture as a function of the temperature catalysts ZC (-----) and ZC-Nd (\_\_\_\_\_) B/E=1/1 mole/mole B(X); EB(•); DEB (o); X+TMB+MEB( )

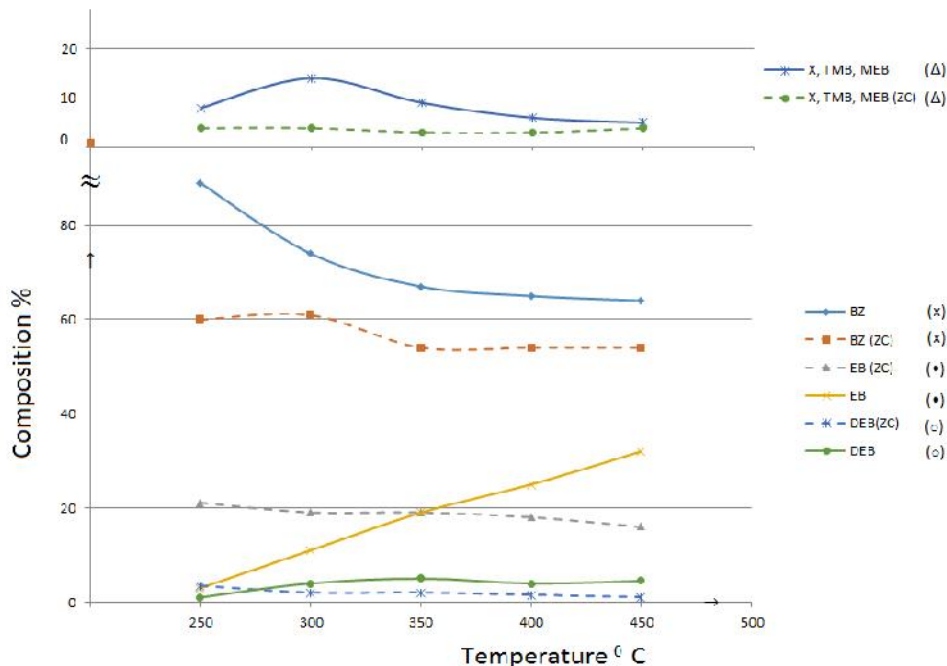


Fig. 6. Concentration of the components in reaction mixture as a function of the temperature catalysts ZC (-----) and ZC-Nd (————). B/E=2/1 mole/mole . B(X); EB(•); DEB (o); X+TMB+MEB( )

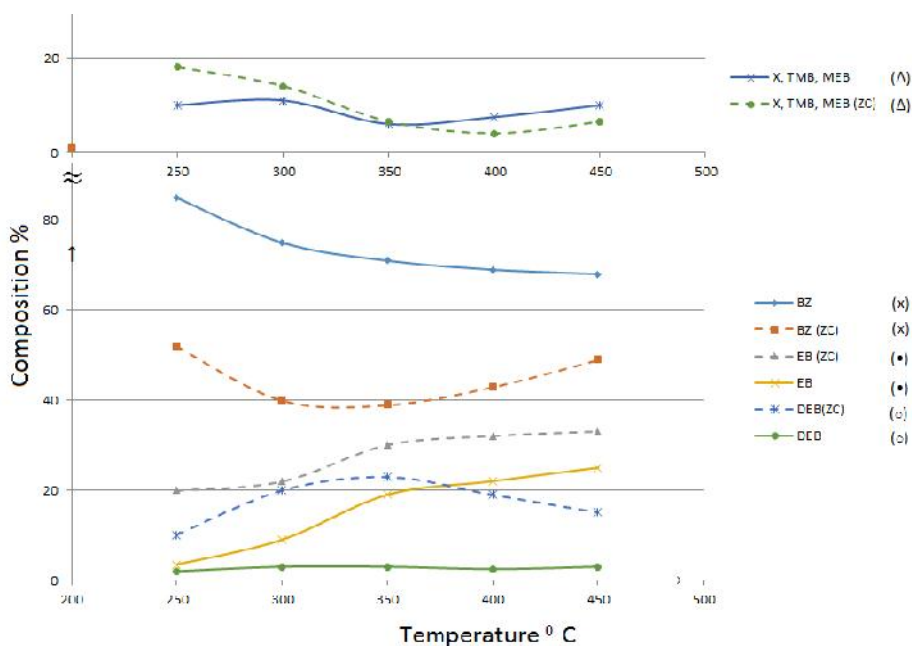


Fig. 7. Concentration of the components in reaction mixture as a function of the temperature catalysts ZC (-----) and ZC-Nd (————). B/E=3/1 mole/mole B(X); EB(•); DEB (o); X+TMB+MEB( )

trimethylbenzene-TMB, Methylethylbenzene- MEB) using ZC and ZC-Nd catalysts are presented on the Figures 5, 6 and 7. Lanthanides (including Pr, Nd) have electrons in „f” sheath (layer) which give the possibility to form complexes and high catalytic activity in chemical reaction as benzene alkylation. From those results we observe a reduction of benzene reactivity (increased concentration of unreacted benzene) in alkylation process in the presence of ZC-Nd catalyst in

comparison with ZC catalyst. We suppose that this phenomenon is explained by the reduction of the total acidity of ZC-Nd catalyst due to the adsorption of Nd cations on the acid centers. The ionic radius of Nd<sup>3+</sup> is 0,995 Å, so it can enter into all micropores (diameter =3.40 nm, table 1) of the catalyst. The concentration of EB in reaction mixture increases with temperature in the region (250-450°C) for all ratios B/E. The modified catalyst with Nd gives a better result increased concentration of EB in comparison with ZC catalyst only for

the ratio B/E=2/1 mole/mole at 350-450 °C. In the case of mixture B/E= 3/1 mole/mole the catalyst ZC-Nd is more selective for DEB than ZC-catalyst ( Fig7, curves DEB and DEB-ZC).

### Conclusions

- The synthesized zeolitic material Z has a well crystallized structure with specific MFI lattice.
- Chemical modification of ZC catalyst with Nd cations decreases its acidity and reactivity of benzene in alkylation process;
- For both catalysts (ZC and ZC-Nd ) the concentration of EB in reaction mixture increases with temperature between 250<sup>0</sup> C -450<sup>0</sup> C for all ratios B/E;
- The catalyst ZC-Nd gives a reaction mixture with a higher concentration in EB, than ZC catalyst only in a particular case: B/E = 2/1 mole/mole and T=350<sup>0</sup> C -450<sup>0</sup> C;
- In the case of initial mixture B/E =3/1 mole/mole, the catalyst ZC-Nd has a higher selectivity for DEB than ZC catalyst.

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