Effects of FAU Zeolites on the Crystallization of Chloronitrobenzenes above the Eutectic Composition

Jeeranun Neaungjumnong, Sasikarn Yairit, Sudarat Pattanapaiboonkul, Pramoch Rangsunvigit, Santi Kulprathipanja

Abstract—Crystallization has been used for the separation of chloronitrobenzene or CNBs, which are isomeric substances (*o*-, *m*- and *p*-CNB) and important intermediates in chemical productions. Effects of feed composition on the crystallization of *m*- and *p*-CNB was first studied. The results conform to the binary phase diagram of *m*- and *p*-CNB. After that, effects of FAU zeolites (NaX, CaX, BaX, NaY and CaY) above the eutectic composition (63.5 and 65.0 wt% *m*-CNB in the feed) was also investigated. The results showed that the FAU zeolites significantly affected the precipitates, the composition of which was shifted from being rich in *m*-CNB to rich in *p*-CNB. Effects of the number of FAU zeolites on the precipitate composition was then studied. The results revealed that the precipitates from the lower number of the zeolites had higher *p*-CNB purity than those from the higher number of zeolite.

Keywords—Chloronitrobenzenes, crystallization, separation, eutectic

I. INTRODUCTION

CHLORONITROBENZENES (CNBs) are isomeric substances, which include *o*-, *m*-, and *p*-CNB. They are important intermediates for the production of azo, and sulfur dyes. Moreover, they are used in the synthesis of preservatives, fungicides, pharmaceuticals, and pesticides [1]. They are prepared commercially by either nitration of chlorobenzene (CB) or chlorination of nitrobenzene (NB) depending on the proportions of *o*-, *m*-, and *p*-CNB in desired products. Furthermore, both *o*- and *p*-CNB are being used more than *m*-CNB because of its industrial applications [2]. There are many commercial processes that have been developed for CNB separation, e.g. fractionation, crystallization, and adsorption. Adsorption is one of the suitable techniques used to separate CNBs into a pure form, because it reduces energy consumption and provides a high-purity product. An appropriate adsorbent is an important factor in the adsorptive separation; therefore, FAU zeolites are widely used in the chemical industry as an adsorbent due to their high adsorption capacity and selectivity.

J. N. is with The Petroleum and Petrochemical College; and Center for Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Soi Chula 12, Phyathai Road, Pathumwan, Bangkok 10330, Thailand (e-mail: jeeranun.ne@gmail.com)

S. Y. was with The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phyathai Road, Pathumwan, Bangkok 10330, Thailand

S. P. was with The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phyathai Road, Pathumwan, Bangkok 10330, Thailand

P. R. is with The Petroleum and Petrochemical College; and Center for Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Bangkok 10330, Thailand (Phone: +66-2-218-4135; fax: +66-2-215-4459; e-mail: pramoch.r@chula.ac.th)

S. K. is with UOP, A Honeywell Company, 50 East Algonquin Rd., Des Plaines, IL 60017, USA.

The other attractive technique for separating CNB isomers is crystallization, which can be carried out either in the presence of solvent (solution crystallization) or the absence of solvent (melt crystallization) [3]. Melt crystallization is attractive because of low-energy required, low costs, and easy operation. This method can separate each isomer by using the difference of melting points. However, the presence of the eutectic point is the obstacle for complete separation of CNB isomers resulting in the low product purity.

The purpose of this research is to study effects of FAU zeolites on the crystallization of CNBs.

II. EXPERIMENTAL

A. Effects of feed composition on *m*- and *p*-CNB crystallization

To study the feed composition of crystallization of *m*- and *p*-CNB, the feed solutions were prepared with different *m*-CNB compositions consisting of below the eutectic, at the eutectic, and above the eutectic composition (61.0, 62.9, and 65 wt% of *m*-CNB in the feed). The crystallization unit is shown in Figure 1. Seven grams of *m*- and *ρ*-CNB solid mixture were melted in the crystallizer to obtain a homogeneous solution. Then, the system was cooled by the cooling water from 30 °C to the crystallization temperature, at which the precipitate was initially formed. The mixed precipitates and mother liquor were collected, washed, and dissolved with hexane. The dissolved crystals were analyzed for the CNB composition by a Hewlett Packard 6890 series gas chromatograph (GC) with a flame ionization detector (FID) and the SUPELCOWAXTH 10 capillary column.
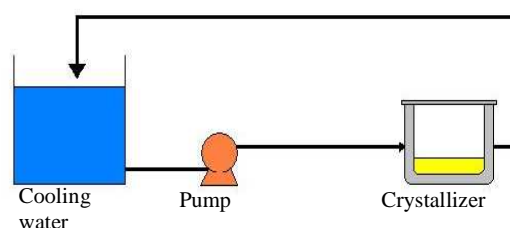

Fig. 1 Crystallization unit

B. Effects of FAU zeolites on *m*- and *p*-CNB crystallization above the eutectic composition

The influence of the number of FAU zeolites on the crystallization was also studied by varying the number of FAU zeolites (5 and 10 grains), compositions (63.5 and 65.0 wt% of *m*-CNB in the feed) and FAU zeolites (NaX, CaX, BaX, NaY, CaY). The CNB liquid mixture was prepared with the same procedure as that in the study on the effects of feed composition on *m*- and *p*-CNB crystallization. Zeolites were

calcined at 350°C for an hour before the experiment. Five grains of a zeolite were added at the center of the CNB mixture in the crystallizer. The mixture was stirred to minimize any concentration gradient in the solution and then collected to check the composition after adding the zeolite by using the GC. The system was cooled by cooling water at the cooling rate of 1°C/hr to the crystallization temperature where the precipitates initially formed. The precipitates from 8 positions in two areas, area (a) and area (b), as shown in Figure 2, were collected, washed, and dissolved with hexane. The dissolved crystals were measured for the CNB compositions by using the GC. The experiment was repeated by using 10 grains of zeolite.
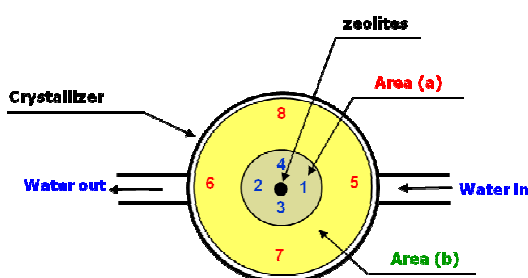

Fig. 2 Locations where precipitates were collected for studying effects of the number of FAU zeolites on the crystallization

III. RESULTS AND DISCUSSION

A. Effects of feed composition on m- and p-CNB crystallization

The CNB compositions of the feeds and precipitates are shown in Table I. Without any zeolite, the result shows that the crystallization of *m*- and *p*-CNB at the eutectic composition or 62.9 wt% *m*-CNB in the feed results in an amorphous form with the CNB composition close to that of the feed at 23.0°C. Above the eutectic composition, the precipitates, which appear in a crystal form, are rich in *m*-CNB, 92.73 wt%, while the opposite is true for the composition below the eutectic composition. These results correspond with binary phase diagram as shown in Figure 3. A possible reason why the precipitate purity is not close to 100% may be from the contamination in the feed. In any case, a single crystallization step cannot produce 100 wt% pure crystals for a variety of reasons, e.g. they can be contaminated with residual solvent or other impurities that have not been removed by washing, or have been incorporated into the crystal interstitially or as liquid inclusion [4].

TABLE I
COMPOSITIONS OF *m*- AND *p*-CNB IN THE FEEDS AND THE PRECIPITATES, AND CRYSTALLIZATION TEMPERATURE

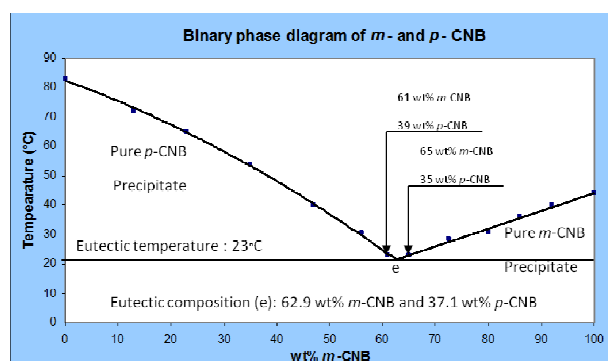| Feed *m*-CNB (wt%)	Feed composition (wt%)		Precipitate composition (wt%)		Crystallization temperature (°C)
	m-CNB	*p*-CNB	*m*-CNB	*p*-CNB	
61.0	61.02	38.98	9.60	90.40	23.0
62.9	62.90	37.10	62.87	37.13	23.0
65.0	64.97	35.03	92.73	7.27	23.0

Fig. 3 Binary phase diagram of *m*- and *p*-CNB [5]

B. Effects of FAU zeolites on m- and p-CNB crystallization above the eutectic composition

The composition of the precipitates obtained from the feed above the eutectic composition is shifted from being rich in *m*-CNB to rich in *p*-CNB. Considering the two areas where the precipitates were collected, area (a) and area (b), the results show that the precipitates located near the zeolites (area (a)) have a higher amount of *p*-CNB than those located far from the zeolites (area (b)) as shown in Table II.

TABLE II
COMPOSITIONS OF *m*- AND *p*-CNB IN THE PRECIPITATES LOCATED NEAR (AREA(a)) AND FAR FROM ZEOLITES (AREA (b)) WITH DIFFERENCE OF *m*-CNB IN THE FEED

Zeolite	Average amounts of *p*-CNB at 63.5 wt% *m*-CNB in the feed (wt%)		Average amounts of *p*-CNB at 65 wt% *m*-CNB in the feed (wt%)	
	Area (a)	Area (b)	Area (a)	Area (b)
NaX	95.45	89.00	91.68	85.15
CaX	92.83	84.74	91.78	85.52
BaX	95.04	86.75	91.46	85.98
NaY	93.98	88.65	92.39	87.92
CaY	93.49	90.46	91.62	85.71

A reason why the precipitate composition in the feed above the eutectic composition is shifted from being rich in *m*-CNB to *p*-CNB may be related to the metastable zone width and interfacial tension. When a suitable foreign particle is present in the system, it can induce nucleation at lower temperature of supercooling than that required for a spontaneous nucleation [4]. This conforms with the crystallization temperature in the presence of zeolite, which is lower than that in the absence of a zeolite because the metastable zone width may become broader.

In order to see the tendency of precipitate compositons clearly, the CNB precipitate compositions in the feed solution

above the eutectic composition with 5 and 10 grains of zeolites were calculated in terms of m-/p-CNB ratio, as seen in Figures 4 and 5. The results show that the crystallization gives almost the same m-/p-CNB ratio of the precipitates at the locations near the zeolite, while the m-/p-CNB ratio at the locations far from the zeolite shows some dependency on the type of the zeolites. With 10 grains of zeolites, as shown in Figure 5, the results revealed that a type of zeolite significantly affects the ratio of the precipitates far from the zeolite.

From Figures 4 and 5, the m-/p-CNB ratio of precipitates near the zeolites is lower than those far from the zeolites, and the high number of a zeolite has more pronounced effects on the ratio than the lower number of the zeolite especially at the locations far from the zeolite. Most crytallization temperatures from 10 grains of zeolites are lower than those from the 5 grains. As a result of high supersaturation, fast nucleation and creation of large number of very small crystal can occur [4]. Ten grains of the zeolites may accelerate the system into nucleation step faster than 5 grains of zeolites, and precipitates from the 10 grains have more time for agglomeration and growth than the 5 grains.

Added into the CNB liquid mixture, a zeolite may act as a foreign particle in the system and center of crystallization. The presence of a zeolite may induce primary nucleation in the heterogeneous nucleation. Mostly, the size of active particle (heteronuclei) in liquid solution is in the range of 0.1 to 1 µm. A zeolite that has an average particle size diameter more than 1 µm can considerably affect heterogeneous nucleation, which usually has a profound effect on the final crystalline product [4].

A possible reason why the number of a zeolite significantly affects the product purity may come from the agglomeration of nuclei in the nucleation step. The agglomeration kinetics is implicated as a function of the supersaturation and the number of particles in the solution [6].

The nuclei in the primary nucleation from the induction by foreign particles are called heterogeneous nuclei. Frequent agglomeration occurs when the number of a zeolite inducing primary nuclei is larger. As the number of primary nuclei is larger and its size is smaller, the purity decreases by agglomeration. The higher number of primary nuclei can also generate the higher number of secondary nuclei in the system. After the secondary nucleation, these nuclei start to agglomerate and grow [4]. Therefore, the purity of agglomerates decreases because the number of elementary crystals constituting agglomerates increase. Moreover, the purity decrease is more substantial when the agglomerate size is smaller.

This can be explained that the number of elementary crystals significantly decreases in the purity since the higher number of nuclei, the greater contact probabilities and collision of nuclei in the system lead to the entrainment of mother liquor during agglomeration [6]. Accordingly, 10 grains of zeolites can induce the number of heterogeneous nuclei more than 5 grains of zeolites leading to the lower p-CNB purity by agglomeration.
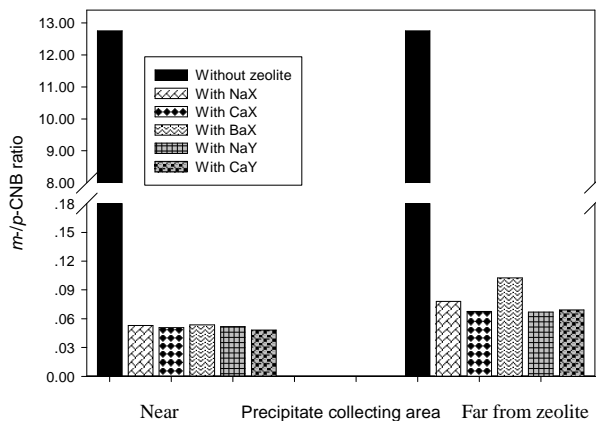

Fig. 4 Comparison of m-/p-CNB ratio of the precipitates with 65 wt% of m-CNB in the feed and 5 grains of zeolites (NaX, CaX, BaX, NaY, and CaY).
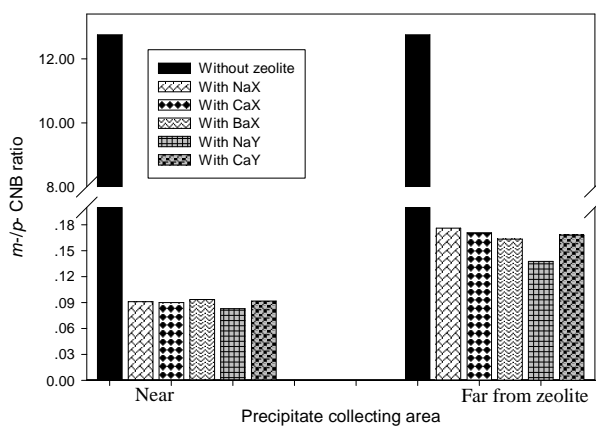

Fig. 5 Comparison of m-/p-CNB ratio of the precipitates with 65 wt% of m-CNB in the feed and 10 grains of zeolites (NaX, CaX, BaX, NaY, and CaY)

IV. CONCLUSIONS

The influence of feed compositions at 61.0, 62.9, and 65.0 wt% m-CNB on precipitate compositions and crystallization temperatures were studied. A mixture containing m- and p-CNB forms a eutectic mixture having a composition of 62.87 wt% m-CNB and 37.13 wt% p-CNB by cooling to 23°C. Below the eutectic composition, the precipitates by cooling to 23°C are rich in the para isomer, 90.4 wt% purity, while above the eutectic composition, the precipitates by cooling to 23°C are rich in the meta isomer, 92.73 wt% purity.

In the feed above the eutectic composition, the effects of zeolites (NaX, CaX, BaX, NaY, and CaY) on the m- and p-CNB crystallization were studied. The zeolites can shift the precipitate composition from being rich in m-CNB to rich in p-CNB. That may be related to the metastable zone width. Moreover, the crystallization of the feed solution with 5 grains of the zeolites results in the precipitates with high p-CNB compositions than that from the solution with 10 grains of the

zeolites. The precipitates near the zeolites have a purity of *p*-CNB higher than those far from the zeolites. A zeolite has considerable effects on the precipitate composition in the area far from the zeolites more than that in the area near the zeolites, especially in the feed with 10 grains of the zeolites.

REFERENCES

[1] W. Priegnitz, "Process for the separation of ortho-chloronitrobenzene," *United States Patent* 4 240 986 to UOP Inc, 1980.

[2] R. Demuth, B.M. Konig, T. Linn, and H.J. Raat, H.M. Weber, E. Zirngiebl, and R. Leiberich, "Continuous adiabatic process for preparing nitrochlorobenzene," *United States Patent*, 0 161 269 to Bayer Corporation, 2002.

[3] L. Roberto, "Separation by crystallization in presence of water," *U.S. Patent*, 3 816 551 to Monsanto Company, 1974.

[4] J.W. Mullin, *Crystallization*. Oxford: Butterworth-Heinemann, 2001.

[5] "Fractional crystallization," *Documenst*, Sulzer Chemtech Ltd., http://www. sulzerchemtech.com/en/PortalData/11/Resources/Brochures/ MTT/Fractional_Crystallization-e.pdf.

[6] K. Funakoshi, H. Takiyama, and M. Matsuoka, "Influences of seed crystals on the agglomeration phenomena product purity of m-chloronitrobenzene crystals in bath crystallization," *Chemical Engineering Journal,* vol. 81, pp 307-313, 2001.