TRANSAKYLATION OF DIETHYLBENZENE WITH BENZENE OVER ZSM-5 CATALYSTS. THE INFLUENCE OF NEODYMIUM CATION, CATALYST ACIDITY AND TEMPERATURE ON THE PROCESS

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In this work four H-ZSM-5 zeolite catalysts with different SiO_2/Al_2O_3ratio have been prepared and characterized. (cat 1, cat 2, cat 3, cat 4) and then modified with neodymium from $NdCl_3$ to obtain Nd 1, Nd 2, Nd 3, Nd 4. The catalysts were applied for gas- phase transalkylation of diethylbenzene (DEB) to ethylbenzene (EB) in reaction with benzene(B). The study has shown that the reactivity of benzene (B) and yield in EB, increase with the total acidity of the catalyst cat 1- cat 4 and, also, with the temperature of the transalkylation reaction. The catalysts Nd1-Nd 4 show a similar reactivity for B as the catalysts cat 1-cat 4, but a maximum yield for EB at $\approx 350^0C$.

Keywords: transalkylation, diethylbenzene, ZSM-5 catalysts, catalyst acidity, modified catalyst

1. Introduction

Ethylbenzene (EB) is industrially one of the largest volume derivate of benzene. Alkylation of benzene (B) with ethylene or ethanol is a major petrochemical process for synthesis of ethylbenzene a raw material for manufacturing of styrene, polystyrene and different copolymers of styrene [1,2,3]. The vapor phase alkylation of benzene with ethylene in the presence of ZSM-5 zeolite (as catalyst) is a commercial process (Mobil-Badger Process) for the synthesis of ethylbenzene [2].

The use of alkylation of enzene with ethanol oraqueous ethanol solution over zeolite catalysts has been reported in different studies [4,5]. In most of the liquid and gas phase processes for the synthesis of ethylbenzene, several competing sidereactiontake place, determining the formation of polyalkylates:

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diethylbenzene (DEB) isomers (ortho, meta and para), triethylbenzene (TEB), ethylmethylbenzene (EMB) etc. [1, 6-11]. During the alkylation about 50-60% polyalkylatedbenzenesare formed whichmainly contain DEB isomers (10-20 %). In order to increase the overall efficiency of the ethylbenzene process, it is necessary to transalkylate DEB isomers with benzene to EB and several zeolitic and non-zeolitic catalysts have been proposed [6,11,12]. An interesting catalyst (trifluoromethanesulphonic acid=triflic acid) have been investigated for synthesis of EB by translakylation of DEB with benzene at atmospheric pressure and law temperature (15-35 ^{0}C). [7].

In this work ZSM -5 catalysts with different acidities were synthetized and the results of transalkylation of DEB with benzene at different temperature were reported. We correlated the acidity of the catalyst and the reaction temperature with the final composition of the reaction mixture. Catalysts ZSM- 5 were modified with neodymium ions ($NdCl_3$), and the metal ion influence on the composition of the final reaction mixture was studied. We compared the influence of catalyst acidity on the EB yield for our catalyst and beta zeolite catalyst having a similar topology (three-dimensional interconected channels) [13].

2.Experimental part

2.1 Materials

DEB (≅90%o-diethylbenzene, ≅5% m-diethylbenzene, $\cong 3\%\ p-$ diethylbenzene, bp=180-182^{0}C, d 25^{0}C= 0,87g/mL, n^{20}_D= 1,4951) and benzene were obtained from Aldrich with high purity. They were used directly without further purification. The catalysts *(*ZSM-5 zeolites) were synthetized and chararacterized in our laboratory according to the methods described in previous works [8, 9,12,14] and the result are presented in table 1.

The mixture of silice and alumina precursors with different molar composition was transformed into a microporous crystalline alumina silicate in the presence of a binding agent HDA (hexamethylenediamine).

The hydrothermal synthesis was done in a stainless-steel autoclave at 70-175^{o}C, pH=12 for 48 hours and under continuous stirring. The product, Na–ZSM-5 was transformed into NH_4-ZSM-5 by ionic exchange with 1M NH_4NO_3 solution and finally a zeolite as dry powder was obtained.

The powder zeolite NH_4-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 (θ=2 mm, L=5 mm) using a plunger–type extruder and the catalyst was dried (80^{0}C, 8hours) and calcined (550^{0}C, 6 hours, 2^{0}C/min) to obtain the final form of H-ZSM (cat 1 –cat 4).

Table 1

Properties of catalysts cat 1-cat 4 and Nd 1- Nd 4

Properties	Cat 1	Nd 1	Cat 2	Nd 2	Cat 3	Nd 3	Cat 4	Nd 4
SiO_2/Al_2O_3 mole/mole	74		32		104		2.80	
Pores diameter, nm	3.62		3.24		3.60		3.42	
BET surface area, m^2/g	320		370		320		350	
Acidity (loss of DEA) $mE_gDEA/g/\%$ Total	1.0636/100		1.3036/100		0.9455/100		0.6621/100	
Weak	0.3768/35.43		0.8695/66.70		0.4814/50.92		0.2384/36.00	
Medium	0.2439/22.93		0.3009/23.08		0.2327/24.61		0.1852/27.97	
Strong	0.4429/41.64		0.9332/10.22		0.2314/24.24		0.2985/36.02	
Nd content %		2.92		2.90		3.01		3.12

The chemical modification of the catalyst (cat 1-cat 4) was achieved by impregnation with 0.1M $NdCl_3$ aqueous solution, dried at 80^0C and calcined at 500^0C to obtain catalysts Nd 1- Nd-4(Nd/dry catalyst=4/100, g/g).

Chemical composition 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 77^0K 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 amodule 951 Thermogravimetric Analyzer.

Desorption of the DEA was carried out by heating the sample from 20^0C to 600^0C in nitrogen atmosphere with 10^0C/min.

The values of catalyst acidity were calculated as the loss of DEA with temperature (150^0C -300^0C-450^0C -575^OC) in m $E_g$of DEA /g catalyst. There are three delimited zones (A, B, C) on the graphs (Figs. 2-5) which are assigned to the weak, medium and strong acidity.

Transalkylation reaction was performed in a metallic reactor Fig. 1. Details about the reactor have been reported earlier [9,12,14]. The experiments were done at 250-400^{0}C at 2 bar pressure with a feeding flow rate of 2.5 mL/min (DEB/B= 1/2 mole/mole). The nitrogen was used as carrier gas (30mL/min). The reaction mixture was analyzed by gas chromatography to establish the chemical composition (Varian CP3800 apparatus coupled with MS Varian 4000).

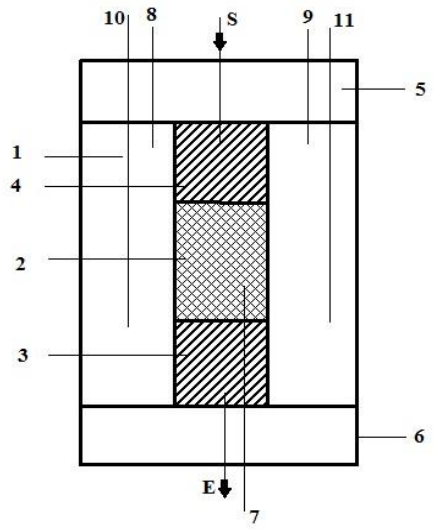


Fig. 1. Transalkylation Reactor 1. Reactor Body, 2. Catalyst zone, 3-4 Inert zones, 5-6 Flanges, 7-11 thermocouples, S – reaction mixture supply, E – exit of reaction products

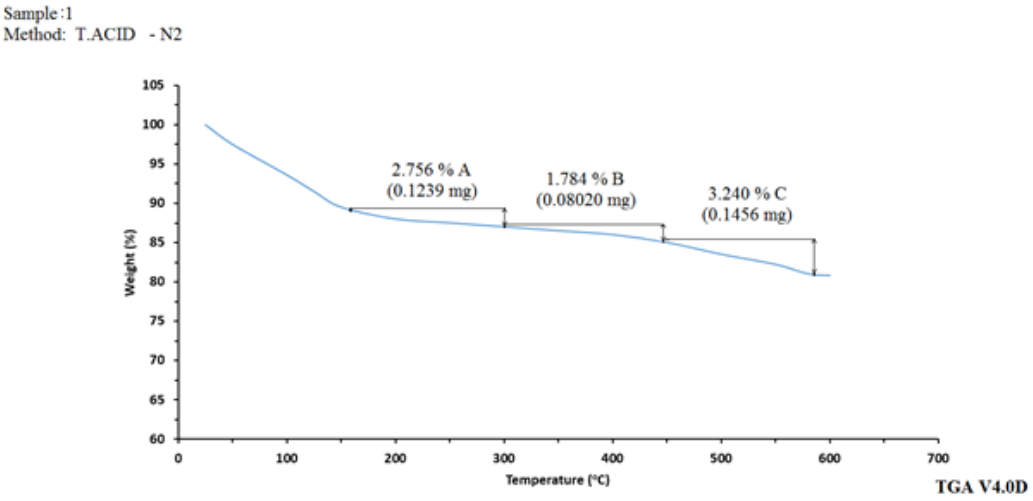


Fig. 2 The loss of DEA with temperature for cat 1

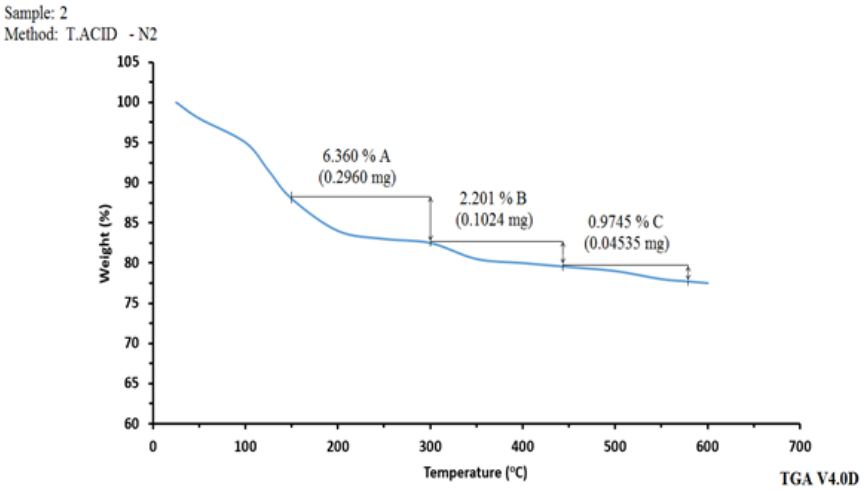


Fig 3. The loss of DEA with temperature for cat 2

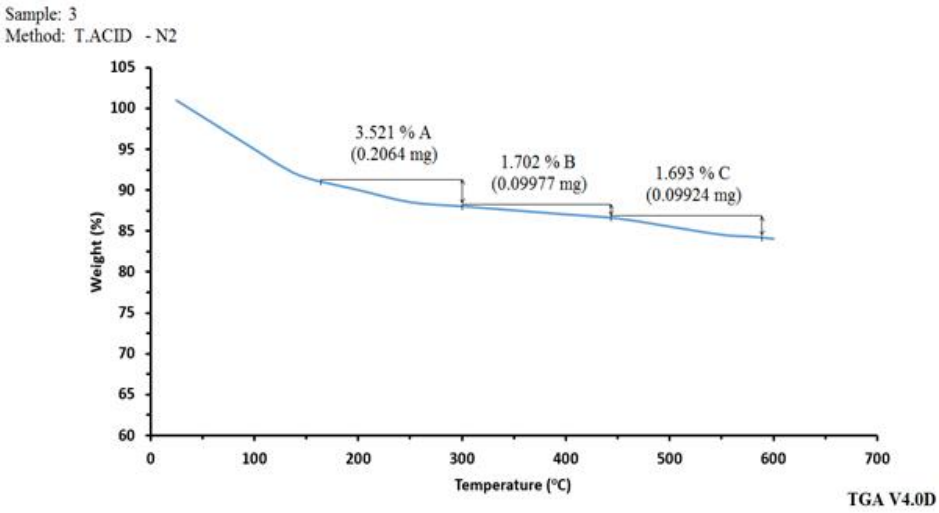


Fig. 4 The loss of DEA with temperature for cat 3

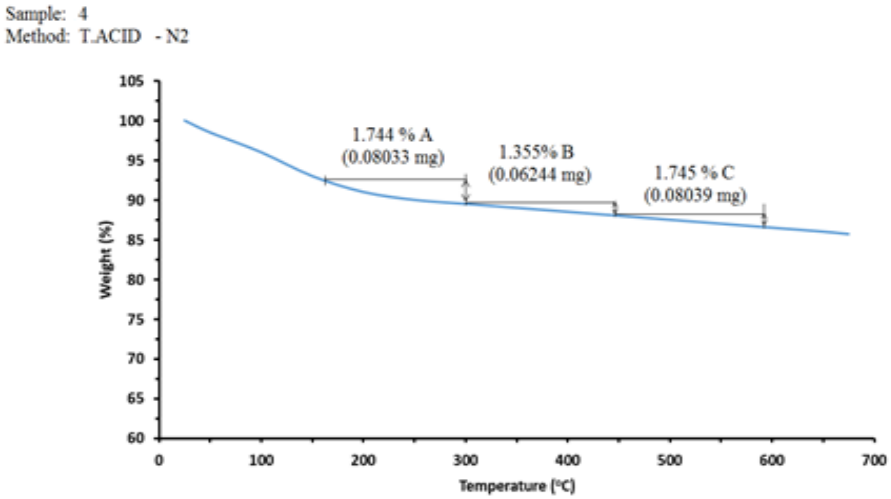


Fig. 5 The loss of DEA with temperature for cat 4

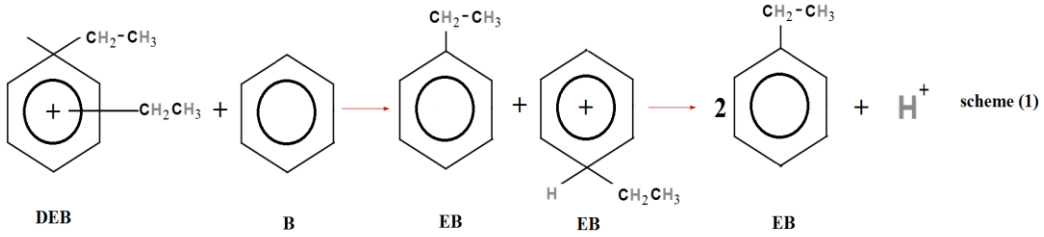
3. Results and discussion

The catalytic activity of H-ZSM-5 zeolites depends on the microporous structure or „topology" (shape distribution and dimensions of the channels), but also on the degree of acidity of the catalyst. (number, strength and location of acid sites) [15,16].

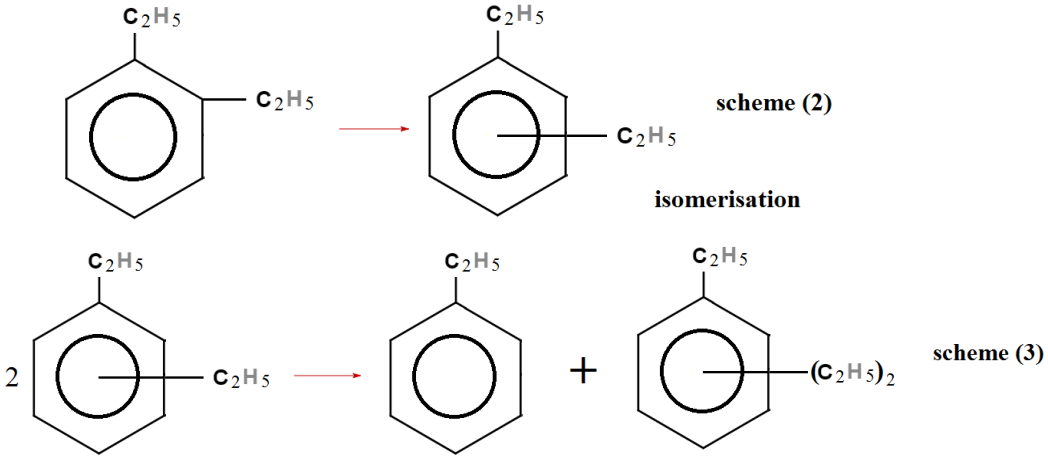
From results presented in table 1, we proved that the total acidity depends on the content Al in catalyst. The total acidity increases with the increase of this content, but the acidity distribution (weak, medium and strong) does not vary in the same way for all catalysts (cat 1 – cat 4), and depends on the distribution of acidic centers in channels or on the surface of the catalyst.

Weak acidity is important in the catalyst with small diameter of the channels (tab 1).

Transalkylation reaction of diethylbenzene isomers with benzene follows the scheme (1) [17].



This is the main reaction, but there are several competing side reactions in transalkylation of DEB with benzene. Some of these reactions (2) and (3) are presented here:



The reaction (2) is confirmed by our gas- chromatography results when we found a different ratio between DEB isomers (o/m/p=87/8/2,%) then initial product (Aldrich) (o/m/p= 90/5/3, %). The influence of the catalyst acidity and the reaction temperature on the chemical composition of the final mixture in transalkylation reaction of DEB with benzene is presented on the Figs. 6, 7.

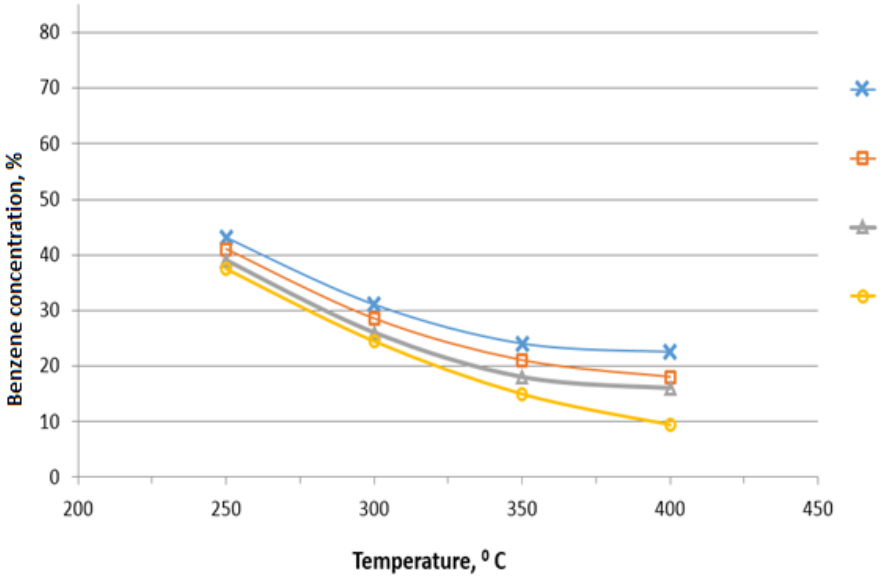


Fig. 6. Benzene concentration (%) in the final reaction mixture using different catalysts and temperatures: :$\Delta - cat\ 1; o - cat\ 2$; □ $- cat\ 3\ and x$-cat 4

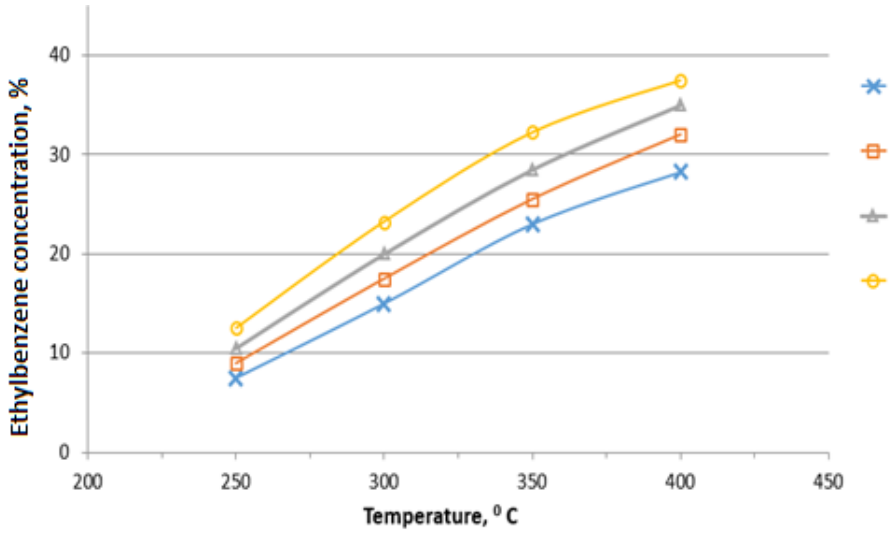


Fig.7 Ethylbenzene concentration (%) in the final reaction mixture using different catalysts and temperatures: $\Delta - Nd\ 1; o - Nd\ 2\ ; \square - Nd\ 3\ and x$-Nd 4

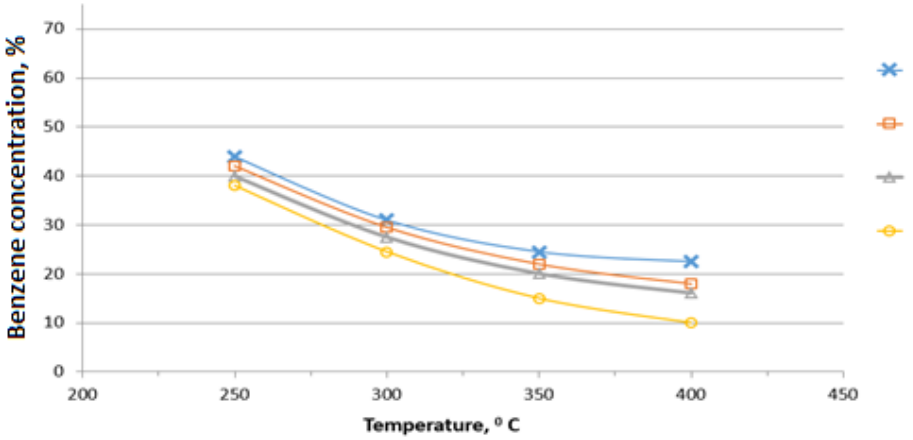


Fig 8 Benzene concentration (%) in the final reaction mixture using different catalysts Nd1- Nd 4 and temperatures: $\Delta - Nd\ 1; o - Nd\ 2\ ; \square - Nd\ 3\ and x$-Nd 4

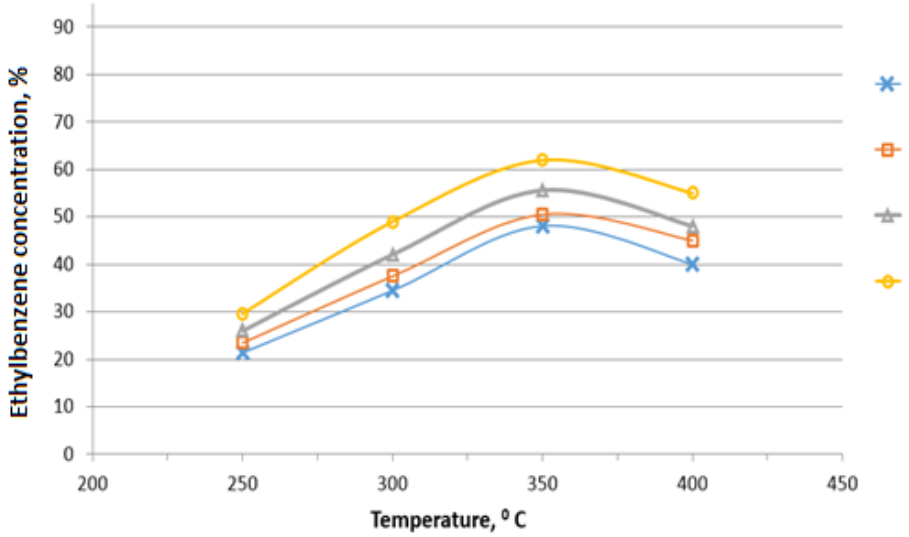


Fig. 9 Ethylbenzene concentration (%) in the final reaction using different catalysts Nd1-Nd 4 and temperatures:$\Delta - Nd\ 1; o - Nd\ 2\ ; \square - Nd\ 3\ and x$-Nd 4

Conversion of the benzene increases with the temperature for all catalysts, but, also with the acidity of the catalyst (Fig. 6). At high temperature (400^0C), the influence of the total catalyst acidity is more important (high benzene conversion).

The concentration of EB in final reaction product increases with temperature, and with acidity of the catalysts (Fig. 7). This behavior is similar to other zeolites with similar topology (three-dimensional network of interconnected channels), for example in the case of the zeolite beta [13] has been found that by increasing the acidity, increases the yield of the EB (test carried out at 300^0C in excess of benzene to DEB).

In our work, the study was conducted at molar ratio B/DEB=2/1 mole/mole. We observed that the use of a H-ZSM-5 catalyst having a topology with three dimensional interconnected channels reduces significantly the formation of coke on the catalyst after 120 h of working. On these results, we suggest to use a H-ZSM-5 catalyst with high ratio Al/Si at 350-400 ^{0}C for transalkylation on reaction of DEB with benzene to obtain EB. By modification of the catalysts (cat 1-cat 4) with neodymium (Nd 1- Nd 4) and after chromatographic analysis of the transalkylation mixture, the reactivity of the benzene is not modified (see Fig. 8), but their yield in EB (Fig. 9) has a maximum value at $\approx 350^0$C.

4. Conclusions

- In this work, 4 zeolite catalysts (H-ZSM-5) with different SiO_2/Al_2O_3 ratios have been prepared and characterized and then modified with Nd.

- EB conversion increases with temperature and total acidity for both cat 1 – cat 4 and for those changed with Nd.

- Concentration of EB in the final reaction mixture increases with the total acidity of the catalyst and with reaction temperature for cat 1- cat 4. For the catalyst Nd1- Nd4 the yield in EB has a maximum value at $\approx 350^0$C.

- On these results, we suggest to use H-ZSM-5 catalyst with high ratio Al_2O_3/SiO_2, and high temperature (350^0C-400 ^{0}C) for transalkylation reaction of DEB with benzene in order to obtain EB. In the case of modified catalysts with Nd, we recommend to work at $\approx 350^0$C.

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