Benzene Alkylation by Ethanol over Catalysts on the Base of Modified Natural Zeolites

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Abstract

Alkylation of aromatic compounds with ethanol was researched on modified natural zeolites of Kazakhstan deposits. These natural zeolites were identified as Clinoptilolite-Heulandite type. Zeolites were treated by hydrochloric acid, which leads to removal of some of the cations and to dealumination. They were modified by metals of II-III groups and mixed with synthetic zeolites Y and ZSM-5. The catalysts were characterized by elemental analysis, scanning electron microscopy, thermal analysis, BET and temperature-programmed desorption of ammonia. It is shown that natural zeolites, treated by acids and modified by metals, as well as synthetic zeolites can be used as catalysts for process of alkylation of benzene by ethanol. They demonstrate high activity and 71% selectivity in synthesis of ethylbenzene.

Introduction

Alkylation of benzene is one of the important methods of processing of hydrocarbon raw materials because products of this reaction – ethylbenzene and styrene - are the basic products of petrochemical synthesis. Ethylbenzene is a component for synthesis of styrene – a monomer of polystyrene production, which output in the world is continuously increasing. In industrial process the alkylation is carried out over ecologically dangerous catalysts such as HF, H_2SO_4, $AlCl_3$, BF_3. Carrying out of this process environmentally friendly, corrosion-resistant and over solid acid catalysts is an important and urgent task. Now synthetic zeolites are widely used as ecologically clean and efficient catalysts for many petrochemical processes, including alkylation. Recently much attention is paid to the development and implementation of zeolite catalysts for the production of ethylbenzene [1-2]. Zeolite catalysts commonly replace traditional catalysts in oil processing and in petrochemistry, due to their unique crystal and adsorption properties, providing a high catalytic activity [3].

According to the Resolution of the Government of the Republic of Kazakhstan on October 13, 2006 №989 diversification of Aktau plant of plastics will be held on the base of complete technological scheme of polystyrene production based on benzene alkylation to ethylbenzene, production of styrene and its polymerization. Production of ethylbenzene will reach 127 thousand tons per year on petrochemical complex on the basis of benzene and para-xylene. In this aspect it is very important to develop highly effective and eco-friendly catalysts for studied process.

Kazakhstan possesses rich deposits of natural zeolites. Synthetic zeolites are usually expensive, so the purpose of this article is an attempt to engage local raw materials – natural zeolites of Kazakhstan for use in the alkylation process. In the present work we investigated zeolites of Kazakhstan deposits, studied their physicochemical modification.

Experimental

The process of alkylation of benzene with alcohols over zeolite catalysts was carried out in a flow type system under atmospheric pressure. Natural zeolites of deposits of Kazakhstan

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(Shankanay and Kerbulak) were used as catalysts. Before the experiments the catalyst was activated in a stream of air at temperature of 600°C during 1 hour. Experiments were carried out in flow-bed reactor under the following conditions: temperature – 450°C, the reactor was fed with reaction mixture of benzene and ethanol with molar ratio of $C_6H_6:C_2H_5OH = 3:1$ at Liquid Hourly Space Velocity (LHSV) of 0.86 h^{-1}.

The catalysts were characterized by elemental analysis, scanning electron microscopy, thermal analysis, BET and temperature-programmed desorption of ammonia. Analysis of the reaction products as performed by Chrom-5 gas chromatograph with a packed bed column 5 m long filled with 10% SE-30 – Chromaton NAW.

Results and Discussion

Treatment of Natural Zeolites

Zeolite of Shankanay deposit has the following composition (% mas.): K_2O – 1,38; Na_2O – 0,95; Fe_2O_3 – 0,16; Al_2O_3 – 10,81; CaO – 2,32; MgO – 0,93. According to the results of physico-chemical analysis Shankanay zeolite has high thermally stability and refers to a group of the high-silicon zeolite Clinoptilolite-Heulandite. Zeolite of Kerbulak deposit is also considered as belonging to a group of Shankanay.

So far, the most studied and widely used natural zeolite is clinoptilolite. In the natural clinoptilolite the molar ratio of mass reaches 9-10 and more [4]. Clinoptilolite belongs to a group of $7(T_{10}O_{20})$ with typical unit cell composition $Na_6[Al_6Si_{30}O_{72}]\times 24H_2O$ [5-6], and overall chemical composition: SiO_2, $6Al_2O_3$, $3Fe_2O_3$, MgO, CaO, Na_2O, H_2O.

Thermal analysis of investigated zeolites by gravimetric method allows for one cycle heating of the sample to obtain information about its sorption capacity of various forms of chemically bounded water, phase of transformation in solids, the threshold of thermal stability and the presence of decomposed substances. Comparison of thermograms of Shankanay zeolite with other types of zeolite, namely stilbit, clinoptilolite, heulandites from the literature [3, 4] showed that this sample is characterized by increased thermal resistance, as well as clinoptilolite.

The DTA curve of the Shankanay zeolite (a) presented on Fig. 1 is similar to the curves obtained from DTA measurements of stilbit (b), clinoptilolite (c) and heulandites (d). These curves showed that all samples have high thermal stability. In addition they have high mechanical strength as compared to synthetic zeolites.

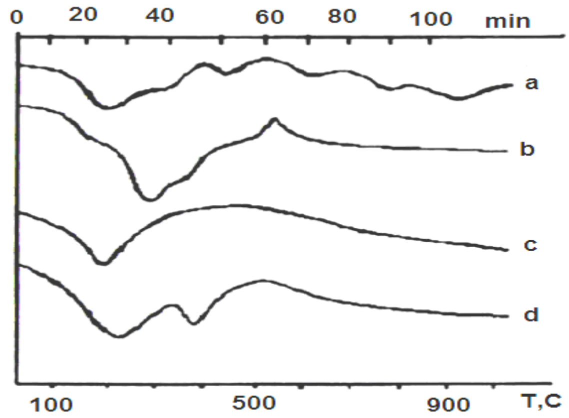

Fig. 1. Thermograms: a – shankanay zeolite; b – stilbit; c – clinoptilolite; d – heulandites.

Natural zeolites are usually catalytically inactive, because of presence of big amounts of unwanted oxides such as iron oxide and others. Therefore it is necessary to activate the natural zeolites, and for this purpose the acid treatment was used.

In [7] it was shown that treatment of natural clinoptilolite with hydrochloric acid leads to removal of cations and dealumination. With increasing of acid concentration the H-form of acid is replaced by the extraction of aluminum and basic cations in the liquid phase. Of course, hydrochloric acid is highly corrosive, but we believe that the use of hydrochloric acid to improve the content of natural zeolites is an optimal method. Method of removing cations from zeolites with ammonium chloride is known, but the preliminary studies of our zeolites showed that it is less effective than the method with hydrochloric acid.

Processing of natural zeolites was carried out with HCl solutions of different concentrations at temperature interval of 50-100°C followed by filtration on vacuum filter and washing of sample with distilled water. We studied the impact of temperature, duration and diffusion factor, the ratio of zeolite: acid. Selection of optimal conditions of acid treatment has been done. The results of elemental analysis of natural zeolites before and after treatment are shown in Table 1.

Alternating of thermal and acid treatment was performed to increase the extraction of aluminum, iron, calcium, sodium, potassium and magnesium from zeolite. Thermal treatment was carried out by heating the zeolite sample in a muffle furnace at 500-550°C for 6-8 hours.

Table 1

The content of oxides in natural zeolites before and after acidic treatment

Oxide	Kerbulak zeolite		Shankanay zeolite	
	before, %	after, %	before, %	after, %
SiO_2	63.0	69.8	62.0	68.9
Al_2O_3	10.2	7.5	9.0	6.4
Fe_2O_3	14.3	4.7	10.5	2.8
CaO	2.7	2.1	2.9	2.1
MgO	2.3	1.8	2.5	2.1
Na_2O	1.9	1.6	1.6	1.4
K_2O	2.5	1.4	2.0	0.8

Acid activation of natural zeolites causes a strong change in the chemical composition of zeolites towards increasing the content of silica and reducing the amount of Fe_2O_3, CaO, MgO, Na_2O and K_2O.The most important observation is that with increasing of acid concentration the content of SiO_2 increases and the content of Al_2O_3 reduces.

XRD analysis of these zeolites before and after acidic treatment showed that their crystalline structure is preserved. Acid activation of natural zeolites in essence does not change the crystalline surface of the zeolite particles and shows that this process involves the release of more effective crystal surface by the removal of foreign substances and the substitution rates of metal ions on the hydrogen ion.

Modification of Natural Zeolites by Metals

Metal ions have significant effect on the activity and selectivity of zeolites in the acid-base reactions. Therefore zeolites are subjected to modification by adding metals. At the beginning we have used a variety of metals-modifiers and their combinations ranked on their catalytic properties. Secondly, for each added metal we analyzed and compared types of active positions of metals in the zeolite matrix to their acidic and catalytic properties.

It was established that the introduction of Group II metals (alkaline earth elements) leads to a change in the distribution of acid sites on the surface of zeolites [8]. The authors of [9] showed that the addition of Ca as a promoter to zeolite reduces coking of catalysts during catalytic reactions. It was established that the modification of zeolites by lanthanide group metals, in particular, La and Ce, increases the thermal stability of catalysts [10]. Introduction of La cations to zeolite also contributes to the selectivity of the process of alkylation of aromatic hydrocarbons. Following metals: La, Ce, Mg have been investigated as modifiers for our catalysts.

We studied the correlation of zeolites acidity with the nature of the metal-modifier. Acidity of zeolites was measured by TPD of ammonia. With changing of the metal the number of weak, moderate and strong acid centers decreases as well as total acidity was also decreased (Table 2).

Table 2

Change of the acid characteristic of the modified Shankanay zeolite

Metal	T_{max} of peak, ^oC			Number of acid centers, mmol NH_3/g cat			∑ Acid centres, mmol/g
	I	II	III	I	II	III	
-	110	250	430	0.38	0.55	1.34	2.27
Mg	100	340	470	0.19	1.21	0.51	1.91
La	120	330	410	0.23	0.75	0.86	1.84
Ce	80	215	400	0.21	0.54	0.85	1.61

This fact is explained by the removal of aluminum from the zeolite – aluminum as we know provides a surface acidity of the zeolite. However, the number of Lewis centers slightly increased with the introduction of transition metals.

Thermo-acidically treated and modified zeolites were tested in the alkylation of benzene with ethanol (Table 3). Initially thermo-acidically treated zeolite showed low catalytic activity. It is shown that the modification by Mg, La, Ce metals decreases the total acidity as well as the number of acid sites of medium strength. The surface of catalysts modified by magnesium and lanthanum contains of number of centers of high acidity and the total acidity is 1.91 and 1.84 mmol/g, respectively. In the case of Ce the total acidity totals to 1.61 mmol/g and the number of centers is significantly reduced, which probably leads to the reduced activity of the catalyst modified with the metal (Table 3).

According to [11] in the zeolite catalysts lanthanides are in the form of oxides and they are uniformly distributed on the surface. La and Ce form new active centers on the surface of the zeolite for the alkylation process. It is also known that the modification of zeolites by metals of Group II changes the distribution of acid sites in zeolites. The authors of the study [12] showed that zeolite catalysts exhibit the maximum activity if there are no strong Bronsted and Lewis acid sites. The most active catalysts have mainly acid sites of medium strength.

Table 3 presents data for the alkylation of benzene with ethanol over the treated natural zeolite modified by metals. By itself, the natural zeolite has a very low activity. Modification of natural zeolite Shankanay increases conversion of benzene from 23 to 64%, the yield of ethylbenzene from 15 to 60% and selectivity to ethylbenzene from 65 to 94%.

Table 3

Alkylation of benzene by ethanol over zeolites modified by metals

Catalyst	Benzene conversion, %	Ethyl-benzene yield, %	Selectivity on ethylbenzene, %
Zeolite (Shankanay)	23	15	65
+ Mg	61	56	92
+ La	64	60	94
+ Ce	62	58	93

The ranking of modifiers by their influence on catalytic activity is:

La > Mg > Ce

We studied the influence of the nature of the precursor – metal salt: nitrates, acetates, chlorides and carbonates on the activity of the modified zeolites. The most active catalysts prepared from magnesium nitrate and lanthanum nitrate increase the maximum conversion of benzene to 64%, the yield of ethylbenzene to 60% and the selectivity to ethylbenzene to 94%. According to these indicators magnesium precursors are arranged in the following: nitrate > carbonate > acetate > chloride. The lanthanum precursors are located in the following series by activity: nitrate > carbonate > chloride > acetate.

Modification of Natural Zeolites by Synthetic Zeolites

In addition to the modification of natural zeolites by metals, synthetic zeolites Y and ZSM-5 were introduced to natural zeolites in the amount of 15-20%.

Catalytic systems prepared three ways: 1 – mechanical mixing of zeolite, 2 – application of synthetic zeolite on natural zeolite, 3 – mixing aqueous suspensions of zeolites. The application of synthetic zeolite on natural zeolites proved to be optimal.

Modification of zeolites leads to higher conversion of benzene from 23 to 60%, yield of ethylbenzene from 15 to 55%, selectivity for the formation of ethylbenzene from 65 to 92% (Table 4). As an additive ZSM-5 was better than Y zeolite. Among the metals La was the best modifier, which increased the conversion of benzene to 64%, yield of ethylbenzene to 60% and selectivity for ethylbenzene to 94%. Twice modified zeolite (with La and by the addition of ZSM-5) showed the maximum benzene conversion 72%, yield of ethylbenzene to 69% and selectivity of 96% (Table 4). The combination of magnesium and lanthanum as modifiers to the Shankanay+ZSM-5 catalyst led to a better results: for benzene conversion 75%, ethylbenzene yield 73% and selectivity on ethylbenzene 97% (Table 4).

Table 4

Alkylation of benzene by ethanol on modified zeolites

Catalyst	Benzene conversion, %	Ethylbenzene yield, %	Selectivity on ethylbenzene, %
Zeolite (Shankanay)	23	15	65
+ Y	54	48	88
+ ZSM-5	60	55	92
+ ZSM-5 + La	72	69	96
+ ZSM-5 + La+ Mg	74	71	96

In industry the synthesis of ethylbenzene by alkylation of benzene with ethylene is conducted on the $AlCl_3$, BF_3 catalysts. The yield is up to 75%. But the selectivity of industrial process is not high because there are a lot of by-products like toluene, isomeric xylenes etc.

The use of ethanol as an alkylating agent is a new and unexplored process. Chosen catalysts must be more active than usual because they must provide the dehydration of ethanol as the first step of this process. The reaction proceeds by following mechanism:

$$C_6H_6 + K - H^+ \rightarrow H^+ - C_6H_6$$
$$CH_3 - CH_2 - OH + K \rightarrow CH_2 = CH_2 + K + H_2O$$
$$H^+ - C_6H_6 + CH_2 = CH_2 \rightarrow C_6H_5 - CH_2 - CH_3$$

The first stage of the process is the interaction of benzene with protonated surface active center forming intermediate surface complex H^+-C_6H_6. In the next step ethanol molecule reacts with different active catalytic centers and dehydration of ethanol takes place to form ethylene. On the third stage protonated complex interacts with gas phase molecule of ethylene to form the final product ethylbenzene.

Table 5 shows the data of the surface area measurements of the catalysts samples by BET method. The surface area of analyst Shankanay + NZSM-5 is reduced by the modification with magnesium and increases with the modification by La and Ce. Pore radius decreases, which is reflected in the decrease in pore volume.

Table 5

BET characteristics of catalysts Shankanay+HZSM-5

Catalyst	S, m^2/g	$V_{ADS\ ml}/g$	V, ml/g	R_{ef}, nm
Shankanay+HZSM-5	307.90	285.20	0.44	1.0-7.7
Mg/Shankanay+HZSM-5	264.28	216.76	0.39	0.8-7.7
La/Shankanay+HZSM-5	321.05	248.85	0.39	0.8-7.6
Ce/Shankanay+HZSM-5	310.72	232.56	0.36	0.8-7.6

It is known that synthetic zeolites have a low mechanical strength. This parameter is very important for industrial processes. As a result of modifying the strength of the synthetic zeolites increases as shown in Table 6. Crushing strength of zeolites was measured by standard methods on the device PC-1. In the case of two zeolites Y and ZSM-5 (clean and with the addition of natural zeolite Shankanay) the mechanical strength increases from 0.001 to 0.08 kg/mm^2 (Table 6).

Table 6

Change of mechanical strength (kg/mm^2) of zeolites

Y	Y+ Shankanay	ZSM-5	ZSM-5+ Shankanay
0.001	0.05	0.002	0.08

Electron-microscopic study of thermo-acidic treated and modified zeolites was carried out (Philips XL30CP CDS Oxford INCA 250). Accumulations of dispersed particles of size ~ 5.0 nm are visible on micrographs of the sample of catalyst, La/Shankanay+HZSM-5 (Fig. 2). Micro diffraction picture of pattern shows continuous rings and the corresponding modification of La_2O_3 (JCPDS, 24-554). Their formation is caused by oxidation of La on the surface of an acidic zeolite. In the present sample there are also local accumulations of dispersed particles of 3.0 nm La_2O_3.

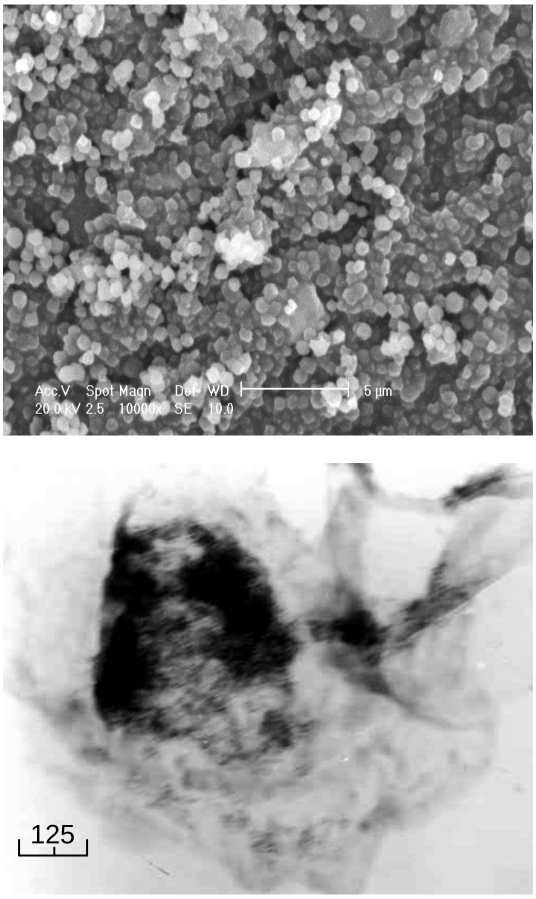

Fig. 2. SEM photographs of La/Shankanay + HZSM-5.

Figure 3 shows a large dense particle size of ~ 120.0 nm. Micro diffraction pattern shows symmetrical strands and can be attributed to the $MgSiO_3$ – clinoenstatite (JCPDS, 35-610).

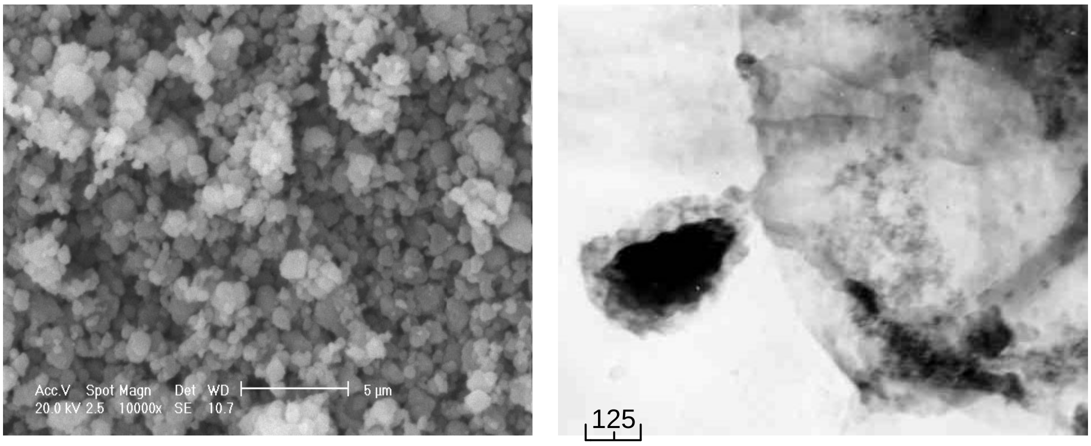

Fig. 3. SEM photographs of Mg/Shankanay + HZSM-5.

On the sample Mg+La/Shankanay+HZSM-5 dispersed particles of size ~ 5.0 nm in the form of clusters of particles were found (Fig. 4). Micro diffraction pattern shows continuous rings and the corresponding modification of La_2O_3.

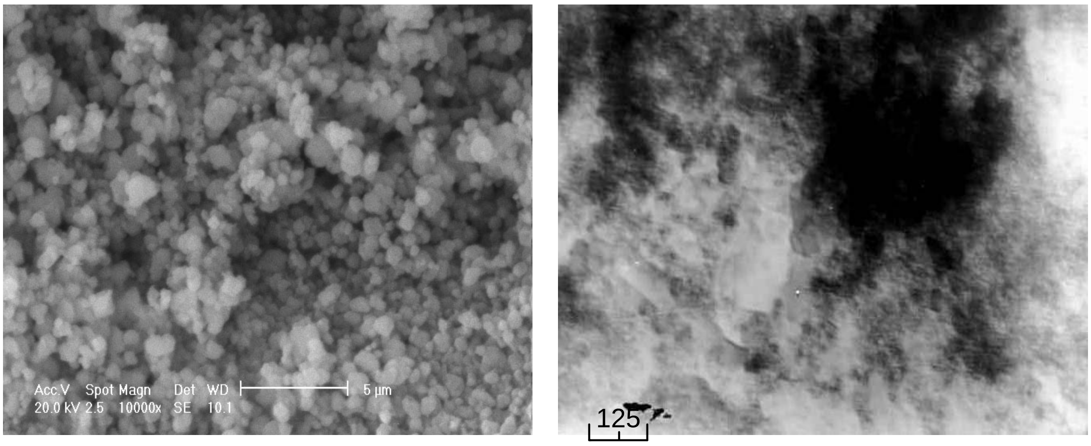

Fig. 4. SEM photographs of Mg+La/Shankanay + HZSM-5

Conclusions

It is shown that natural zeolites from Kazakhstan deposits can be used as catalysts in acid-base catalytic processes. Natural zeolites (from Kerbulak and Shankanay deposits) were investigated by gravimetric method and identified as Clinoptilolite-Heulandite type. But usually they are inactive in chemical processes.

By acidic treatment almost all unnecessary oxides were removed according to the data of elemental analysis. Then after double modification (by metals of II-III groups and by synthetic zeolites Y and ZSM-5) natural zeolites obtain high catalytic activity in process of alkylation of benzene with ethanol: conversion of benzene – 74%, yield of etheylbenzene up to 71% and selectivity of ethylbenzene formation 96%.

The data of electron microscopy, BET and temperature-programmed desorption of ammonia revealed the catalyst's optimal acidity, particles sizes and content modifiers which are necessary for preparing the best catalyst

Thus, thermo-acidic treated and twice modified natural zeolites showed high activity in a new process of alkylation of benzene with ethanol. They have some advantages over synthetic zeolites – cheapness, high thermal stability and mechanical strength.

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