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Synthesis and Characterization of HS, X and HS + X Type Zeolites from Kaolin and the Study of Their Ion Exchange Capacity for Cu^{2+}, Ni^{2+} and Co^{2+}

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HS, X and HS + X type zeolites are synthesized from kaolin clay having a large amount of impurities such as quartz (39 %) by hydrothermal treatment with NaOH in presence of sodium chloride. The zeolites are crystallized under the optimum hydrothermal conditions and characterized by XRD, FT-IR spectroscopy, BET surface area and SEM-EDS methods. The effects of aging time, crystallization time and crystallization temperature in synthesis of these zeolites are also investigated. Cation exchange capacity (CEC) of X, HS and X + HS (mixed crystallized) zeolites for Cu^{2+}, Ni^{2+} and Co^{2+} were determined that they act selectively for exchanging of Cu^{2+} cation. The cation exchange capacity of these zeolites for mentioned cations were increases as follows: X + HS > X > HS. The XRD patterns of cation exchanged zeolites are also investigated.

Key Words: Zeolite, Kaolin, Hydrothermal, Cation exchange capacity.

INTRODUCTION

Zeolites are crystalline aluminosilicates with uniform pores, channels and cavities and have tremendous industrial applications due to their properties like ion exchange, sorption and catalytic activity. Structurally they have aluminosilicates framework, which are based on an infinitely extending three dimensional network of AlO_4 and SiO_4 tetrahedra link to each other by sharing all of their oxygens. The negative charge on AlO_4 is compensated by cations like sodium[1].

Zeolites have been widely used and studied as ion exchangers, adsorbents and catalysts in industrial processes. For catalytic applications, transition metal ions are often introduced by ion exchange. These metal ions often have easy access to other oxidation states and can coordinated more selectively to guest molecules than filled shell cations, so their introduction into the zeolite allows new mechanisms for their function as adsorbents and catalysts[2]. Zeolites containing transition metal cations have been shown to catalyze a wide range of organic reactions, such as: hydroformylation of olefins[3,4], hydrosulfurization of alcohols[5,6], oxidation of alkenes[7,8], conversion of olefins to thiols[9], decomposition of nitromethane[10], Fischer-Tropsch catalysis[11], *etc*.

Transition metal exchanged zeolites can be prepared in many ways (a) by ion exchange, either from aqueous solutions[12-18] or by solid state reaction[19-21], (b) by hydrothermal synthesis[22] and (c) by adsorption and decomposition of volatile organometalic compounds[23].

According to the process of synthesis of zeolites, kaolin type clays are suitable starting materials for supplying part of the desired constituents. In this research work, we synthesized HS, X and X + HS type zeolites from kaolin of Zonouz zone of Azerbaijan province of Iran. Zonouz kaolin mineral has great amounts of quartz (SiO_2, 39 %), alunite [$KAl_3(OH)_6(SO_4)_3$] (5 %) and oxides of potassium, sodium, magnesium, calcium, iron and titanium (21 %) impurities[24].

The effect of different factors such as time and temperature of aging and crystallization and presence of an alkali metal chloride on synthesis of zeolites and their transformation to other types were investigated. Moreover the ion exchange capacity of the synthesized zeolites was also investigated.

EXPERIMENTAL

The powder XRD spectra of the investigated samples were recorded using Cu-Kα X-ray source on XRD D500 Siemens apparatus. FT-IR spectra were recorded using KBr discs on bruker tensor 27. Atomic absorption spectroscopy analysis was performed on a Shimadzu AA-670G atomic absorption spectrophotometer. Samples were mounted on aluminum using double-sided adhesive tape, coated with gold in HUS-SGB vacuum coating unite and observed in Leo 440i scanning electron microscope. Elemental analysis was carried out using link, ISIS-300, Oxford EDS (energy dispersion spectroscopy) detector. BET (Brunauer-Emmett-Teller) surface areas of samples measured in an all-glass high vacuum system by N_2 adsorption at 77 K. Crystallization of the samples was done within a teflon vessel surrounded by a stainless steel reactor. Kaolin was obtained from Zonouz kaolin mine Co. Other reagents were purchased from Merck.

Synthesis of HS type zeolite: 20 g Kaolin was calcinated at 700°C for about 3 h. The obtained metakaolin was mixed with 34.5 g sodium hydroxide, 7.2 g sodium chloride and 120 mL H_2O. The mixture was filtered after 2 d stirring in room temperature. The obtained material was shaped as granules and then dried in room temperature and mixed again with the filtered mother solution and stayed at room temperature for 2 d.

The crystallization was proceed in 120°C and completed after 26 h. The obtained zeolite crystals were filtered and washed with distilled water till pH = 10, then dried at 140°C. The crystals were characterized by means of powder XRD method and FT-IR spectra.

Synthesis of X type zeolite: 10 g Kaolin calcinated at 700°C for about 3 h. The obtained metakaolin was mixed with 12.8 g sodium hydroxide, 2 g silicic acid, 10 g sodium chloride and 100 mL H_2O. After 72 h stirring at room temperature 5.6 mL hydrochloric acid (conc.) was added to the mixture. The mixture was crystallized at 100ºC during 48 h. The obtained zeolite crystals were filtered and washed with distilled water till pH = 10 and dried at 140ºC. The crystals were characterized by means of powder XRD method.

Ion exchange process: 0.7 g of the synthesized zeolites were mixed with 50 mL of 0.1 M Cu^{2+}, Ni^{2+} or Co^{2+} chloride solutions and stirred for 72 h at room temperature. The cation exchanged zeolites were filtered and washed with distilled water for several times to remove the unexchanged compound. In order to analyze the exchanged amount of the cations, the cation exchanged material was digested in the HF/HNO_3 system and then diluted and measured by atomic absorption spectroscopy and standard addition method. It is worth to be mention here, dehydrated zeolite was made by heating it at 400°C.

RESULTS AND DISCUSSION

Chemical composition[24] of Zonouz kaolin is summarized in Table-1.

TABLE-1
CHEMICAL COMPOSITION OF ZONOUZ KAOLIN

Oxides	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	K_2O	Na_2O
%age	70.05	18.44	0.32	< 0.05	1.45	0.15	0.14	< 0.05

Although kaolin type minerals have a chemical composition which makes them suitable to be as reactants for synthesis of crystalline zeolites. It has been found that Zonouz kaolin type material must has under gone a particular thermal treatment before use[25]. By thermal treatment kaolin shows several transitions when heated in air for a sufficient length of time. These transition observed to begin at about 550-600°C, where the crystalline silicate sheets are apparently altered or disordered, yielding a product, which is essentially amorphous in XRD pattern. This metastable phase is referred to as metakaolin, dehydrated kaolin or dehydroxylated kaolinit[25].

Synthesis of zeolites

After thermal treatment of kaolin that converts it to metakaolin a mixture of reagents is prepared depending on the zeolite type and then undergone a digestion procedure within the aging step. Then the mixture was crystallized. The reagents used are sodium hydroxide and sodium silicate that is needed for preparation of reagent mixtures with suitable molar ratios of SiO_2/Al_2O_3 and SiO_2/Na_2O for synthesis of desired zeolites. The reagent ratios and starting materials are important in present work. Although the nature of the reactions occurring in aging time is not completely understood, however, the aging time is necessary and important for crystallization in next step. In crystallization step, the reagent mixtures of the reactants positioned at 75-120°C at auto genius pressure to gives the desired zeolite crystals.

In order to eliminate some of impurities in preparation of zeolite with desired cation we used sodium chloride. Although the allowed amount of added salt was reported 0.1-5 mol for each mole of Al_2O_3[25], but we obtained the best result in the case of 10 mol sodium chloride for each mol of Al_2O_3.

Synthesis of HS type zeolite

In synthesis of HS type zeolite, in order to obtain the optimized conditions, the effects of different factors were studied.

Washing with acid: Strong inorganic acids such as hydrochloric acid, sulfuric acid, nitric acid, *etc*. are useful for washing. Metakaolin was stirred in hydrochloric acid for 2 h. During this time iron impurity of metakaolin and some of the other impurities are eliminated. The obtained material was filtered and washed till pH = 7. Fig. 1 shows the XRD patterns for zeolite HS obtained from the washed and unwashed metakaolin. The peaks at d = 5.04, 4.82, 3.35 are eliminated in Fig. 1b in comparison to Fig 1a.

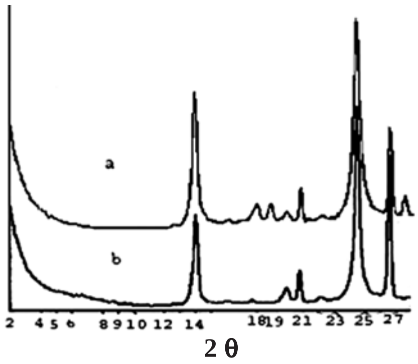

Fig. 1. XRD pattern of HS type zeolite obtained from (a) unwashed metakaolin with acid and (b) washed metakaolin

Increasing of aging time: Increasing of aging time results in more digestion of the quartz (impurity of kaolin) and so the intensity of the peaks related to quartz in the XRD pattern of the obtained zeolite decreases (Fig. 2). However, aging times more than 96 h has no effect on the composition of the obtained material.

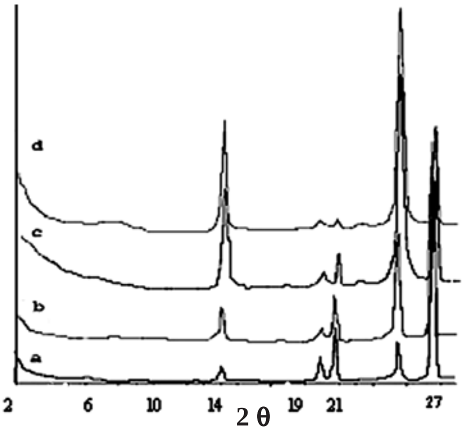

Fig. 2. XRD patterns of HS type zeolite obtained at different aging times (a: 12 h b: 24 h c: 48 h d: 96 h) (crystallization time and crystallization temperature for all of them were 26 h and 100°C respectively)

Shaping and crystallization time: The obtained material after 72 h aging time was filtered. The solid material was shaped as granules and dried at room temperature and then added to the remained solution obtained from filtration. By this way the conversion of metakaolin to zeolite occurs more (Fig. 3) crystallization process is completed within 26 h and after this time no increasing in intensity of the XRD peaks was observed.

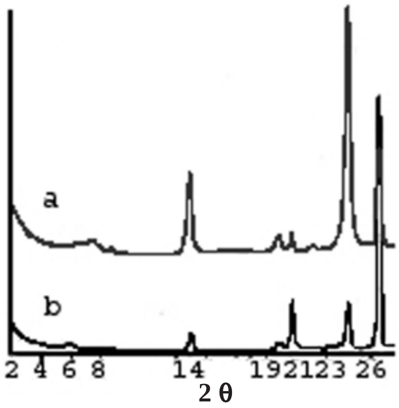

Fig. 3. XRD pattern of HS type zeolite obtained from (a) shaping and (b) non shaping solid material obtained (aging time: 72 h, crystallization time: 62 h and crystallization temp. 100°C)

Increasing of the crystallization temperature: Increasing of the crystallization temperature from 100 to 120°C, when aging time is 96 h, results supports the formation of the quartz and conversion to HS zeolite.

As shown in Fig. 4, the peaks related to the quartz were disappeared completely and the intensity of the peaks related to HS type zeolite were increased and a highly pure zeolite was obtained. Table-2 represents the powder XRD data of the obtained HS zeolite.

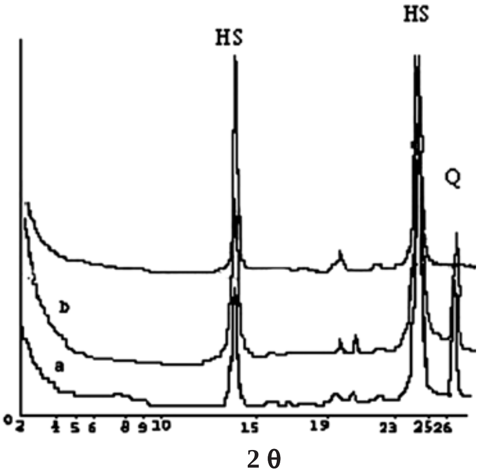

Fig. 4. XRD patterns of results of increasing crystallization temperature (a: 100°C, b: 110°C, c: 120°C). (Aging time and crystallization time for all of them was 96 and 26 h respectively)

TABLE-2
POWDER XRD DATA OF HS TYPE ZEOLITE

d (experimental)	d(ASTM)[2]	d (experimental)	d(ASTM)[2]
6.29	6.28	2.37	2.37
4.46	4.44	2.09	2.09
4.00	3.97	1.98	1.99
3.64	3.63	1.89	1.88
3.12	3.13	1.81	1.81
2.81	2.81	1.74	1.74
2.56	2.56	1.62	1.62

Fig. 5 shows FT-IR spectra of obtained HS zeolite. The peak at 1456 cm^{-1} is related to HS type zeolite[26].

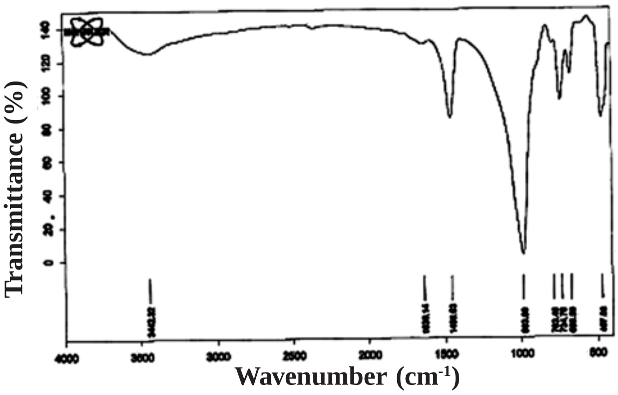

Fig. 5. FT-IR spectra of HS type zeolite

Synthesis of X type zeolite

Synthesis of X type zeolite carried out in presence of NaCl and HCl: Synthesis of X type zeolite was not successful when it was proceed according to the literature in the absence of NaCl and HCl[25].

Optimum ratio of Na_2O/Al_2O_3 and H_2O/Na_2O in synthesis of X type zeolite for starting materials are 5.92, 45.8, respectively. HCl was added to the reaction mixture at the end of aging step, before crystallization step.

Fig. 6 and 7 represents XRD pattern and FT-IR spectrum of the synthesized X type zeolite respectively. FT-IR spectrum is comparable with those of literature[26]. The d values of the XRD pattern of X zeolite are given in Table-3.

TABLE-3
THE d VALUES OF XRD PATTERN OF X-ZEOLITE[2]

d(ASTM)	d(experimental)	d(ASTM)	d(experimental)
14.530	14.505	4.419	4.420
8.878	8.875	4.226	4.226
7.558	7.548	3.946	3.943
5.740	5.741	3.808	3.802
4.819	4.811		

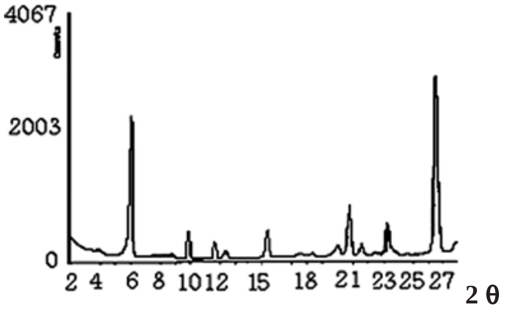

Fig. 6. XRD pattern of obtained X type zeolite (aging time, crystallization time and crystallization temperature were 72 h, 48 h and 100°C respectively)

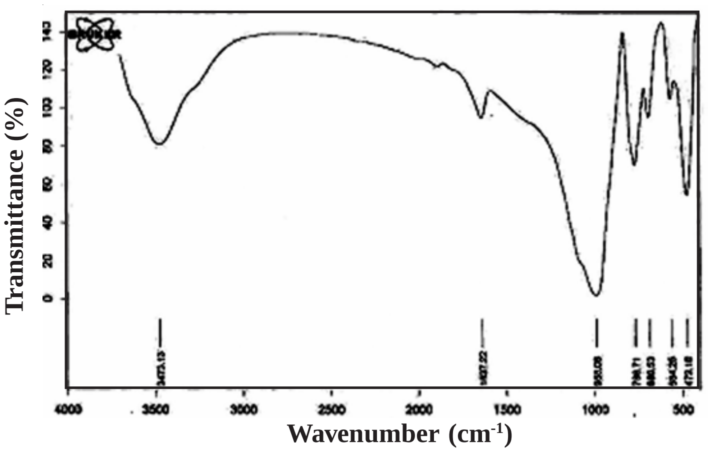

Fig. 7. FT-IR spectra of obtained zeolite (X type zeolite)

It is worth to mention that the peaks at d = 4.266, 4.42 and 3.34 relate to both of X zeolite and quartz.

SEM image of the obtained X zeolite, after hydrothermal treatment is shown in Fig. 8. The size of largest crystal of obtained X zeolite is 2 µm and the energy dispersive X-ray (EDS) of it's are shown in Table-4.

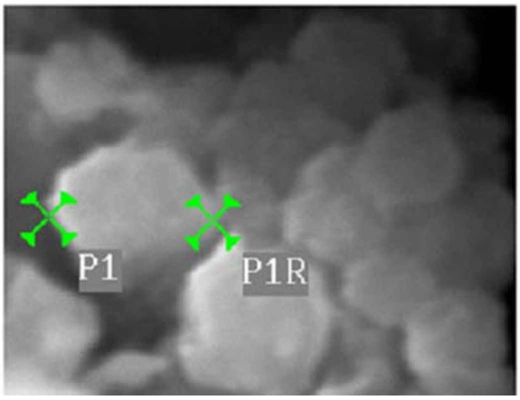

Fig. 8. SEM image of X type zeolite EHT = 25.00 kv WD = 28 mm mag = 10.00 k x

TABLE-4
ENERGY DISPERSIVE X-RAY TABLE OF X TYPE ZEOLITE

Element	Spect. Type	Element (%)	Atomic (%)
Al K	ED	8.62	13.40
Si K	ED	10.65	15.91
Ti K	ED	80.73	70.70
Total		100.00	100.00

The addition of NaCl to the reaction mixture in preparation of X zeolite reduces some of the impurities and is necessary to formation of X zeolite. In the absence of NaCl, only the HS type zeolite accompany with some impurities is formed.

Aging and crystallization time: Increasing of crystallization time, results in the more crystallization of X type zeolite until 48 h. Fig. 9 shows results of increasing of crystallization time from 10 to 48 h. After this time, increasing of crystallization time X zeolite is going to transfer to HS type (Fig. 10) and HS type zeolite was crystallized together with X type zeolite and the intensities of the peaks related to X zeolite are reduced (Fig. 10). It is noted that X type zeolite is metastable phase and HS type is stable[27].

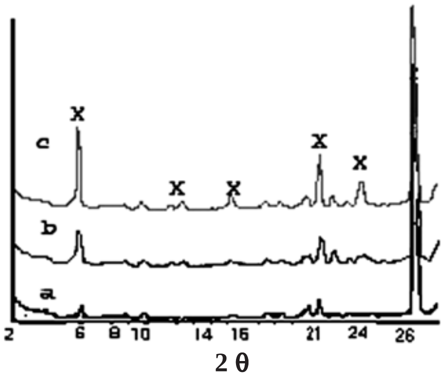

Fig. 9. XRD Patterns of X zeolite (aging time; 72 h, crystallization time was (a: 10 h, b: 24 h, c: 48 h)

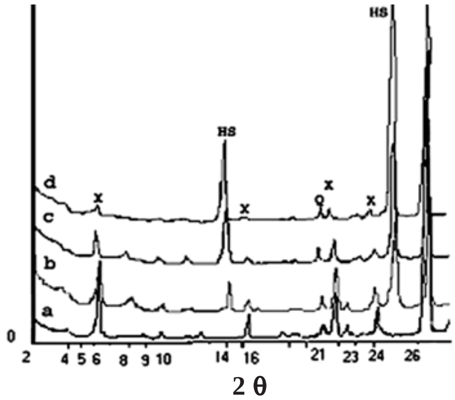

Fig. 10. XRD patterns of obtained zeolite when aging time was 72 h and crystallization time were increased (a: 48 h, b: 58 h, c: 65 h, d: 72 h)

By increasing the aging time over 72 h, HS type zeolite was crystallized together with X type zeolite. The reason is a more digestion takes place on the quartz existing in kaolin composition that converts to HS type zeolite. In this way the mixed crystal (HS + X) is formed. Fig. 11 represents the changes occurring in XRD patterns of obtained zeolite product when the aging time was increased.

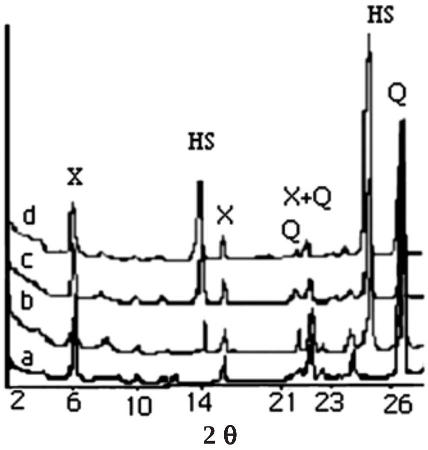

Fig. 11. XRD patterns of obtained zeolite when crystallization time was 48 h and aging time were increased (a: 72 h, b: 85 h, c: 90 h, d: 96 h)

Cation exchanging of zeolites

Cation exchanging of X, HS and (X + HS) (mixed crystallized) zeolites with Cu^{2+}, Ni^{2+} and Co^{2+} were investigated. The zeolites were allowed to experience a cation exchange reaction during 72 h in 0.1 M solutions of the appropriate chloride salts. The amount of the exchanged cations was measured by AAS analysis by using a standard addition method. The results are shown in Table-5. The synthesized zeolites act selectively for exchanging of Cu^{2+} in contrast with the other cations.

TABLE-5
THE AMOUNT OF EXCHANGED CATIONS OF X, HS AND (X + HS) TYPE ZEOLITES

Zeolite	Co(II) (mg/g zeo.)*	Ni(II) (mg/g zeo.)*	Cu(II) (mg/g zeo.)*
X (hydrated)	95	150	220
HS (hydrated)	55	40	205
(X + HS) (hydrated)	110	180	250
X (dehydrated)	48	56	98
HS (dehydrated)	32	28	85
(X + HS) (dehydrated)	56	68	102

*Milligram of cations/1 g of zeolite.

The amounts of the exchanged cations in dehydrated zeolites are much less than in hydrated zeolites. The reduction is due to the changing of pore size of the zeolites because of structural deformation, during heating on dehydration[2].

It is worth to mention the amount of exchanged cation in (X + HS) is more than the individual X and HS zeolites. Cu^{2+} exchanging of zeolites decreases the surface area of the initial zeolites (Table-6).

TABLE-6
THE SURFACE AREA OF INITIAL X AND HS TYPE ZEOLITES AND Cu^{2+} EXCHANGED

Zeolite	HS	HS + Cu^{2+}	X	X + Cu^{2+}
BET (mg/m^2)	113	27	178	28

Conclusions

Zeolites were synthesized from Zonouz kaolin by hydrothermal treatment with NaOH in presence of sodium chloride. The zeolites were crystallized under the optimum hydrothermal conditions. Optimal conditions for NaHS zeolite were 120ºC for crystallization, 96 h aging time and 26 h crystallization time. For NaX zeolite 100ºC for crystallization, 72 h aging time and 48 h for crystallization. Investigations show that, increasing of aging time causes HS and X zeolite mixed crystallized and crystallization time causes the X type zeolite to convert to HS type zeolite by the absence of NaCl in reactants mixture no X type zeolite was crystallized.

Investigations show that the cation exchange capacities of these zeolites are good and selective for Cu^{2+}. Synthesized zeolites have small crystal size and large surface area and the surface area of zeolites decreases by cation exchanging.

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