

SYNTHESIS AND CRYSTALLIZATION OF ZEOLITE A

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ABSTRACT

Zeolite A is a crystalline aluminosilicate, represented by the formula $\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O}$. It has a wide range of applications as ion exchangers. One of these is in a detergent builder, suggested in the 1970's to replace the phosphate builder for environmental reasons. The crystalline material is usually prepared by combining sources of silica, alumina and alkali to form an aluminosilicate gel. The product obtained is depend on the composition of the reaction mixture and reaction condition. This paper outlines some of the factors affecting zeolite crystallization.

INTRODUCTION

Syntheses of zeolites have been reported over considerable period. In 1862, Deville reported the production of "Levynite" by heating sodium aluminate and potassium silicate in a sealed glass tube at 170°C . Since then, zeolites have been developed into key materials in the chemical industry for a wide field of applications ranging from ion exchange to the catalysis of petrochemical processes.

In 1987, the production of synthetic zeolites had grown to estimated 460,000 metric tons worldwide (Chen et al., 1988). More than three hundred types of zeolites are known at the moment, however only few of these types are actually produced. One of them is zeolite A. In 1987, 375,000 metric tons of zeolite A were produced worldwide only for the detergent industry (Dietrich et al., 1987). The product should be free of impurities and should have a small average particle size (approximately 4mm or less) and narrow particle size distribution.

FACTORS AFFECTING ZEOLITE CRYSTALLIZATION

Many investigators have studied a number of variables which determine the kinetics of zeolite A crystallization. Most of the studies were carried out in a batch crystallizer. Table 1 lists a number of studies performed on zeolite A crystallization. Zeolites are often metastable and their formations depend not only on the composition of the reaction mixture and the synthesis temperature, but also on the nature of the starting materials, method used to prepare the gel and the degree of agitation of the reactant.

Initial composition of reaction mixture

Many data have been obtained and published on the influence of composition of the initial mixture on the final result of the zeolite synthesis. Breck and Flanigen (1968) have established a relationship between the synthetic zeolite product and the starting composition of the reaction mixture for $\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$ system at 100°C . These are illustrated in reaction diagram, shown in Figure 1 where the areas identified by letters refer to compositions of the reaction mixture that yield the designated zeolite. Meise and Schwochow (1973) found that addition of K^+ ions into the gels delayed the formation of A and leads to the formation of relatively large particle sizes.

Temperature

Hu et al. (1990) has studied the crystallization of zeolite A at different temperatures. Their plots of percent crystallization versus time form an S-shaped curve as shown in Figure 2. This curve implied that there is an existence of an induction period. The induction periods are shorter at a higher temperature. They concluded that rates of nucleation and crystallization of zeolite A increase as the temperature increase. Hu et al. (1990) found the activation energy for nucleation and crystallization are 15.0 kcal/mol and 10.9 kcal/mol respectively for zeolite A.

Stirring Rate

Thompson et al. (1985) studied the effect of stirring rate and agitator hardness. They observed that a higher stirrer speed produced more particles of smaller average sizes as shown in Figure 3. This is due to an enhancement of nucleation by increase in the stirring rate.

Alkali concentration

An increase in the concentration of NaOH in the liquid phase of the gel caused a corresponding increase in the rate of crystallization of zeolite A (Meise et al., 1973, Subotic et al., 1982). Meise and schwochow (1973) found that higher concentrations of NaOH present in the liquid phase of aluminosilicate gels resulted in more rapid crystallization of zeolite A and produced finer crystals than those crystallized from lower NaOH concentrations. The types of zeolite obtained is dependent on the concentration of OH^- ion in the liquid phase.

Seeding

Studies have been carried out to see the effect of seeding on the crystallization of zeolite A. Breck and Flanigen (1968) noticed that the addition of seed to the reaction mixture brought about an acceleration to the crystallization rate but no significant increase to crystal size. The crystallization rate increase is due to the increase in total external surface area over which new crystals can nucleate. Higher crystallization rates were observed when the seed crystals were smaller than the large single crystal seed

Reaction Time

Many zeolites are known to be metastable and transform to other more stable phase. The transformation is usually undesirable since it will contaminate the product. Longer synthesis time will result in the transformation of product.

CONCLUSION

Zeolites are known to be metastable. As discussed earlier, the purity and particle size of the zeolite product are influenced by reaction composition and reaction condition. Thus the knowledge on the factors affecting zeolites formation are very important in order to produce desired product.

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Table 1 : Some of the studies on zeolite A synthesis.

Author	Mode of crystallizer	Parameter studies	Remark
Clric, 1968	Batch	SiO ₂ /Al ₂ O ₃ , alkali, and stirring rate	Solution phase mechanism
Subotic et al., 1982	Batch	Transformation of zeolite A into zeolite P	
Meise et al., 1973	Batch	Temp., alkali, SiO ₂ source & K ⁺ ion	
Hu et al., 1990	Batch	Temp. & composition	nucleation and crystallization rates
Culfaz et al., 1973	Batch	Temp., & seeding	Solution phase mechanism
Thompson & Dyer, 1985	Batch	Agitation intensity, agitator hardness & seeding	Secondary nucleation is not important
Kerr, 1966	Batch	Alkali, seeding, & volume of NaOH	
Dutta et al., 1986	Batch	Influence of starting composition esp. Si/Al.	Solution phase mechanism
Tassopoulos et al., 1987	Batch and semibatch	Transformation behaviour of zeolite A	
Culfaz et al., 1977	CSTR	Retention time of the feed in the reactor	

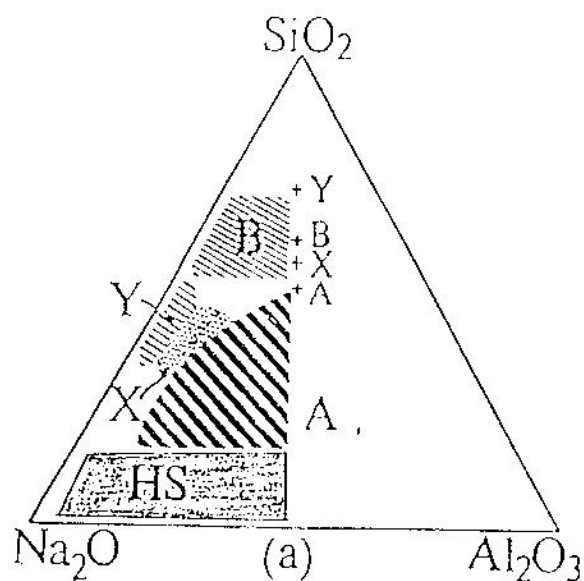


Figure 1: Reaction composition diagram. Projection of the Na₂O-SiO₂-Al₂O₃-H₂O system at 100°C. H₂O content of gels is 90-98 mol %. (Breck et al., 1968).

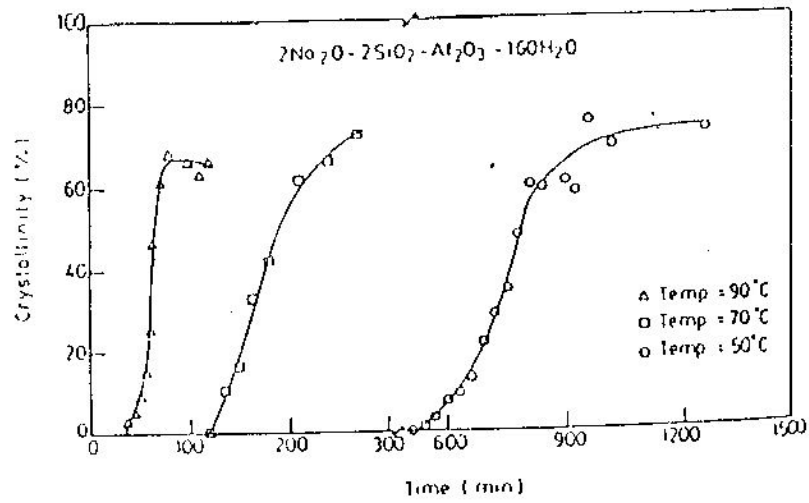


Figure 2: Crystallinity (%) versus time for different temperatures of zeolite A synthesis. (Hu et al., 1990).

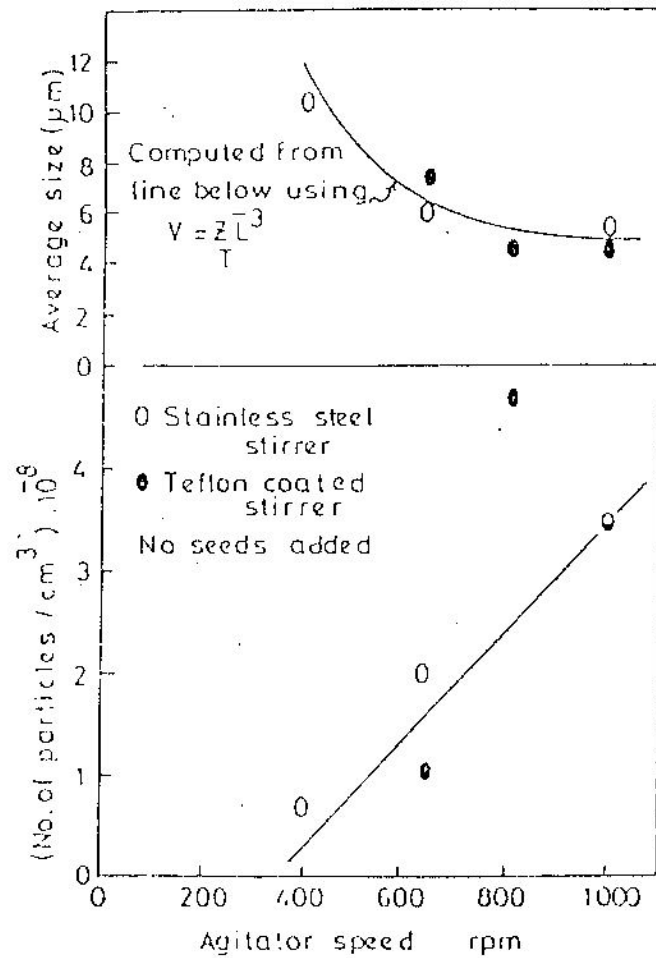


Figure 3: Total number of crystals formed and their average sizes as a function of agitator speed (Thompson et al., 1985).