

Studies of the Solid - Liquid Phase Mass Transfer during the LTA type Zeolite Crystallization from Metakaolin

O. S. Travkina*, B. I. Kutepov, M. L. Pavlov

Institute of Petrochemistry and Catalysis of RAS, Ufa, Russia

*Corresponding author: simchanka@mail.ru

Received December 12, 2012; Revised January 15, 2013; Accepted February 28, 2013

Abstract Mass transfer between the liquid and solid phases of the reaction mix during the metakaolin crystallization into the powdered Zeolite LTA has been studied. The metakaolin crystallization has been shown to occur through the formation stage of the amorphous sodium aluminosilicate close by its composition to the Zeolite LTA (Linde type A). It has been established that during thermochemical processing of the metakaolin in aqueous sodium hydroxide solution the solid-liquid mass transfer occurred already at 30°C on account of the interaction of the metakaolin with polyhydroxy complexes of sodium. The stage rate grows as the temperature is elevated, and the sodium hydroxide concentration in the liquid phase of the reaction mix increased. All the above mentioned witnesses the crystallization centers to arise at the boundary of the solid and liquid phases of the reaction mix.

Keywords: Mass transfer, metakaolin, crystallization, Zeolite LTA

1. Introduction

The highly dispersed Zeolite LTA (Zeolite A) is usually crystallized from aqueous solutions of sodium aluminate and sodium silicate [1]. In such a case, according to the existing concept [2,3,4], the feed reagents mixing at 20-30°C results in the formation of aluminosilicate hydrogels. The processes of ripening and undergrowth that occur in the course of hydrogel aging in aqueous solutions give rise to the particle size growth. During the following hydrothermal treatment stage of 70-100°C the rapid crystal growth of Zeolite A, X, or Y is in progress. The newly formed hydrogel compositions are closest to the compositions of slots being synthesized and are preset at the feed solution mixing stage.

Alternative techniques developed for the synthesis of Zeolite A aimed at the feedstock source expansion, technology simplification, and reduction of the obtained product cost make use of enriched kaolins as a single source of aluminum and silicon. The enriched kaolins contain one basic component kaolinite, the clay mineral with the layered lattice [5,6,7,8,9]. The Si/Al ratio values in the latter and in Zeolite A are close.

Due to the high stability of the kaolinite's layered lattice in alkaline solutions, a product of the thermal kaolinite dehydration at 500-900°C, namely, the amorphous aluminum disilicate or metakaolin possessing the chemical composition of the formula $Al_2Si_2O_5$ is used for the zeolite crystallization. The product composition differs from that of Zeolite A, primarily by the absence of sodium; therefore the crystallization of metakaolin is performed in sodium hydroxide solutions. Thus, the major distinction between the crystallization of Zeolite A from metakaolin and the crystallization of the same structure

type zeolite from solutions of sodium silicate and sodium aluminate is the presence from the very beginning of the synthesis of the solid and liquid phases significantly different in their composition. Hence, the mass transfer between those phases during the metakaolin crystallization in sodium hydroxide solutions assumes the specific importance; however, the reference data on it are not available.

In connection with the above, this work was aimed at the kinetic studies of the liquid - solid phase mass transfer during synthesis of the high dispersed Zeolite A from metakaolin in alkaline solutions of different sodium hydroxide concentrations within the temperature range of 30 thru 80°C.

2. Experimental Part

For the experiments we used the powdered metakaolin prepared from the kaolin of the Prosyantov deposit by means of thermal processing at 600-650°C in the air for 4-6 hours [9]. The prepared metakaolin contained 97.0-98% of aluminum and silicon oxides in the presence of impurities, such as iron, calcium, and titanium oxides. Thermochemical processing of the metakaolin was conducted in aqueous solutions of sodium hydroxide with the concentrations of 132, 170, and 332 g/dm³ counted on Na₂O basis, at the temperature of 30, 60, and 80°C for 4-24 hours.

The chemical composition of the solid and liquid phases was determined by weighing and Alkalimetric methods, the method of flame photometry on the device type "PFA-311" and complexometric titration [10].

The phase composition of the solid phase prior and after thermal processing was determined using automated PHILIPS PW 1800 XRD meter and the powder technique

by the Debye-Sherrer. The XRD (X-ray diffraction) pattern detecting conditions was as follows: $\theta/2\theta$ - scanning; the sample holder spinning of 1 RPS; the copper anode; the scattering angle range of $5-55^\circ/2\theta$; the angle pitch of 0.05° ; the exposure time per pitch of 2s; the anode voltage and current of 40 KV and 30 MA, respectively. XRD patterns were identified using the reference diffraction data [11].

3. Results and Discussion

In Figure 1 the data on the effect of the metakaolin holding time span at 30°C in aqueous sodium hydroxide solutions on the kinetics of the change in sodium, aluminum, and silicon concentrations in the liquid phase of the reaction mix (RM) are given.

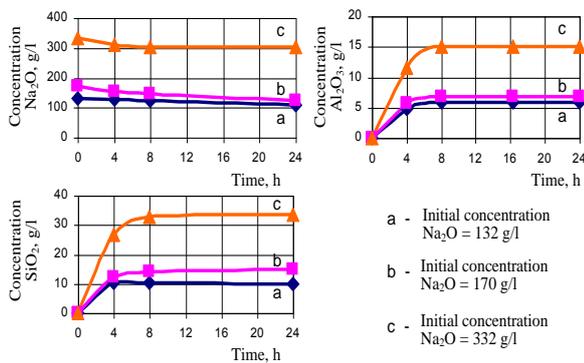


Figure 1. Effect of the duration of the metakaolin thermal processing in aqueous sodium hydroxide solutions of different initial concentrations at 30°C on the content of the crystal-forming components in the liquid phase of the RM

It is seen that in the course of the entire holding time span the concentration of sodium in the solution slowly decreases. Simultaneously with the transfer of sodium into the solid phase the ions of aluminum and silicon move from the metakaolin into the solution. Their concentration is gradually increased and in 8 hrs reaches its maximum values of 5.1 and 7.4% of the concentration in the metakaolin, respectively. A further increase in the processing duration does not result in any variation in sodium and silicon concentrations in the liquid phase of the RM. Thus, the mass transfer between the liquid and solid phase occurs already at 30°C on account of the chemical interaction between the metakaolin and polyhydroxycomplexes of sodium. Meanwhile, the transformation of the metakaolin into the amorphous sodium aluminosilicate is started. The crystal-forming component ratios in the above mentioned phases are given in Table 1.

Table 1. The crystal-forming component ratio in the liquid and solid phase of the RM after 8 hour processing at 30°C in sodium hydroxide solutions of different concentration

Concentration of Na_2O in the solution, g/dm^3	Molar ratio in the liquid phase			Molar ratio in the solid phase		
	Na_2O	Al_2O_3	SiO_2	Na_2O	Al_2O_3	SiO_2
132	35.0	1.0	3.5	0.2	1.0	2.0
170	35.0	1.0	3.5	0.3	1.0	2.0
332	37.0	1.0	3.6	0.5	1.0	2.0

It is seen that those values differ greatly from one another as well as from the proportion between sodium, aluminum, and silicon in Zeolite A.

When the crystallization temperature is elevated to 60°C (see Figure 2), the concentration of sodium oxide decreases just for the first 6 hours, and remains constant thereafter.

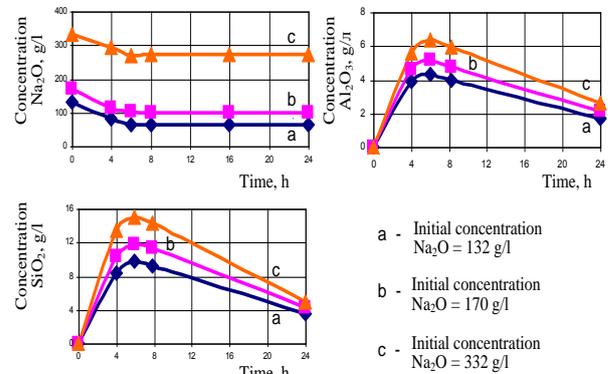


Figure 2. Effect of the duration of the metakaolin thermal processing in aqueous sodium hydroxide solutions of different initial concentrations at 60°C on the content of the crystal-forming components in the liquid phase of the RM

During this period the concentrations of silicon and aluminum oxides in the liquid phase of the RM grow and in 6 hrs reach the maximum of 4.2 and 6.7% of their content in the metakaolin, respectively. If the processing duration is increased further, those concentrations are gradually decreased.

Thus, at 60°C the mass transfer between the solution and metakaolin is more intense than at 30°C . The amorphous sodium aluminosilicate is formed in the solid phase (see Table 2), and after 6 hours processing its sodium oxide/aluminum oxide ratio already matches that in Zeolite A (or a little bit higher), and the crystallization actually begins.

Table 2. The crystal-forming component ratio in the liquid and solid phase of the RM after 6 hours processing at 60°C in sodium hydroxide solutions of different concentration

Concentration of Na_2O in the solution, g/dm^3	Molar ratio in the liquid phase			Molar ratio in the solid phase		
	Na_2O	Al_2O_3	SiO_2	Na_2O	Al_2O_3	SiO_2
132	24.0	1.0	3.3	1.0	1.0	2.0
170	35.0	1.0	3.4	1.1	1.0	2.0
332	89.0	1.0	4.3	1.3	1.1	2.0

According to the XRD data, by that moment Zeolite A has already started to form in the solid phase and its content is about 5% by mass. If the processing duration is increased further, the concentrations of silicon and aluminum in the liquid phase of the RM are gradually decreased. The crystallization is complete in 20 hours and results in the formation of the high dispersed Zeolite A with the degree of crystallinity close to 96%.

When the crystallization temperature is elevated from 60 to 80°C (see Figure 3), the concentration of sodium counting on the sodium oxide basis decreases just for the first hour, and remains constant thereafter.

During this period the concentrations of silicon and aluminum in the liquid phase grow and reach their maximum. If the processing duration is increased further, those concentrations are decreased.

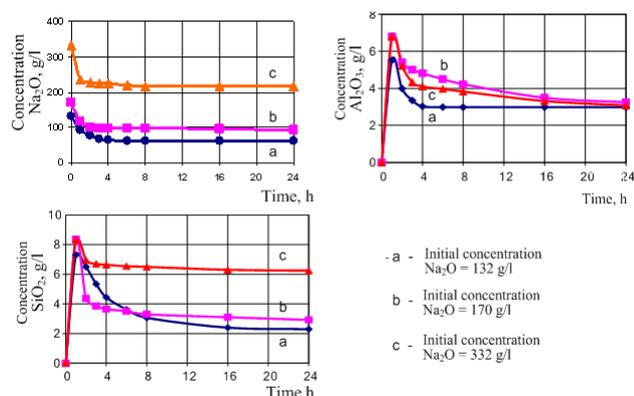


Figure 3. Effect of the duration of the metakaolin thermal processing in aqueous sodium hydroxide solutions of different initial concentrations at 80°C on the content of the crystal-forming components in the liquid phase of the RM

At 80°C the amorphous sodium aluminosilicate close by its composition to that of Zeolite A is formed already in 1 hour, and its crystallization begin (see Table 3).

Table 3. The crystal-forming component ratio in the liquid and solid phase of the RM after 1 hour processing at 80°C in sodium hydroxide solutions of different concentration

Concentration of Na ₂ O in the solution, g/dm ³	Molar ratio in the liquid phase			Molar ratio in the solid phase		
	Na ₂ O	Al ₂ O ₃	SiO ₂	Na ₂ O	Al ₂ O ₃	SiO ₂
132	27.7	1.0	2.2	1.0	1.0	2.0
170	28.1	1.0	2.2	1.0	1.0	2.0
332	56.7	1.0	2.2	1.6	1.0	2.0

Apparently, the crystallization centers are formed on the solid-liquid phase boundary as early as the temperature is low. The nucleation process is followed by the crystal growth stage; as the temperature gets higher, the rate of growth increases. A shortage in the “construction material” for the ever growing crystals is probably made up from the solution at the expense of the aluminum and silicon cations emerged into the solution earlier. At 80°C the crystallization is complete in 12 hrs and results in the formation of the high dispersed Zeolite A with the degree of crystallinity close to 97%.

4. Conclusions

It has been established that during thermochemical processing of the metakaolin in aqueous sodium

hydroxide solution the solid-liquid mass transfer occurred already at 30°C on account of the interaction of the metakaolin with polyhydroxy complexes of sodium. The amorphous sodium aluminosilicate formed in the process possessed the crystal forming component ratios greatly different from one another and from those of sodium, aluminum, and silicon in Zeolite A.

The amorphous sodium aluminosilicate has been shown to be formed in the solid phase at 60°C; the sodium/aluminum oxide ratio in it after 6 hour processing already matched that of Zeolite A and the crystallization actually began.

The transformation of the metakaolin particles into sodium aluminosilicate containing sodium cations in the equivalent quantity of the content of aluminum cations has been found to be essential for the metakaolin crystallization into Zeolite A. If the Na₂O/Al₂O₃ ratio in the aluminosilicate exceeds 1, it does not crystallize into Zeolite A.

References

- [1] Breck D.W., *Zeolite Molecular Sieves: Structure, Chemistry and Uses*, Wiley, New York, 1973.
- [2] Barrer R.M. *Hydrothermal Chemistry of Zeolites*. Academic Press, London, 1982.
- [3] Zhdanov S.P., Egorova E.N. *Chemistry of zeolites (in Russian)*. Science, Leningrad, 1968.
- [4] Fenelonov V.B. *Introduction into the physical chemistry of the supramolecular structure formation in adsorbents and catalysts (in Russian)*. Novosibirsk. Publishing of the SD of RAS. 2004.
- [5] Chandrasekhar S., Pramada P. N. Microwave assisted synthesis of zeolite A from metakaolin, *Microporous and Mesoporous Materials*. 108(1-3): 152-161, 2008.
- [6] Vilma Sanhueza U. K., R. C., Synthesis of molecular sieves from Chilean kaolinites: 1. Synthesis of NaA type zeolite, *Journal of Chemical Technology and Biotechnology*. 74(4): 358-363, 1999.
- [7] Imbert, F.E.; C. M.; A. M., Venezuelan natural aluminosilicates as a feedstock in the synthesis of zeolite A, *Zeolites*. 14(5): 374-378, 1994.
- [8] Chandrasekhar S. Influence of metakaolinization temperature on the formation of zeolite 4A from kaolin, *Clay Minerals*. 31: 253-261, 1996.
- [9] Pavlov M.L., Travkina O.S., Kutepov B.I. Development of the synthesis of a powdered A-type zeolite from kaolin, *Petroleum processing and chemistry*. 4-5: 59-61, 2008.
- [10] Kreshkov A.P., Yaroslavets A.A. *The treatise of analytical chemistry*. Chemistry. Moscow.1975.
- [11] Treacy M.M.J., Higgins J.B. *Collection of Simulated XRD Powder Patterns for Zeolites*. Amsterdam - London - New York - Oxford - Paris - Shannon - Tokyo. Elsevier. 2001.