

Catalysts for Purification of Waste Gas on the Basis of Natural Zeolites of Kazakhstan

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The results of X-ray structure analysis of clinoptilolite of the Republic of Kazakhstan deposits – Chankanai and Taizhuzgen are represented in comparison with synthetic zeolite of ZSM-5 grade. The article also comprises data about their thermal stability, ductileness and strength of compositions on their base. Metals particles morphology and dispersity are studied by the method of electronic microscopy. These particles were used as active components of synthesized catalysts.

1. Introduction

Rapid development of new technologies goes along with poor conditions of environment, therefore it is required to search for ways stabilizing ecological situation (Koutsonikolas et al., 2013). Among the main pollutants of large cities where there are a number of thermal power stations, industrial enterprises (Mikulčić et al., 2013), a lot of automotive transports, gas emissions is a considerable hazard (Da Silva and Oliveira, 2013). Among the existing methods of gas wastes deep purification the most perspective one is catalytic one in the paper by Akimkhan (2012). High cost of conventional catalysts based on synthetic zeolites containing platinum and palladium considerably limit their practical appliance. Catalyst work efficiency depends on content and nature of active component, presence of modifying agents and technology of producing catalysts by Ono et al. (2011). The catalyst carrier determines thermal and chemical endurance, work stability and catalyst durability in certain conditions of catalytic process (Krylov and Matyshak, 1996), as well as final cost of commercial catalyst in the paper by Rivera (2000). Currently positive results were achieved only on ZSM-5 zeolites. The given article for the first time consider the opportunity to use natural zeolites of Kazakhstan as catalyst carrier in the form of granules, tablets, and blocks for gas purification catalyst in order to create technology of producing effective, cheap and available catalyst for conversion NO_x, CO and hydrocarbons of thee gas wastes from thermal power stations and vehicles.

2. Methodology of carrying out experimental researches

As research objects natural zeolites of Kazakhstan and widely applied synthetic zeolite of ZSM-5 grade were used. Natural zeolites were taken from Chankanai deposit (located in Kerbulak region of Almaty oblast) a Taizhuzgen deposit (located in Tarbagatai region of East-Kazakhstan oblast). Synthetic zeolites are produced are produced at “Angarsknefteorgsintez” (Si / Al = 40) as Novikova (2013).

Zeolites samples were in crude form as tuff that was crashed, and also granulated as well as in the form of tablets and blocks. X-ray structure analysis of the zeolites samples was carried out on diffractometer "Ultima IV" produced by Rigaku (Japan) and on X'Pert PRO produced by "PANalytical" (Holland). For this purpose original zeolite had been crushed to the 10 μm - sized particles, put it into the X-ray dish and surfaced the powder in the dish.

Electron microscope investigation of the samples was carried out on analytic scanning electron microscope of Hitachi SU70 mark.

For scanning electron microscope samples preparation was carried out by spreading the sample in the form of powder on two-side electro conductive scotch and further spraying on the conductive base. Prepared in such manner samples are suitable for topography analysis and particles size as well as quality element material composition.

Researches on raster electron microscope (mark JSM-6390LV) produced by company "JEOL Ltd" (Japan) with the system energy-dispersive microanalysis INCA Energy company "OXFORD Instruments Analytical Limited" (UK) were carried out in the laboratory of engineering profile "IRGITAS" at D. Serikbayev EKSTU (Ust- Kamenogorsk, Kazakhstan).

Samples for raster electron microscope are prepared as common metallographic sections by grinding and further gritting. In order to prepare samples for analysis it's necessary to meet certain requirements. Thus samples surface must be completely flat without any scratches and relief, the researched sample must be exceptionally clean.

Moulding materials were produced by compound and to refraction temperature varying in the wide interval on the basis of domestic natural materials. Moulding materials were used for producing samples of catalyst carrier in the form of pellets, granules and blocks (Mukhlyonov, 1989) and their ductileness and mechanical resistance were studied according to methodology described by Wu (2007).

Samples of synthesized granulated and block zeolite (Regalbuto, 2006) containing carriers that have optimal properties of ductileness and mechanical resistance among the studied ones were applied with catalyst systems Cu-Ce, Cu-Ni-Cr, Ti-V, Ti-V-W, TiO₂-V₂O₅ as in Palma et al. (2013). Their effectiveness in conversion NO_x was determined due to CO or C₃H₆ under conditions of hyper-stoichiometric oxygen concentrations (Schwarz, 1995).

3. Results

It is known that the main disadvantage of natural zeolites that limit their practical appliance is changeability of their chemical composition by Mansouri (2013). Main characteristics of natural zeolites are identical to famous deposits of Ukraine (Sokirnitskoye), Georgia (Tedzamskoye), Russia (Kholinskoye, Kulikovskoye, Vaginskoye), as well Japan (Sainokai), that are widely used in different sectors of the national economy. Comparison characteristics of domestic natural zeolites of different deposits with famous foreign analogues and main characteristics of synthetic zeolite ZSM-5 are presented in Table 1 and Table 2, respectively.

Table 1: Comparison characteristics of natural zeolites of different deposits

Composition	Concentration (%)					
	Chankanai (Kazakhstan)	Taizhuzgen (Kazakhstan)	Kulikovskoye (Russia)	Sokirnitskoye (Ukraine)	Tedzamskoye (Georgia)	Sainokai (Japan)
SiO ₂	60.0-74.0	62.5-68.7	77.2	70.5	59.1	72.1
Al ₂ O ₃	14.0-15.0	13.4-19.2	12.8	12.1	13.4	11.4
TiO ₂	0.1-0.7	-	0.2	-	-	0.2
Fe ₂ O ₃	1.4-5.8	1.3 -4.6	2.9	0.9	-	1.4
MnO ₂	0.1-0.2	0.1	0.1	0.2	-	0.1
MgO	0-2.1	0.8-1.1	0.2	1.1	1.4	2.2
CaO	0.1-6.4	1.0-4.2	1.2	2.1	5.2	1.0
Na ₂ O	0.6-5.5	1.5-3.9	1.4	2.4	2.3	1.3
K ₂ O	0.7-4.0	2.9-4.2	3.9	2.7	1.5	0.5
P ₂ O ₅	0.1-0.2	-	0.1	0.1	0.5	-
H ₂ O	0-4.1	5.7-10.0	-	8.0	-	4.7

Table 2: Comparison and processing properties of synthetic zeolite ZSM-5

Zeolite	Composition oxides	%	Processing properties		SiO ₂ / Al ₂ O ₃
ZSM-5	Al ₂ O ₃	4.2	water vapour	no more 0.1	40
	Na ₂ O	0.1	intan	no more 0.14	
	Fe ₂ O ₃	0.1	BET general surface m ² /g	315	
	ППП	no more 55	external surface m ² /g	70.0	
			overall pore volume cm ³ /g	0.235	

Table 3: Influence of torrefaction temperature on the structure of zeolite Chankanai

Temperature (°C)	Time of heating (h)	Intensity of reflexes (relative unit)				
		SiO ₂ (3.34)	Clinoptilolite (8.95)	Na[AlSi ₃ O ₈] (3.18)	CaCO ₃ (3.03)	Fe ₂ O ₃ (2.52)
100	3	100	210	102	47	30
500	3	170	-	86	40	22
700	5	104	-	210	-	25
1,000	5	94	-	91	-	45

Diffraction patterns of powdered zeolites ZSM-5 from Chankanai and Taizhuzgen after heating in the air at the temperature 500 °C are shown on Figure 1a. It is visible that structures of high-silicon synthetic zeolite and natural aluminosilicates are in general similar they only differ in intensity of peaks from main components that is connected with composition of every sample.

It's known that crystal lattice of aluminosilicates with relation Si/Al more than 20 is resistant to high temperature action (Canafoglia, 2009). In fact, previously zeolite ZSM-5 was researched Rabo (1980) by X-ray phase analysis and the researches proved that high temperature heating in the air (100 °C 3 h, 500 °C 3 h, 800 °C 5 h, 1,100 °C 5 h) doesn't change intensity of synthetic zeolite reflexes. This proves that zeolite lattice is safe and stable. Behavior of natural zeolites was different as in Hagiwara (2002). Initial structure of natural clinoptilolite Chankanai after heating at the temperature 100 °C is presented by reflexes of quartz, clinoptilolite, albite, calcite, and hematite. Further zeolite heating temperature rising results in disappearance of the signal from clinoptilolite after heating to 500 °C and in decrease of reflexes of other body components and its further complete disappearance (Table 3).

Comparative characteristics of thermal treatment influence on zeolites of various types revealed that after heating in air for an hour at 500 °C, the initial structure of natural clinoptilolite is characterised by reflexive actions densification of quartz, by reflexive actions reduction for calcite, albite and hematite, and reflexive actions disappearance of clinoptilolite. Nothing but reflexive actions of quartz with cristobalite structure and feldspar remain on the Chankanai zeolite diffraction pattern after heating-up in air at temperature of 700 ÷ 1,000 °C. Figure 1 demonstrates thermal tolerance of Taizhuzgen zeolite heated-up in air at gradual elevation of temperature during 1 h. It is seen that after initial sample being heated-up at the temperature range of 500 ÷ 1,000 °C the intensity of reflexive actions represented by clinoptilolite (9.9056), quartz (26.7130) and albite (27.89) change. Gradual temperature evaluation of heating-up to 700 °C results in reflexive actions densification of quartz, albite and disappearance of clinoptilolite. After heating-up at 1,000°C nothing but reflexive actions of quartz and albite remain on the diffraction pattern.

On the next stage the influence of incorporation of various transition metals-active catalysts on thermal tolerance of zeolites was examined (Arcoya, 1994). Figure 2 demonstrates the spectra of X-ray fluorescence analysis (XFA) of Taizhuzgen zeolite initial nature and synthetic ZSM-5 zeolite as well as catalysts catalysts based on them after heating-up in air at 500 °C for 1 h.

It is stated that incorporation of transition metal ion on all occasions serves to modification of aluminosilicate crystalline structure particularly after hyperthermal bakeout. Incorporation of cations elements of group III

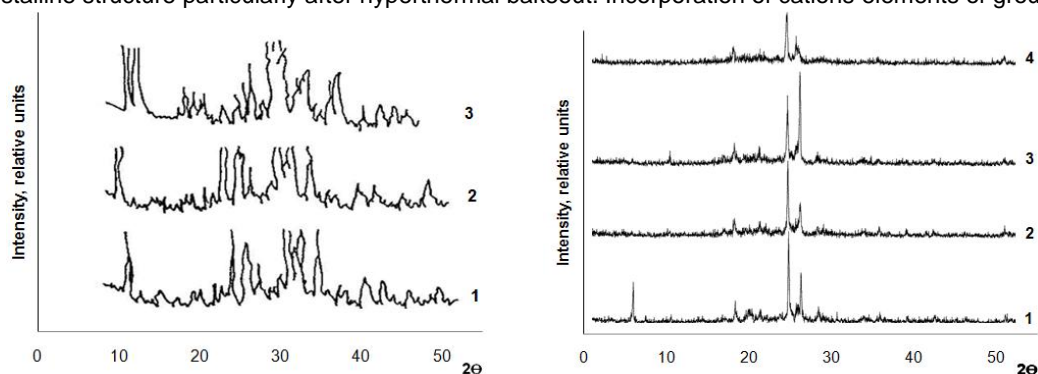


Figure 1a: Spectrums of X-ray phase analysis of different zeolites after heating in the air at the temperature 500 °C: 1 - zeolite Chankanai; 2 - zeolite Taizhuzgen; 3 - zeolite ZSM-5

Figure 1b: Spectrums of X-ray phase analysis of zeolite Taizhuzgen after high-temperature heating for 1 hour: 1 - initial, 2 – at the temperature 500 °C, 3 - at the temperature 700 °C; 4 - at the temperature 1,000 °C

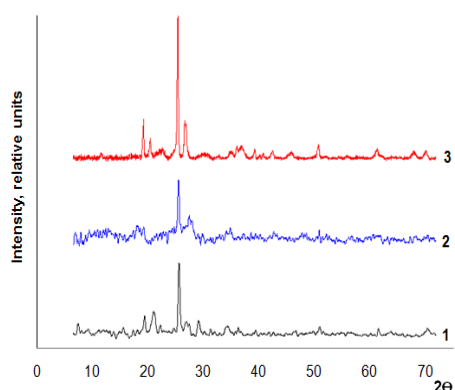


Figure 2a: XRD spectra of Taizhuzgen zeolite and catalysts on its basis after heating-up in air at 600°C: 1 - zeolite; 2 - Cu-Ce/zeolite; 3 - Cu-Ni-Cr/zeolite

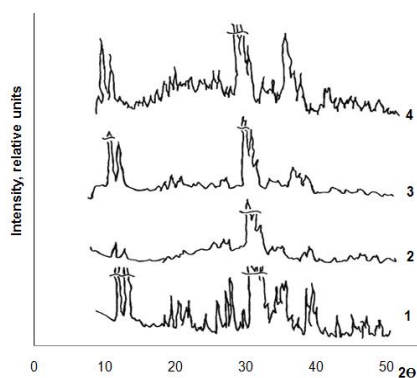


Figure 2b: XRD spectra of ZSM-5 zeolite catalysts on its basis after heating-up in air at 500°C: 1 - ZSM-5; 2 - Cu/ZSM-5; 3 - Ce/ZSM-5; 4 - Cu/Ce/ZSM-5

cerium and group VIII cobalt helps to preserve zeolite frame and to prevent tenorite formation (Figure 2b). It has been found that the amount of CeO_2 changes accordingly to the method and the order of cerium application (Rikhtegar, 2013).

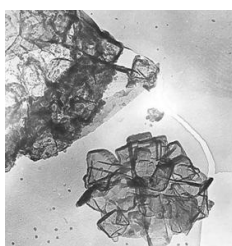
Thus, experimental data show that dissimilarity from ZSM-5, which displays thermal tolerance up to 1,000°C, the initial structure of Cu / ZSM-5, on XRD evidence, at temperature of 500 °C begins to change dramatically, that result in amorphous aluminosilicate formation with copper densification and bakeout temperature elevation. On the other hand we can observe crystal phase of CuO formation on the external surface of support structure. The crystal phase of CuO formation increases at presence of reviewed co-exchangable elements of groups I and II and decreases in the event of cerium and cobalt cations content besides Cu.

Figure 3 demonstrates electron micrograph of original ZSM-5 and Chankanai zeolites, the image was increased 24,000 times. It is seen that ZSM-5 is composed of well-cut crystals primary with domatic shaping when a natural clinoptilolite is composed of crystals of mono-metrical shaping.

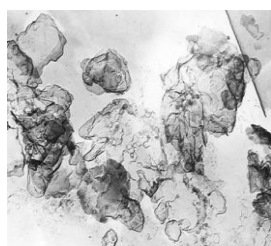
It has been found out that copper and other active components in ZSM-5, as well as in Chankanai zeolite after heating in air at 500 °C appear as fine-grained, drop-shaped particles as big as 2, seldom 4-5 nm. The method of copper incorporation to the matrix of support structure affects the dispersiveness of particles in a minor way.

Figure 4 demonstrates the investigation data of mechanical resistance of the samples obtained in the process of varying of compositions and moulding materials bake out temperatures (Li, 2000). The data were monitored with program product Statistics application.

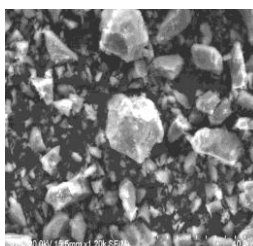
Correspondences analysis shows that when the bake out temperature as well as content of zeolite in moulding material increases from 50 % to 70 %, mechanical resistance of zeolite-containing ceramic support structure strengthens significantly and gets its peak value that is 29.70 MPa when humidity is 15 %, squeeze pressure is 1.5 t, and bake-out temperature is 1,000 °C.



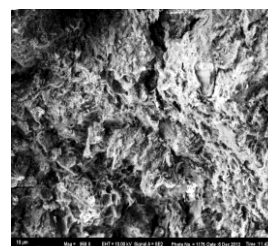
the image is increased in 24,000 times
zeolite ZSM-5



Chankanai zeolite



the image is increased in 1,200 times
Cu-Ni-Cr/Tayzhuzgen



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Cu-Ce/Tayzhuzgen

Figure 3: Electron micrograph of zeolites and catalysts on based on them

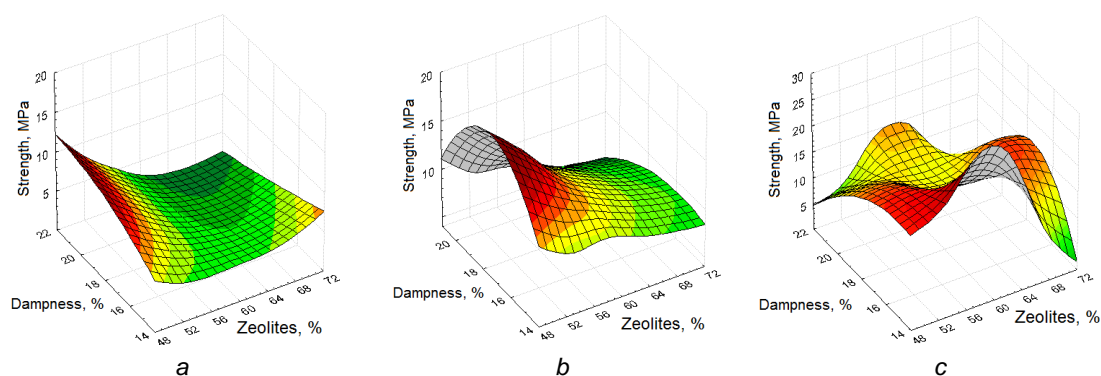


Figure 4: Mechanical resistance of premolds made from zeolite-containing support structure depending on the amount of zeolite and humidity at bake out temperature variation: a - 500 °C; b - 750 °C; c - 1,000 °C

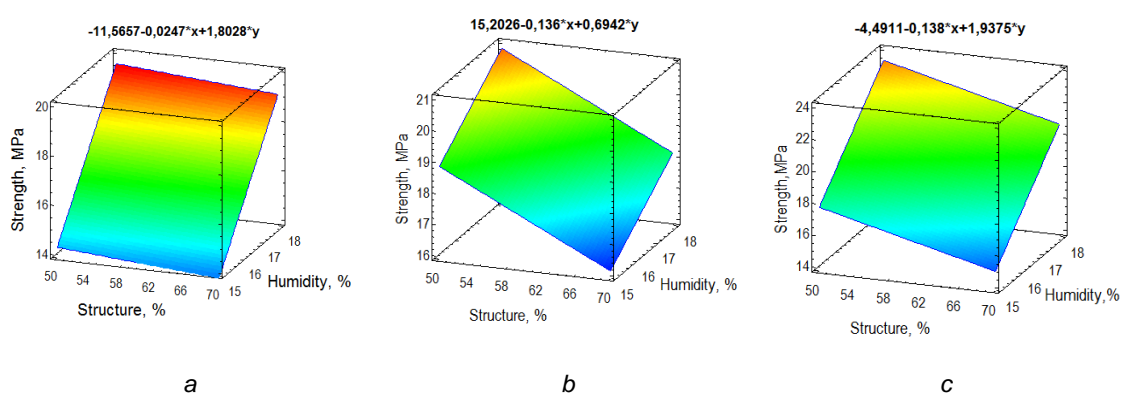


Figure 5: Mechanical resistance of premolds made from zeolite-containing support structure depending on the amount of zeolite at constant bakeout temperature: 750 °C and squeeze pressure variation, t: a - 0.5; b - 1.0; c - 1.5

The influence of squeeze pressure on mechanical resistance of the samples investigated is examined with graphic editor Stat graphics usage. Graphic editor Stat graphics makes it possible to obtain not only elemental statistics and correlative matrixes but also execute basic mathematic-analytical procedures (component, regressive, dispersive, discriminant and clustering analysis of the data) (Figure 5).

It is shown, that mechanical resistance of premolds made from zeolite-containing support structure during reconstruction by means of zeolite amount increasing from 50 % to 70 % strengthening from 19 to 24 MPa in direct proportion with squeeze pressure elevating from 0.5 to 1.5 t.

4. Conclusions

Thus, the data of X-ray diffraction analysis testify insufficient thermal tolerance of natural zeolite in comparison with synthetic one as when being heated up at 500 °C in air, alteration of its crystalline structure begins. In consequence of this alteration we gain the mixture of various minerals and oxides and the number of combinations may be magnified more than 2 times depending on heating-up temperature.

On the electron micrographs of the investigated samples of zeolitized massive material we can observe accumulations of needle-shaped microcrystals as well as in the form of elongated prismatic units that form in the sides of interstices and cracks. All this indicates the complex micro surface profile shaped by microcrystals and units represented by fine-grained substance.

Obtained data as well as the analysis of literary sources by Hagiwara (2003) let us to conclude that the structure of natural zeolite may be improved by means of various modifiers in corporation (Zaleska, 2008) and by means of regime fitting of thermal training of samples.

It is demonstrated that developed compositions of moulding materials for manufacturing the support structure for catalysts of gas cleaning in the form of granules and premolds meet the demands concerning plastic properties and mechanic resistance (Tatsumi, 1999). It is stated that the optimal value of mechanic resistance is 27.6 MPa is provided when the ratios of zeolite / bentonite in moulding materials makes 60 / 40 and heating-up temperature equals 1,000 °C during per hour in air.

On the ground of above-mentioned facts we may conclude that natural zeolites of the Republic of Kazakhstan after further investigation and modification their properties can be real alternative to synthetic zeolites in various sectors of national economy as they are obtainable and cheap mineral raw materials.

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