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Synthesis of Zeolitic Material on the Basis of Natural Raw Material Volcanic Ash in Presence of Tetraethylammonium Iodide

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Abstract

Zeolitic material as Na-mordenit ($SiO_2/Al_2O_3 = 10$) was synthesized on the basis of natural raw material volcanic ash, in presence of organic components tetraetilamonium iodide (TEAI). The ash sample used in the laboratory experiments contains 67%, 56% SiO_2 and 12.48% Al_2O_3, abundances. The reaction time as well as the influence of TEAI was studied in the zeolitic materials crystallization. The experiments were carried out under hydrothermal conditions, autogenic pressure and temperature of 220˚C, as well as reaction time from 48 to 240 h. Products from this hydrothermal treatment were identified by the rentgenophase analysis methods on the apparatus of BRUKER D2 PHASER and weight-spectroscopic analysis method on the apparatus of ICP-MS Agilent 7700. Of the zeolitic material, the Na-mordenit zeolite was found to be the most effective for the retention of cations Pb^{2+}, Zn^{2+} and Ba^{2+}.

Keywords

Zeolites, Mordenit, Ash, Synthesis, Organic Cations

1. Introduction

The modern scientific and technological progress resulted in the rapid growth of industry and agriculture is accompanied by involvement in economic circulation of non-traditional types of mineral raw materials, one of which is zeolites [1] [2].

It is no secret that the specific crystal structure of zeolite determines the number of very valuable properties, such as thermal stability, adsorption, catalytic activity, acidity, cations exchange and molecular sieves; zeolites

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have important applications in refining processes at the petrochemical industry, as well as gas separation, water purification at mining industry and environmental catalysis [2].

Obtaining of zeolites for drying natural gas, purification of gas and liquid industrial waste from environmentally harmful components, increasing the productivity of a number of branches of agriculture (animal husbandry, aviculture, crop and so on) is particularly important. The rapidly growing demand for zeolites necessitated their production [3]-[9].

Most zeolites are synthesized from commercial (Martucci *et al.*, 2009; Tanaka *et al.*, 2009; Trejda *et al.*, 2010; Morales-Pacheco, 2011; Xue *et al.*, 2012) and natural raw (fly ash, kaolin, bentonite and others) (Moriyama *et al.*, 2005; Terzano *et al.*, 2005; Tanaka *et al.*, 2008; Walek *et al.*, 2008; Font *et al.*, 2009; Kumar *et al.*, 2009; Ríos *et al.*, 2009; Goni *et al.*, 2010; Ahmaruzzaman, 2010) materials. Many of them have been synthesized, at a given temperature and crystallization time, from gels containing Na_2O-Al_2O_3-SiO_2-H_2O. Some sources of silicon are: Na-silicate HS-40 (Sig and Seung, 2004, Chen *et al.*, 2009), Na-silicate, Cab-O-Sil M-5 fused silica (Rivallan *et al.*, 2010), fumed silica (Xu *et al.*, 2010), UltraSil silica TMA-SiO_2 and Cab-O-Sil TMA-SiO_2 (Shvets *et al.*, 2008). On the other hand, some of the sources of aluminum that have been employed are: Na-aluminate (Anuwattana and Khummongkol, 2009, Gupta *et al.*, 2009) and Al-isopropylate (Tosheva *et al.*, 2005). Surfactants of different chain lengths have been used as templates. Among them, the following can be mentioned: $C_{16}H_{33}(CH_3)_3$N-OH/Cl, $C_{12}H_{25}(CH_3)_3$ N-OH/Cl, $C_{14}H_{29}(CH_3)_3$N-Br, C_{16}TMA-OH and C_8TMA-Br (Han *et al.*, 2009, Sakthivel *et al.*, 2009). The use of such synthetic and natural materials leads to the synthesis of such zeolites as the chabazite, phillipsite, analcime.

The aim of the present work is the synthesis of zeolite mordenite based on natural raw materials and structure-forming component tetraetilamonium iodide (TEAI).

In addition it should be noted that the synthesis of the zeolite mordenite is carried out using local raw materials, what leads to a reduction cost price desired product.

This fact motivated us to evaluate the possibility of investigating the reactivity of ash as a raw material in the formation of zeolites and or zeolitic materials [10] [11].

2. Experimental

This article is devoted to the study of the process of preparing a zeolite with an organic component tetraetilamonium iodide (TEAI). The study of zeolitization process in the systems with participation organic component is particularly interesting, because it affects the structure and properties of zeolites (thermal stability, adsorption and catalytic properties). From literature data it is known that if the synthesis is carried out in the presence of large cations such as TEA, then crystallizing the composition of the zeolites become more high silica than normal samples [1].

Also during the synthesis volcanic ash was used from the deposit by named Dzheyranchel of Azerbaijan Republic.

Based on the above synthesis of zeolites based on natural raw materials presents both scientific and practical interest.

The volcanic ash sample was dried at room temperature, ground and the grain size employed in the synthesis was less than 200 mesh. With the aim of converting the volcanic ash into zeolite or zeolitic materials, several experiments were done. The experiments (**Table 3**) were carried out in Parr steel autoclave reactor in static conditions under hydrothermal conditions, autogenic pressure, temperature of 220˚C, with high and low concentrations of TEAI and reaction time from 48 to 192 h. Once the run was completed and the system cooled down, the products were washed off with abundant distilled water and dried at 120˚C for 15 h. The calcinations of samples prepared with template agent were carried out in air at 600˚C for 6 h.

Natural raw material and products from this hydrothermal treatment were identified by the rentgenophase analysis methods (RFA) on the apparatus of BRUKER D2 PHASER and weight-spectroscopic analysis method on the apparatus of ICP-MS Agilent 7700 and X-ray analysis methods (RSA). Of the zeolitic material the Na-mordenit zeolite was found to be the most effective for the retention of cations Pb^{2+}, Zn^{2+}, and Ba^{2+}.

3. Results and Discussion

The chemical composition of the ash was determined by X-ray fluorescence (XRF; **Table 1**), and it was used to carry out the experiments. The volcanic ash (molar ratio SiO_2/Al_2O_3 = 9.2) was collected at the bottom of the

Jeyranchol volcano. Minerals found correspond mainly to kaolinite $Al_2(OH_4)(Si_2O_5)$ (7.17_x, 1.49_9, 3.58_8) and clayey mineral montmorillonite $Al_2(OH)_2{\cdot}(Si_4O_{10}){\cdot}\ mH_2O$ ($9.5 - 20_x$, 4.48_8, 2.55_8) followed by minor amounts of quartz SiO_2 (3.34_x, 4.22_2, 1.81_1); cakhcholonq SiO_2 (4.05_x, 2.494_9, 1.611_8); carbonate $CaCO_3$ (3.03_x, 1.87_3, 3.85_3); feldspar $Ca(Al_2Si_2O_8)$ (3.20_x, 2.509_6, 2.135_6); gypsum $CaSO_4{\cdot}2H_2O$ (4.29_x, 2.87_7, 3.06_6); cordierite $(Mg,Fe)_2Al_3(AlSi_5O_{18})$ (3.00_x, 3.34_9, 8.29_8) and others which probably come from the volcanic ash (**Table 2**).

The reaction product is the result of a chemical reaction between the volcanic ash, NaOH 0.5 M solution at 220˚C temperature reaction whether in presence of TEAI, respectively. Mordenit-like zeolite crystallized at 144 h of reaction time.

As can be seen from **Figure 1** and **Table 3** along with mordenite, analcime and quartz is obtained, wherein

Table 1. Major elements composition of the volcanic ash.

Oxide	Volcanic ash (wt%)
SiO_2	67.56
TiO_2	0.33
Al_2O_3	12.48
Fe_2O_3	1.06
MnO	0.054
MgO	1.51
CaO	4.15
Na_2O	1.95
K_2O	2.31
P_2O_5	0.12
SO_3	0.45
E.C.	7.27
Total	99.24

Table 2. The diffractometeric dates of the volcanic ash.

Volcanic ash		Quartz	Cakhcholonq	Montmorillonite	Illite	Kaolinite	Feldspar	Carbonate	Gypsum	Cordierite
d (Å)	I	d (Å)	d (Å)	d (Å)	d (Å)	d (Å)	d (Å)	d (Å)	d (Å)	d (Å)
17.46	23			17.46						
16.13	22			16.13						
9.96	38				9.96					
8.30	37									8.30
7.68	19								7.68	
7.14	13					7.14				
6.48	21			6.48						
6.36	16						6.36			
4.98	10				4.98					
4.50	26				4.50					
4.43	33			4.43	4.43	4.43				
4.03	74									4.03
3.64	42				3.64					
3.34	100	3.34	3.34		3.34	3.34	3.34			3.34
3.28	28						3.28			
3.19	100			3.19			3.19			
2.79	8					2.79				
2.56	15			2.56	2.56	2.56		2.56		
2.38	15		2.38		2.38	2.38	2.38			

the percentage content of these foods varies depending on synthesis conditions. But the order of present study was to obtain mordenite zeolite, so further research has gone into the synthesis of pure zeolite mordenite. At the beginning of crystallization (0 hour) crystallinity degree of the sample taken from solid phase of RM is equal to 10 wt%. This value corresponds to the amount of preliminarily introduced in RM crystal seed. Dependence of change of static adsorption capacity from duration of crystallization of volcanic ash in sodium silicate solution shows that after 144 hours of crystallization mordenite type zeolite achieves maximum (for this type zeolite) adsorption capacity. This value corresponds to 100% crystallinity degree of zeolite and it is confirmed with RFA data (**Figure 2**).

In **Table 4**, it has been shown the diffractometric datas of the synthesized zeolite mordenite.

After identification of the obtained pure zeolite mordenite by RSA method has been found that the silicate modulus of zeolite is $SiO_2/Al_2O_3 = \alpha = 10$.

Table 3. Experimental conditions and reaction products related to the chemical reaction between the volcanic ash with low and high TEAI concentrations and a 0.5 M NaOH solution.

Run	Volcanic ash (g)	TEAI ml	Time (day)	Reaction products
1	1.00	0.87	6	An + Mor 30%
2	1.00	0.87	10	An + quartz
3	1.00	0.87	8	Analcim
4	2	1.75	6	Mordenite
5	2	1.75	8	An + Mor
6	2	1.75	10	Analcim

Table 4. The diffractometeric dates of the zeolite mordenit.

d (Å)	I	h	k	l
10.210	8	0	2	0
9.007	59	2	0	0
6.697	35	2	2	0
6.549	53	1	1	1
6.398	42	1	3	0
6.034	17	0	2	1
5.783	30	3	1	0
5.119	5	0	4	0
5.016	8	2	2	1
4.801	3	1	3	1
4.515	30	3	3	0
4.840	10	0	4	1
4.129	11	4	2	0
4.000	60	1	5	0
3.760	18	0	0	2
3.463	100	2	0	2
3.386	72	3	5	0
2.888	92	5	1	1
5.016	33	4	0	2

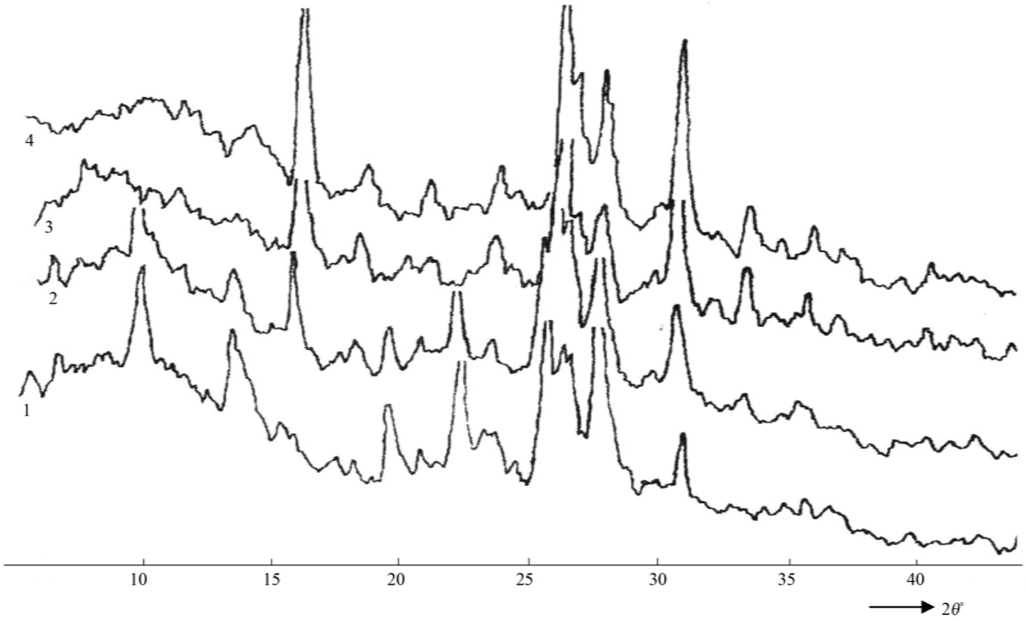

Figure 1. Diffraction patterns of samples obtained during crystallization of volcanic ash-NaOH-TEAI: 1) mordenite; 2) mordenite-analsime; 3) analsime; 4) analsime-quartz.

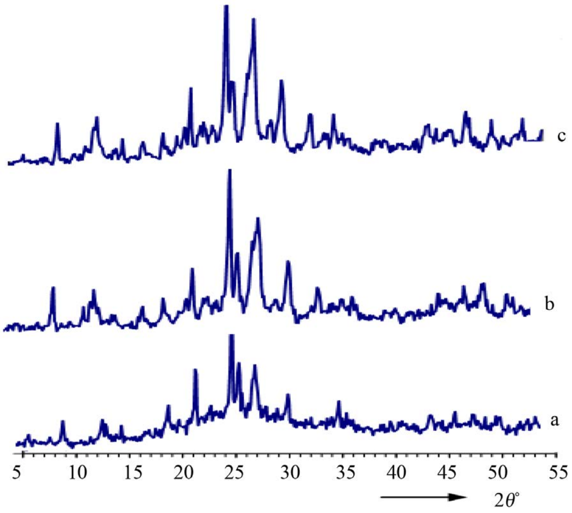

Figure 2. Diffraction patterns of mordenite samples obtained during crystallization of volcanic ash in sodium silicate solution in presence of organic components for: (a) 2 hours; (b) 4 hours; (c) 6 hours.

4. Conclusion

Thus, increase of the crystallization speed of mordenite type zeolite from volcanic ash (compared with known methods) is achieved due to high alkalinity of RM and introduction of crystal seed. Implementation of the developed method allows extending the raw materials base, simplifying the synthesis and reducing the cost of powdery mordenite type zeolite.

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