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COMPARATIVE STUDY OF ZEOLITE A SYNTHESIS IN BATCH AND SEMIBATCH REACTORS

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ABSTRACT

Synthesis of Zeolite A from Natrium Silicate and Natrium Aluminate solutions were studied using batch and semibatch reactors. Sample were taken at one hour interval times. Solid samples were analyzed using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Malvern Mastersizer. Performance of both mode of operations were compared. Semibatch process produced zeolite A faster and larger than those of batch process. Scanning Electron Micro graph of the solid sample indicated a change in the crystal habit and size due to change in mode of operation.

INTRODUCTION

Molecular sieve zeolites are a class of aluminosilicate compounds suitable for use in a variety of industrial process such as adsorption, separation and catalytic reaction due to their internal structure and surface characteristics. Zeolites are synthesized from alkaline aluminosilicate gel consisting of a heterogeneous phase in which amorphous solid and aqueous solution phases coexist.

Molecular sieve zeolites are synthesized primarily in batch crystallizer. There are only two known reports of continuous stirred tank syntheses (Culfaz et. al (1977), Culfaz et. al. (1981)) and two known reports of tubular reactor syntheses (Rollman et. al. (1980), Wolf et al.(1982). Both of these reactor types give poorer performance (i.e. lower conversion, smaller crystal and ununiform size distribution) than the same sized batch reactor. As reported earlier (Ramli (1993)), zeolites are metastable and their formation depend on reaction mixture composition and reactor operating variable such as temperature, agitation etc.

The purpose of this present work is to report a recent study of zeolite crystallization in batch and semibatch crystallizer. In semibatch mode, crystallization is allowed to proceed during the time of the reactor is being filled and no effluent stream is withdrawn until the crystallization process is completed. The solid product from both reactors are analyzed using XRD, SEM, and Malvern Mastersizer.

EXPERIMENTAL

All experiments were carried out in a 2L stainless steel laboratory scale crystallizer at 100°C with reflux at ambient pressure. Stirring was constant at 700 rpm in each experiment using turbine type stirrer. Materials used in these experiments were Natrium Silicate, Natrium Aluminate and distilled water. 107.66 g of Natrium Aluminate (41 wt% Na_2O, 54 wt% Al_2O_3, 5 wt% H_2O)was dissolved in 1220ml of distilled water to make Natrium Aluminate solution. Natrium Silicate solution was prepared by adding 650ml water to 240 g Natrium Silicate (16 wt% Na_2O, 32 wt% SiO_2, 52 wt% H_2O).

For the batch process, Natrium Silicate solution was added to Natrium Aluminate solution in the crystallizer in a very short time. On the other hand, for semibatch process Natrium Silicate solution was added gradually into the crystallizer containing Natrium Aluminate.

Sample were taken out from the reaction vessel at chosen time interval, filtered through a 0.2 μm membranes filter and separated into solid and liquid. The solid portion was washed with a large quantity of distilled water until the pH of wash is below 10, then dried in oven at a temperature of 60°C overnight. The solid sample was analyzed using XRD for qualitative and quantitative measurements. The crystal size distribution was determined by Malvern Mastersizer. The crystal morphology of the crystalline phase was examined using a Scanning Electron Microscope.

RESULT AND DISCUSSION

The solid sample was analyzed for percent crystallinity, size, and morphology.

Percent Crystallinity

The X-ray diffraction pattern of zeolite A was shown in Figure 1. The percent crystallinity of zeolite A in the process was estimated using X-ray diffraction pattern of the sample. Percent crystallinity of zeolite A is defined from the ratio of the total peak area of a number of very intense peaks of the product sample to that of the reference sample. The crystallinity curves for both batch and semibatch processes were shown in Figure 2. Based on the plot, it can be concluded that the semibatch process requires shorter time for the zeolite to achieve 100% crystallinity. This finding also was in agreement with the result obtained by Hu et. al. (1990). They found out that the ratio of SiO_2/Al_2O_3 in the reaction mixture had some influence on the crystallization process.

Size Analysis

Size analyses of the solid sample were done using Malvern Mastersizer. Only final products were analyzed. Results of size analysis were shown in Figure 3. The result shown that the semibatch process produced larger crystal size than batch process. Semibatch process produced larger crystal because the concentration of reactants in the reactor were lower, thus number of nuclei were small. Crystal with small number of nuclei will grow faster than crystal with large number of nuclei because of smaller surface area available.

Crystal Morphology

Scanning Electron Microscope was used to determine the morphology of the zeolite crystal. Micro graphs of zeolite A were shown in Figure 4. Crystals obtained in a batch system were cubic; on the other hand, crystals produced in a semibatch system were cubic with beveled edges. The small different in shape is perhaps due to the influence of SiO_2/Al_2O_3 ratio in the reaction mixture.

CONCLUSIONS

It has been shown that Zeolite A can be produced in high yields in a semibatch crystallizer. The crystals produced in a semibatch mode were larger than those produced in a batch mode for the same reaction condition. The morphology of the crystals were affected by the mode of operation.

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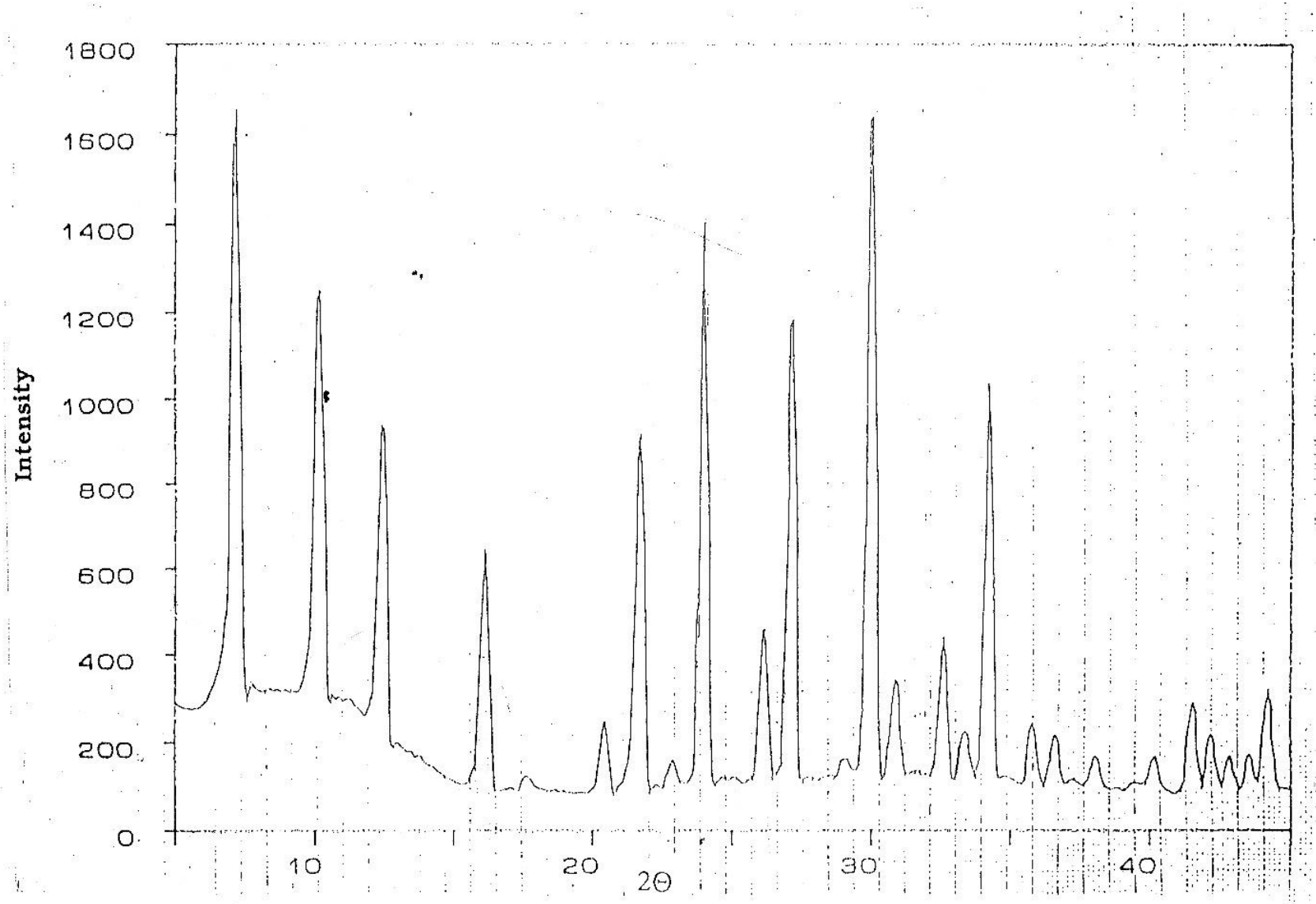


Figure 1: X-Ray diffraction pattern of the solid sample obtained from semibatch process

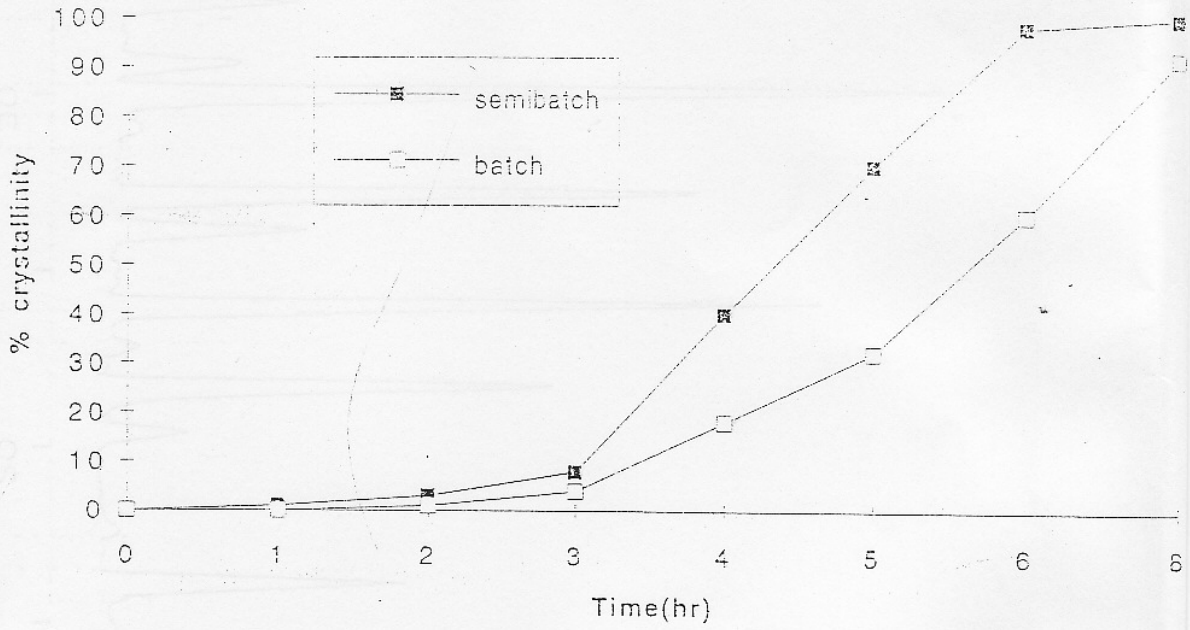
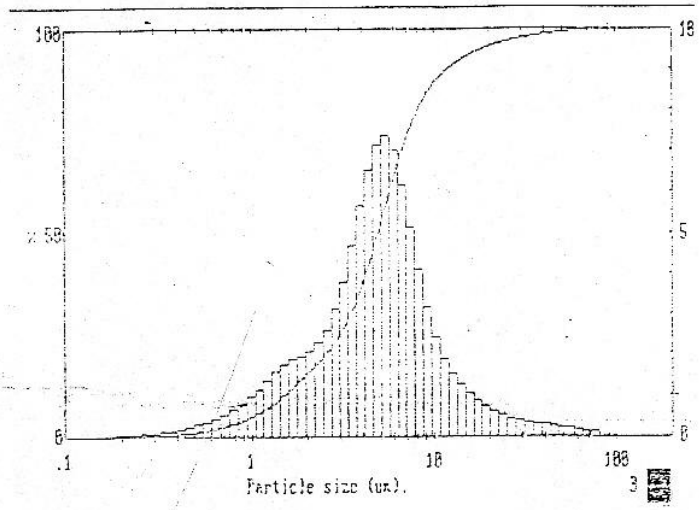


Figure 2: Change of percent crystallinity of solid phase as a function of time for batch and semibatch reactors.

a)

High Size	In %	High Size	In %	High Size	In %	High Size	In %	High Size	In %	High Size	In %	Span 2.08
80.0	0.1	24.9	0.5	7.75	5.1	2.41	2.3	0.75	0.5	0.23	0.0	D[4,3] 6.60µm
71.9	0.1	22.4	0.6	6.97	6.2	2.17	2.1	0.68	0.4	0.21	0.0	
64.7	0.2	20.1	0.7	6.27	7.1	1.95	2.0	0.61	0.4	0.19	0.0	D[3,2] 3.06µm
58.2	0.2	18.1	0.9	5.64	7.4	1.75	1.9	0.55	0.3	0.17	0.0	
52.3	0.2	16.3	1.1	5.07	7.2	1.58	1.8	0.49	0.2	0.15	0.0	
47.1	0.3	14.6	1.3	4.56	6.6	1.42	1.6	0.44	0.2	0.14	0.0	D[v,0.5] 11.62µm
42.3	0.3	13.2	1.5	4.10	5.7	1.28	1.4	0.40	0.1	0.12	0.0	
38.1	0.3	11.8	1.9	3.69	4.7	1.15	1.1	0.36	0.1	0.11	0.0	
34.2	0.4	10.7	2.5	3.32	3.8	1.03	1.0	0.32	0.1	0.10	0.0	D[v,0.1] 1.49µm
30.8	0.4	9.58	3.2	2.98	3.1	0.93	0.8	0.29	0.1			
27.7	0.5	8.62	4.1	2.68	2.6	0.83	0.7	0.26	0.1			

Source = :Sample	Mean length = 2.2 µm	Model indp	D[v,0.5] 4.66µm
Focal length = 45 mm	Residual = 0.339 %	Volume Conc. = 0.0100%	
Presentation = std	Obscuration = 0.2035	Sp.S.A 1.9576 m²/cc.	
	Volume distribution		



b)

High Size	In %	High Size	In %	High Size	In %	High Size	In %	High Size	In %	High Size	In %	Span 2.20
80.0	0.0	24.5	0.7	7.75	5.7	2.41	2.0	0.75	0.7	0.23	0.1	D[4,3] 7.26µm
71.9	0.1	22.4	1.0	6.97	6.7	2.17	1.8	0.68	0.6	0.21	0.1	
64.7	0.1	20.1	1.2	6.27	6.6	1.95	1.6	0.61	0.5	0.19	0.0	D[3,2] 2.54µm
58.2	0.1	18.1	1.5	5.64	6.3	1.75	1.5	0.55	0.4	0.17	0.0	
52.3	0.1	16.3	2.1	5.07	4.8	1.58	1.5	0.49	0.4	0.15	0.0	
47.1	0.2	14.6	2.7	4.56	4.0	1.42	1.3	0.44	0.3	0.14	0.0	D[v,0.5] 14.06µm
42.3	0.2	13.2	3.3	4.10	3.5	1.28	1.2	0.40	0.3	0.12	0.0	
38.1	0.3	11.8	3.5	3.69	2.6	1.15	1.1	0.36	0.2	0.11	0.0	
34.2	0.3	10.7	4.1	3.32	2.1	1.03	1.0	0.32	0.2	0.10	0.0	D[v,0.1] 1.38µm
30.8	0.4	9.58	5.1	2.98	2.7	0.93	0.9	0.29	0.1			
27.7	0.5	8.62	5.3	2.68	2.4	0.83	0.8	0.26	0.1			

Source = :Sample	Mean length = 2.2 µm	Model indp	D[v,0.5] 5.76µm
Focal length = 45 mm	Residual = 0.308 %	Volume Conc. = 0.0117%	
Presentation = std	Obscuration = 0.2085	Sp.S.A 2.0256 m²/cc.	
	Volume distribution		

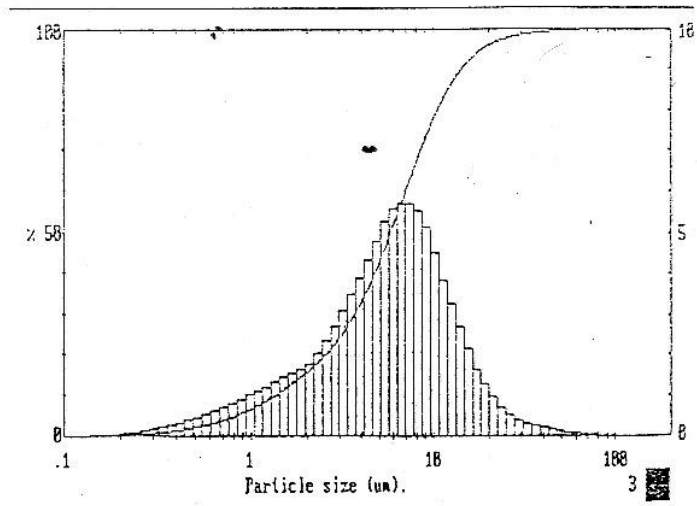
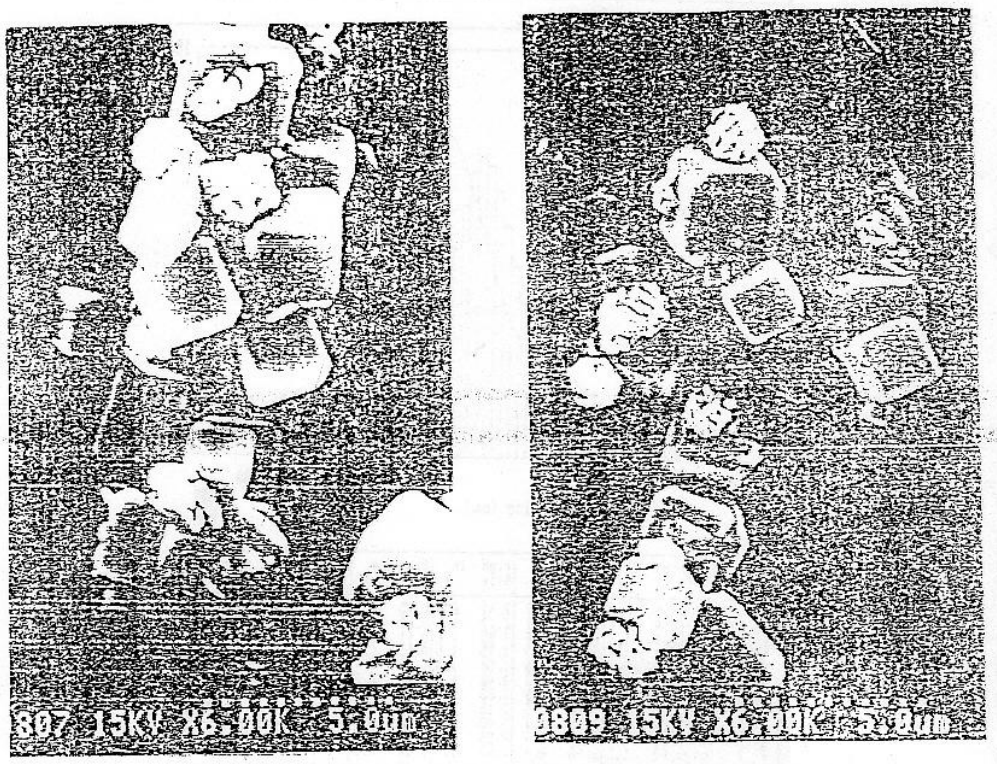


Figure 3: Crystal size distribution for batch and semibatch production of zeolite A.
a) Batch reactor b) Semibatch reactor



a) b)

Figure 4: Scanning electron micrograph of zeolite A crystal for
a) Batch crystallizer b) Semibatch crystallizer