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PRACTICAL REALIZATION OF HYPOTHETICAL STRUCTURE OF ZEOLITE «m»

S.B.Aliyeva*[1], G.M.Aliyeva[2]

[1]*«OilGasScientificResearchProject» Institute, SOCAR, Baku, Azerbaijan;*
[2]*Institute of Catalysis and Inorganic Chemistry NAS Azerbaijan*

A b s t r a c t

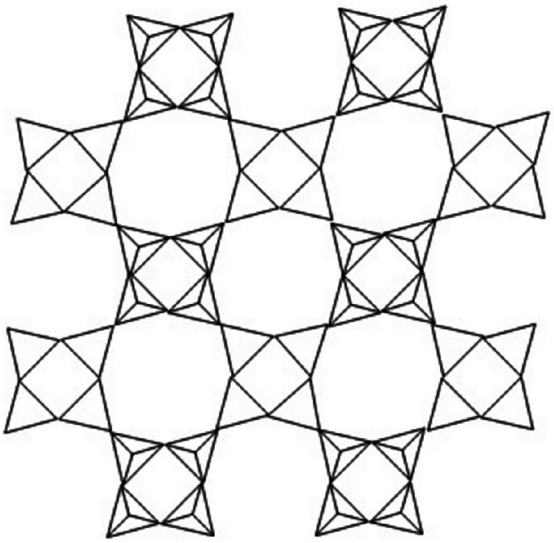
The new version of practical realization of zeolite 'm' from the mixture of metakaoline and obsidian has been given. Formation of initial samples-tablets was proceeded by the dry pressing. The synthesis was realized by hydrothermal crystallization in Na_2O-Al_2O_3-SiO_2-H_2O system at 150 °C. The samples were crystallized in NaOH medium. The study of kinetics and elucidation of mechanism of zeolite 'm' crystallization has been carried out. Phase and chemical composition of crystallization products have been determined by the methods of X-Ray phase, thermographic and X Ray - spectral.

Keywords:
Zeolite «m»;
Hypothetical structure;
Hydrothermal synthesis;
Kinetics.

Introduction

Various structurally possible hypothetical zeolite frameworks were suggested recently [1-3]. However the number of practically realized zeolite frameworks is insignificant in compare with the amount of hypothetical structures. The forecasting of hypothetical structure of zeolites by taking into account of the size of zeolite forming cations with the hydrate cover, the amounts and locations of the pores of the bulk, Si/Al correlation in elementary cell and the conditions of their practical realization stimulate the activities to look for new zeolites in corresponding alumosilicate systems.

One of the forecasting structurally-possible and practically realized zeolite is the zeolite «m» [4, 5]. Its hypothetical structures with cubic symmetry and parameter of elementary cell a=19.5±0.5Å, has the chemical formula $Na_{16}Al_{16}Si_{112}O_{256}{\cdot}64H_2O$. This structure was presented in the figure 1.



$Na_{16}Al_{16}Si_{112}O_{256} \cdot 64H_2O$
Fig.1. Hypothetical structure of zeolite «m»

Experimental

The synthesis was realized by hydrothermal crystallization in Na_2O-Al_2O_3-SiO_2-H_2O system at 150ºC treated with dilute HCl natural glass of kaoline composition and synthetic oxides mixture corresponding to the composition of treated kaolinite.

Initial reaction masses have the following compositions: Na_2O / Al_2O_3 = 5.5 - 6.5;
SiO_2/Al_2O_3 = 21-27;
H_2O/Al_2O_3 = 60-120.

Phase and chemical composition of crystallization products have been determined by the methods of X-Ray phase (DRON-2.5; CuKα-radiation; Ni-filtr), thermographic (Derivatograph Q-1500D, Poulic- Poulic-Ardey) and X Ray - spectral (SRM-18).

Results and Discussions

In this paper the new version of practical realization of zeolite «m» has been given. The purpose of this research is to study kinetics and elucidation of mechanism of zeolite «m» crystallization from the mixture of metakaoline and obsidian. Unlike the earlier work [5] this

*E-mail: samiraaliyevab@gmail.com

Table

The amount of oxides mol for 1 mol Al_2O_3 in reaction mass and products, phase composition of synthezed crystals

№	Composition of initial reaction mass			Product composition			Phase composition of obtained products
	Na_2O	SiO_2	H_2O	Na_2O	SiO_2	H_2O	
1	4.8	22	60	-	-	-	-
2	5.4	21.5	60	1	16	8	«m»
3	6.0	23	60	1	16.2	81	«m»
4	6.6	25	60	1	15.9	8	«m»
5	7.4	24	60	-	-	-	-

synthesis was carried out in the presence of zeolite forming agent- metakaoline as an etching agent which was added to the initial mass-treated with HCl obsidian. In this case the synthesis also was carried out at the 150 °C in the NaOH solution of various concentrations. The chemical compositions of initial reaction masses, the products and phase compositions of obtained crystals are given at the table.

The compositions of the initial reaction masses were prepared in accordance with the method worked out before [5]. The conditions of zeolite «m» synthesis on the base of obsidian in the presence of metakaoline etching were chosen to take into account of the nature and concentration of thermal solution, SiO_2/Al_2O_3 correlation in initial reaction mass and structural feature of expected product.

(Table) the comparably weak crystallizations proceed at Na_2O/Al_2O_3 = 4.8 and 7.4; beyond of these scopes zeolite «m» crystallized feebly. However between above said correlation, zeolite «m» undergoes crystallization with a high degree of crystalline.

The kinetics of zeolite «m» crystallization has been studied. Z% - conversion degree of initial reaction mass into zeolite «m» in a time – τ, hour, was controlled by the method of X Ray – phase analysis and by determination of moisture capacity of samples at the standard conditions.

The kinetic curves of zeolite « m» crystallization from shown at the Table compositions have been drawn up (fig.2). The drawn before kinetic curve [5] of zeolite « m» crystallization also has been presented at figure 2.

The comparison of this curve with other ones has revealed the rate of crystallization of mass with etching twice as much the rate of crystallization of mass without the kaoline at the same concentrations of thermal solutions (curves III and VI).

The analysis of kinetic curves shows:

1. reaction masses 1 and 5 convert into zeolite «m» approximately at 15 and 30% accordingly;
2. the rate of zeolite «m» crystallization from reaction masses 2-4 considerably increases with the small increasing of Na_2O amount in initial reaction mass;
3. zeolite «m» from reaction masses 2-4 crystallizes with the high degree of crystalline;
4. the rate of crystallization of zeolite «m» from reaction masses 2-4 containing metakaoline etching considerably higher than the rate of its formation from same reaction mass without etching.

It will be noted that the reaction mass, without etching as in previously published work [5] crystallization was realized after the stage of «aging» at the room temperature. Zeolites of mordenite and analsime types form from the same reaction mass without of stage of «aging».

Revealed kinetic regularities of crystallization from above mentioned reaction mass are very interesting for elucidation of zeolite « m»

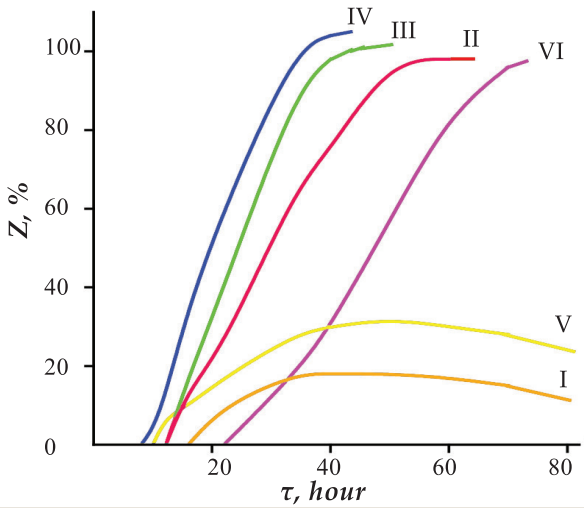


Fig.2. Kinetic curves of zeolite «m» crystallization from reaction mass with following composition:

I – $4.8Na_2O \times Al_2O_3 \times 22SiO_2 \times 60H_2O$
II – $5.4Na_2O \times Al_2O_3 \times 21.5SiO_2 \times 60H_2O$
III – $6.0Na_2O \times Al_2O_3 \times 23SiO_2 \times 60H_2O$
IV– $6.6Na_2O \times Al_2O_3 \times 25SiO_2 \times 60H_2O$
V – $7.4Na_2O \times Al_2O_3 \times 24SiO_2 \times 60H_2O$
VI – $6.0Na_2O \times Al_2O_3 \times 26SiO_2 \times 60H_2O$

crystallization mechanism.

The initial samples were prepared from the metakaoline and obsidian mixture as a tablets with diameter – 8 mm and this – 3-4 mm, in which the metakaoline also was added to obsidian as etching. Formation of initial samples-tablets was proceeded by the dry pressing. The samples were crystallized in NaOH medium.

The time of full crystallization was determined by investigation of process kinetics. It was shown the samples after crystallization preserve their forms. X Ray – patterns show the full crystallization process of zeolite «m» proceed in form of tablets as it is also in the case of powdery initial samples conversion into zeolite. The parameters of cubic elementary cell obtained crystals: a = 19.60 ± 0.2Å were determined. These data are consistent well with the parameters of hypothetical variation and known before real crystals of zeolite «m».

As stated above the reaction masses containing metakaoline in comparison with the kaoline free mass convert into zeolite «m» with the high rate. Their kinetic curves of crystallization testify about it (fig.2). It means that the increasing of crystallization rate was connected with the presence in reaction mass of metakaoline being the centre of crystallization.

Apparently, the zeolite «m» crystals origins have been formed around the metakaoline. After this process oktaedric groups [AlO_6] in layers turn into tetraedric units [AlO_4]:

$Al_2[Si_2O_7] \rightarrow [(Al,Si)_2O_7]$

Coupling with $(Al,Si)O_4$ tetraedrs in glass these structural units form around the cations of thermal solution the silica – alumina – oxygen skeleton: $[(Al,Si)O_4 + (Al,Si)_2O_7]$. The schematic picture of this process is given at figure 3.

Namely these discrete chains form eight numerated rings. In this case Si^{4+} ions were substituted in tetraedrs by Al^{3+} ions statistically files of discrete diortogroups Si_2O_7 convert into chain of $[Si_4O_{12}]$ (fig.3.). Diortogroups in this simplest metasilicate chains couple and form batisite chain:

$(Si_2O_7 + Si_2O7) \rightarrow [Si_2+2O_{12}] \rightarrow [Si_4O_{12}]_\infty$

It is to be noted that abovementioned chain was found in batisite mineral. «Pure» batisite chain contains only silica tetraedrs and the period of repetition along the chain axis equal to two diortogroups. The four numerated rings $[(Al,Si)_4O_{12}]$ have been formed from this association. By coupling with side oxygen atoms these four numerated rings form eight numerated rings which connect with each other via four numerated rings of silica – alumina – oxygen tetraedrs and form the frameworks of zeolite «m» (fig.3). Hydrated sodium cations are situated into the pores of balk. Elementary cell contains 16 sodium ions and 128 tetraedric units $(Al,Si)O_4$.

The structural features of proposed hypothetical framework, X Ray – data practically realized zeolite «m» and kinetic regularities of its crystallization, preservation of geometric forms of samples allow us to elucidate the mechanism of whole crystallization process of the zeolite under consideration.

Scheme (fig.3) allows us to express an opinion about the mechanism of zeolite crystallization. Apparently, crystallization of zeolite from investigated reaction mass proceeds in consequence of regrouping of structural elements of reaction mass solid phase on the boundary of solid phase – solution.

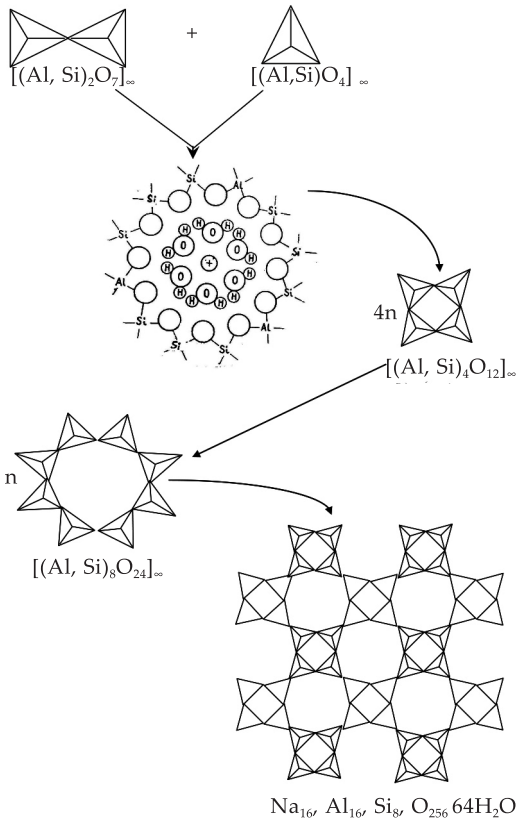


Fig.3. Schematic picture of zeolite «m» crystallization mechanism

It should be noted that after crystallization the forms of initial samples have been preserved i.e. they have the tablet forms. In other words, crystallization proceeds in solid phase by diffusion of hydrated cations inside. In the proposed scheme of mechanizm hydrated cation acts as pattern in consequence of regulation of alumosilicate grating. This mechanizm has been testified by series of observations and date on investigation of zeolite crystallization.

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Практическая реализация гипотетической структуры цеолита «m»

С.Б.Алиева[1], Г.М.Алиева[2]
[1]НИПИ «Нефтегаз», SOCAR, Баку, Азербайджан;
[2]Институт катализа и неорганической химии им.М.Ф.Нагиева НАН Азербайджана, Баку, Азербайджан

Реферат

Приведен новый вариант практической реализации цеолита «м» из смеси метакаолина и обсидиана. Формирование исходных образцов-таблеток производилось методом сухого прессования. Синтез осуществлен методом гидротермальной кристаллизации в системе Na_2O-Al_2O_3-SiO_2-H_2O при 150 °С. Образцы кристаллизовали в среде NaOH. Проведено исследование кинетики и выяснение механизма кристаллизации цеолита «m». Фазовый и химический состав продуктов кристаллизации определен методами рентгенофазового, термографического и рентгеноспектрального.

Ключевые слова: цеолита «m»; гипотетическая структура; гидротермальный синтез, кинетика.

«m» seolitinin hipotetik quruluşunun praktiki reallaşdırılması

S.B.Əliyeva[1], Q.M.Əliyeva[2]
[1]«Neftqazelmitədqiqatlayihə» İnstitutu, SOCAR, Bakı, Azərbaycan;
[2]Azərbaycan MEA M.F.Nağıyev adına Kataliz və Qeyri-üzvi Kimya İnstitutu, Bakı, Azərbaycan

Xülasə

Metakaolin və obsidian qarışığından «m» seolitinin praktik olaraq reallaşdırılmasının yeni üsulu verilmişdir. Ilkin nümunələr-tabletlər quru pressləmə üsulu ilə hazırlanmışdır. Seolitin sintezi Na_2O-Al_2O_3-SiO_2-H_2O sistemdə 150 °C temperaturda hidrotermal kristallaşma metodu ilə aparılmışdır. Nümunələr qələvi mühitdə kristallaşdırılmışdır. «m» seolitinin kristallaşma kinetikası və kristallaşma mexanizminin tədqiqi verilmişdir. Kristallaşma məhsullarının faza və kimyəvi tərkibi rentgenfaza, termoqrafik və rentgenspektral analiz üsulları ilə tədqiq edilmişdir.

Açar sözlər: «m» seoliti; hipotetik quruluş; hidrotermal sintez; kinetika.