



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Effect of Feed Composition on *m*- and *p*-CNB Crystallization

The starting liquid mixtures at 61.0, 62.9, and 65.0 wt% *m*-CNB were studied without any zeolite in order to investigate precipitate compositions and temperatures that the precipitates were formed. Seven grams of solid *m*- and *p*-CNB were melted to obtain a homogeneous liquid solution. The liquid mixture was measured for the CNB compositions by using the GC. Then, the liquid mixture in the crystallizer was cooled by the cooling water from 30°C to a crystallization temperature. All precipitates were collected from the crystallizer, washed, and dissolved with hexane. The dissolved precipitates were measured for the CNB compositions by using the GC. The CNB compositions with different starting liquid mixtures without any zeolite are shown in Table 4.1.

Table 4.1 Composition of *m*- and *p*-CNB in the feeds and precipitates, and crystallization temperatures

| Feed | Feed composition (wt%) | | Precipitate composition (wt%) | | Crystallization temperature (°C) |
|--------------------------------|------------------------|---------------|-------------------------------|---------------|----------------------------------|
| | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> -CNB | <i>p</i> -CNB | |
| Below the eutectic composition | 60.97 | 39.03 | 8.92 | 91.08 | 23.0 |
| At the eutectic composition | 62.90 | 37.10 | 62.95 | 37.05 | 23.0 |
| Above the eutectic composition | 65.02 | 34.98 | 89.85 | 10.15 | 23.5 |

The result shows that the precipitates appear in a crystal form with 61 wt% *m*-CNB (below the eutectic composition) and 65 wt% *m*-CNB (above the eutectic composition) in the feed, while the precipitates from 62.9 wt% *m*-CNB (at the eutectic composition) in the feed is a solid mixture of *m*- and *p*-CNB. Below the eutectic composition, the precipitates are rich in *p*-CNB, 91.08 wt% purity. Above the eutectic composition, the precipitates are rich in *m*-CNB, 89.85 wt% purity. The precipitate composition and crystallization temperature at each feed composition are shown in Table 4.1. These results conform with binary phase diagram as shown in Figure 4.1. 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 (Mullin, 2001). These are possible reasons why the purity of precipitate is not close to 100 wt%.

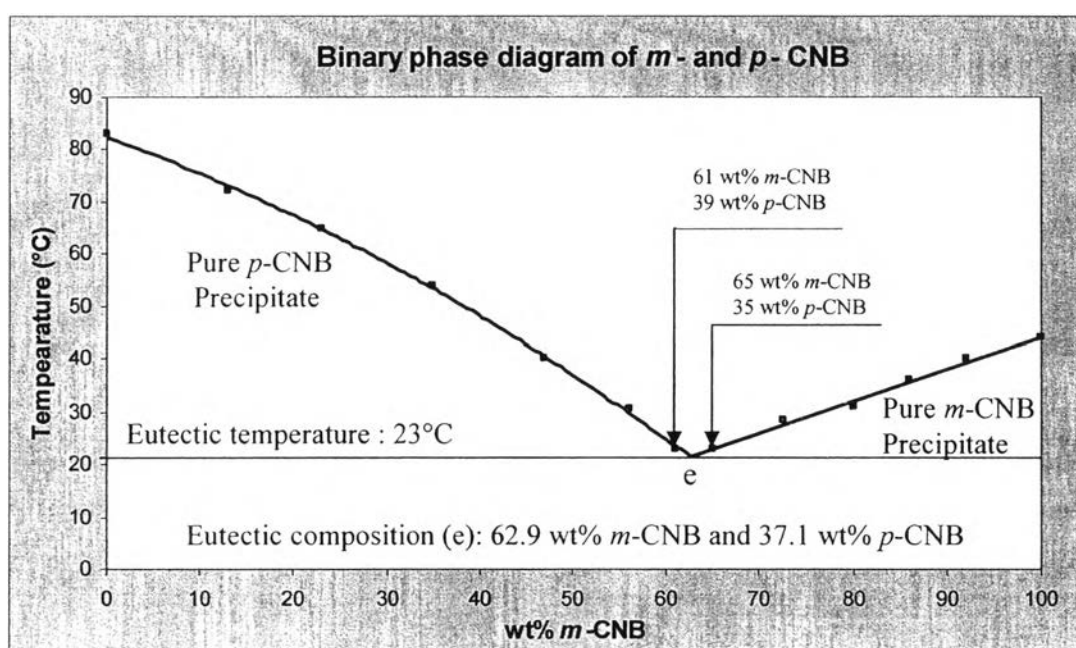


Figure 4.1 Binary phase diagram of *m*- and *p*-CNB (Sulzer Chemtech Pte., Ltd).

4.2 Effect of the FAU Zeolite on the *m*- and *p*-CNB Crystallization

4.2.1 Effect of FAU Zeolites on the CNB Feed Solution Compositions

To investigate the effects of the number of zeolites on the feed composition, an experiment was carried out with 61 wt% *m*-CNB or below the eutectic composition in the feed or starting liquid mixture: 7 g of 0.61 and 0.39 mass fraction of *m*-CNB and *p*-CNB. The mixture was melted to obtain a homogeneous liquid mixture. The zeolites used in this work were prepared by calcinations at 350°C for an hour before adding into the CNB mixture. After a given time, the mixture was stirred to minimize any concentration gradient in the solution. Then, the mixture compositions after adding a zeolite were measured by the GC. The results are shown in Tables 4.2 and 4.3. The feed compositions before and after adding the zeolites are about the same regardless the number of the zeolite. It appears that the studied number of zeolites hardly affects the *m*- and *p*-CNB compositions in the liquid mixture.

Table 4.2 *m*- and *p*-CNB composition in the feed with 61 wt% of *m*-CNB before and after adding 5 grains of zeolites at 30°C

| Zeolite | Feed composition before adding zeolite (wt%) | | Feed composition after adding zeolite (wt%) | | % difference* |
|---------|---|---------------|--|---------------|------------------|
| | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> -CNB | <i>p</i> -CNB | |
| NaX | 60.98 | 39.02 | 60.93 | 39.07 | -0.05 |
| CaX | 60.97 | 39.03 | 60.93 | 39.07 | -0.04 |
| BaX | 61.00 | 39.00 | 61.02 | 38.98 | +0.02 |
| NaY | 61.04 | 38.96 | 60.98 | 39.02 | -0.06 |
| CaY | 60.95 | 39.05 | 60.97 | 39.03 | -0.02 |

* %difference is the difference between the *m*-CNB composition in the feed with and without a zeolite.

Table 4.3 *m*- and *p*-CNB composition in the feed with 61 wt% of *m*-CNB before and after adding 10 grains of zeolites at 30°C

| Zeolite | Feed composition before adding zeolite (wt%) | | Feed composition after adding zeolite (wt%) | | % difference* |
|---------|---|---------------|--|---------------|------------------|
| | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> -CNB | <i>p</i> -CNB | |
| NaX | 61.04 | 38.96 | 60.98 | 39.02 | -0.06 |
| CaX | 60.97 | 39.03 | 60.95 | 39.05 | -0.02 |
| BaX | 60.95 | 39.05 | 60.93 | 39.07 | -0.02 |
| NaY | 61.00 | 39.00 | 60.94 | 39.06 | -0.06 |
| CaY | 61.03 | 38.97 | 60.98 | 39.02 | -0.05 |

* %difference is the difference between the *m*-CNB composition in the feed with and without a zeolite.

4.2.2 Effect of the Number of Zeolites on the CNB Precipitate Compositions and Crystallization Temperature

To study effect of the number of a zeolite on the precipitate composition, a CNB mixture with 5 grains and 10 grains of a zeolite was cooled by cooling water at the cooling rate of 1°C/hr from 30°C until precipitates were formed. The precipitates were collected, washed and dissolved with hexane. The CNB precipitate composition (Run#1) was analyzed by the GC. The experiment was repeated by heating the mixture back to homogeneous phase. The liquid mixture was taken to check the composition and then cooled the system until the precipitates were formed again. The CNB precipitate composition (Run#2) was analyzed. The precipitates were taken from 8 positions in two areas; the 1-4 positions near the zeolites (area (a)) and the 5-8 position far from the zeolites (area (b)) as shown in Figure 4.2.

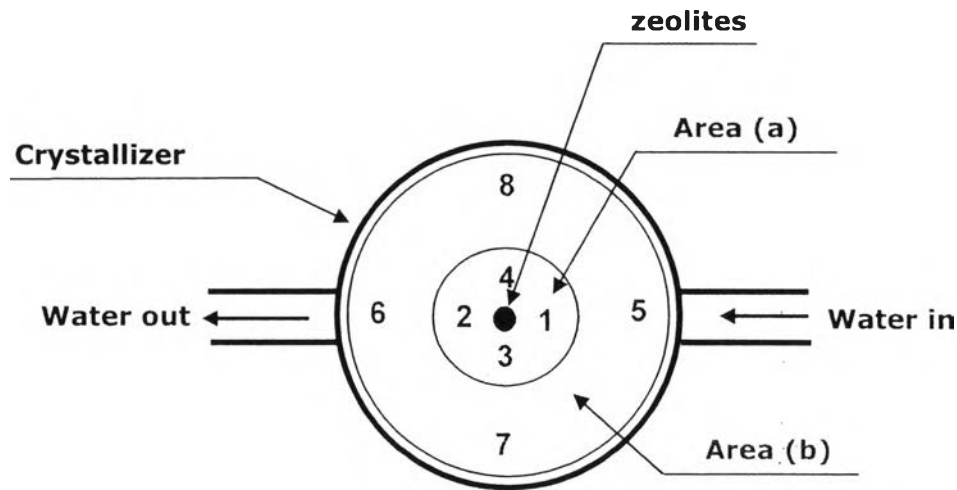


Figure 4.2 Locations where precipitates were collected for *m*- and *p*-CNB composition analysis.

From Tables 4.4-4.7, the presence of the zeolites in the system with 61 wt% *m*-CNB or below the eutectic composition in the feed resulted in precipitates rich in *p*-CNB. It can be clearly seen that the precipitates near the zeolites (area(a)) have a purity of *p*-CNB higher than those far from the zeolites (area(b)). The crystallization of the feed solution with 5 grains of the zeolites resulted in the precipitates with high *p*-CNB compositions (Tables 4.4-4.5) than that from the solution with 10 grains of the zeolites (Tables 4.6-4.7). And that is true for both areas, near and far from the zeolites.

Table 4.4 Composition of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#1) with 61 wt% of *m*-CNB in the feed and 5 grains of zeolites

| Zeolite | Precipitate near zeolite | | | Precipitate far from zeolite | | |
|---------|--------------------------|---------------|---------------------------|------------------------------|---------------|---------------------------|
| | Composition (wt%) | | | Composition (wt%) | | |
| | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> -/ <i>p</i> -CNB | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> -/ <i>p</i> -CNB |
| NaX | 6.20 [1] | 93.80 [1] | 0.0661 | 10.39 [5] | 89.61 [5] | 0.1159 |
| | 7.85 [2] | 92.15 [2] | 0.0852 | 8.39 [6] | 91.61 [6] | 0.0916 |
| | 6.25 [3] | 93.75 [3] | 0.0667 | 13.14 [7] | 86.86 [7] | 0.1513 |
| | 4.43 [4] | 95.57 [4] | 0.0464 | 9.29 [8] | 90.71 [8] | 0.1024 |
| CaX | 4.74 [1] | 95.26 [1] | 0.0498 | 4.25 [5] | 95.75 [5] | 0.0444 |
| | 4.16 [2] | 95.84 [2] | 0.0434 | 6.56 [6] | 93.44 [6] | 0.0702 |
| | 5.17 [3] | 94.83 [3] | 0.0545 | 6.84 [7] | 93.16 [7] | 0.0734 |
| | 6.32 [4] | 93.68 [4] | 0.0675 | 9.67 [8] | 90.33 [8] | 0.1071 |
| BaX | 4.79 [1] | 95.21 [1] | 0.0503 | 5.58 [5] | 94.42 [5] | 0.0591 |
| | 6.09 [2] | 93.91 [2] | 0.0648 | 4.23 [6] | 95.77 [6] | 0.0442 |
| | 4.65 [3] | 95.35 [3] | 0.0488 | 6.49 [7] | 93.51 [7] | 0.0694 |
| | 4.40 [4] | 95.60 [4] | 0.0460 | 4.14 [8] | 95.86 [8] | 0.0432 |
| NaY | 6.41 [1] | 93.59 [1] | 0.0685 | 8.34 [5] | 91.66 [5] | 0.0910 |
| | 5.84 [2] | 94.16 [2] | 0.0620 | 7.37 [6] | 92.63 [6] | 0.0796 |
| | 4.14 [3] | 95.86 [3] | 0.0432 | 8.04 [7] | 91.96 [7] | 0.0874 |
| | 6.27 [4] | 93.73 [4] | 0.0669 | 6.91 [8] | 93.09 [8] | 0.0742 |
| CaY | 7.67 [1] | 92.33 [1] | 0.0831 | 6.47 [5] | 93.53 [5] | 0.0692 |
| | 4.79 [2] | 95.21 [2] | 0.0503 | 9.24 [6] | 90.76 [6] | 0.1018 |
| | 6.89 [3] | 93.11 [3] | 0.0740 | 7.33 [7] | 92.67 [7] | 0.0791 |
| | 6.06 [4] | 93.94 [4] | 0.0645 | 8.88 [8] | 91.12 [8] | 0.0975 |

* The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

Table 4.5 Composition of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#2) with 61 wt% of *m*-CNB in the feed and 5 grains of zeolites

| Zeolite | Precipitate near zeolite | | | Precipitate far from zeolite | | |
|---------|--------------------------|---------------|---------------------------|------------------------------|---------------|---------------------------|
| | Composition (wt%) | | | Composition (wt%) | | |
| | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> -/ <i>p</i> -CNB | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> -/ <i>p</i> -CNB |
| NaX | 6.07 [1] | 93.93 [1] | 0.0646 | 9.88 [5] | 90.12 [5] | 0.1096 |
| | 4.66 [2] | 95.34 [2] | 0.0489 | 9.60 [6] | 90.40 [6] | 0.1062 |
| | 6.04 [3] | 93.96 [3] | 0.0643 | 8.17 [7] | 91.83 [7] | 0.0890 |
| | 7.07 [4] | 92.93 [4] | 0.0761 | 10.66 [8] | 89.34 [8] | 0.1193 |
| CaX | 7.51 [1] | 92.49 [1] | 0.0812 | 7.23 [5] | 92.77 [5] | 0.0779 |
| | 5.63 [2] | 94.37 [2] | 0.0597 | 10.67 [6] | 89.33 [6] | 0.1194 |
| | 7.71 [3] | 92.29 [3] | 0.0835 | 8.86 [7] | 91.14 [7] | 0.0972 |
| | 5.97 [4] | 94.03 [4] | 0.0635 | 10.07 [8] | 89.93 [8] | 0.1120 |
| BaX | 4.27 [1] | 95.73 [1] | 0.0446 | 8.03 [5] | 91.97 [5] | 0.0873 |
| | 7.02 [2] | 92.98 [2] | 0.0755 | 10.52 [6] | 89.48 [6] | 0.1176 |
| | 4.93 [3] | 95.07 [3] | 0.0519 | 9.68 [7] | 90.32 [7] | 0.1072 |
| | 5.70 [4] | 94.30 [4] | 0.0604 | 7.99 [8] | 92.01 [8] | 0.0868 |
| NaY | 4.66 [1] | 95.34 [1] | 0.0489 | 10.74 [5] | 89.26 [5] | 0.1203 |
| | 4.07 [2] | 95.93 [2] | 0.0424 | 7.07 [6] | 92.93 [6] | 0.0761 |
| | 7.11 [3] | 92.89 [3] | 0.0765 | 8.10 [7] | 91.90 [7] | 0.0881 |
| | 5.98 [4] | 94.02 [4] | 0.0636 | 8.38 [8] | 91.62 [8] | 0.0915 |
| CaY | 7.88 [1] | 92.12 [1] | 0.0855 | 13.64 [5] | 86.36 [5] | 0.1579 |
| | 7.80 [2] | 92.20 [2] | 0.0846 | 8.39 [6] | 91.61 [6] | 0.0916 |
| | 5.06 [3] | 94.94 [3] | 0.0533 | 6.75 [7] | 93.25 [7] | 0.0724 |
| | 4.14 [4] | 95.86 [4] | 0.0432 | 6.88 [8] | 93.12 [8] | 0.0739 |

* The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

Table 4.6 Composition of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#1) with 61 wt% of *m*-CNB in the feed and 10 grains of zeolites

| Zeolite | Precipitate near zeolite | | | Precipitate far from zeolite | | |
|---------|--------------------------|---------------|--------------------------|------------------------------|---------------|--------------------------|
| | Composition (wt%) | | | Composition (wt%) | | |
| | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> / <i>p</i> -CNB | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> / <i>p</i> -CNB |
| NaX | 7.15 [1] | 92.85 [1] | 0.0770 | 10.63 [5] | 89.37 [5] | 0.1189 |
| | 6.28 [2] | 93.72 [2] | 0.0670 | 13.35 [6] | 86.65 [6] | 0.1541 |
| | 9.25 [3] | 90.75 [3] | 0.1019 | 11.66 [7] | 88.34 [7] | 0.1320 |
| | 7.10 [4] | 92.90 [4] | 0.0764 | 12.32 [8] | 87.68 [8] | 0.1405 |
| CaX | 8.54 [1] | 91.46 [1] | 0.0934 | 12.15 [5] | 87.85 [5] | 0.1383 |
| | 7.24 [2] | 92.76 [2] | 0.0781 | 12.40 [6] | 87.60 [6] | 0.1416 |
| | 7.50 [3] | 92.50 [3] | 0.0811 | 10.13 [7] | 89.87 [7] | 0.1127 |
| | 6.35 [4] | 93.65 [4] | 0.0678 | 10.35 [8] | 89.65 [8] | 0.1154 |
| BaX | 5.19 [1] | 94.81 [1] | 0.0547 | 7.71 [5] | 92.29 [5] | 0.0835 |
| | 5.99 [2] | 94.01 [2] | 0.0637 | 8.88 [6] | 91.12 [6] | 0.0975 |
| | 6.98 [3] | 93.02 [3] | 0.0750 | 7.36 [7] | 92.64 [7] | 0.0794 |
| | 7.16 [4] | 92.84 [4] | 0.0771 | 8.39 [8] | 91.61 [8] | 0.0916 |
| NaY | 7.53 [1] | 92.47 [1] | 0.0814 | 9.88 [5] | 90.12 [5] | 0.1096 |
| | 6.35 [2] | 93.65 [2] | 0.0678 | 8.96 [6] | 91.04 [6] | 0.0984 |
| | 6.24 [3] | 93.76 [3] | 0.0666 | 10.83 [7] | 89.17 [7] | 0.1215 |
| | 7.01 [4] | 92.99 [4] | 0.0754 | 9.85 [8] | 90.15 [8] | 0.1093 |
| CaY | 7.12 [1] | 92.88 [1] | 0.0767 | 12.20 [5] | 87.80 [5] | 0.1390 |
| | 6.93 [2] | 93.07 [2] | 0.0745 | 14.58 [6] | 85.42 [6] | 0.1707 |
| | 7.24 [3] | 92.76 [3] | 0.0781 | 13.49 [7] | 86.51 [7] | 0.1559 |
| | 10.05 [4] | 89.95 [4] | 0.1117 | 15.27 [8] | 84.73 [8] | 0.1802 |

* The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

Table 4.7 Composition of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#2) with 61 wt% of *m*-CNB in the feed and 10 grains of zeolites

| Zeolite | Precipitate near zeolite | | | Precipitate far from zeolite | | |
|---------|--------------------------|---------------|--------------------------|------------------------------|---------------|--------------------------|
| | Composition (wt%) | | | Composition (wt%) | | |
| | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> / <i>p</i> -CNB | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> / <i>p</i> -CNB |
| NaX | 9.24 [1] | 90.76 [1] | 0.1018 | 14.06 [5] | 85.94 [5] | 0.1636 |
| | 9.05 [2] | 90.95 [2] | 0.0995 | 15.96 [6] | 84.04 [6] | 0.1899 |
| | 11.78 [3] | 88.22 [3] | 0.1335 | 13.68 [7] | 86.32 [7] | 0.1585 |
| | 10.35 [4] | 89.65 [4] | 0.1154 | 13.40 [8] | 86.60 [8] | 0.1547 |
| CaX | 8.08 [1] | 91.92 [1] | 0.0879 | 13.99 [5] | 86.01 [5] | 0.1627 |
| | 10.12 [2] | 89.88 [2] | 0.1126 | 14.11 [6] | 85.89 [6] | 0.1643 |
| | 8.89 [3] | 91.11 [3] | 0.0976 | 12.86 [7] | 87.14 [7] | 0.1476 |
| | 7.43 [4] | 92.57 [4] | 0.0803 | 12.89 [8] | 87.11 [8] | 0.1480 |
| BaX | 8.90 [1] | 91.10 [1] | 0.0977 | 11.28 [5] | 88.72 [5] | 0.1271 |
| | 6.92 [2] | 93.08 [2] | 0.0743 | 9.25 [6] | 90.75 [6] | 0.1019 |
| | 8.67 [3] | 91.33 [3] | 0.0949 | 11.77 [7] | 88.23 [7] | 0.1334 |
| | 7.62 [4] | 92.38 [4] | 0.0825 | 9.13 [8] | 90.87 [8] | 0.1005 |
| NaY | 7.61 [1] | 92.39 [1] | 0.0824 | 12.59 [5] | 87.41 [5] | 0.1440 |
| | 8.34 [2] | 91.66 [2] | 0.0910 | 11.34 [6] | 88.66 [6] | 0.1279 |
| | 7.14 [3] | 92.86 [3] | 0.0769 | 11.10 [7] | 88.90 [7] | 0.1249 |
| | 8.04 [4] | 91.96 [4] | 0.0874 | 10.38 [8] | 89.62 [8] | 0.1158 |
| CaY | 10.16 [1] | 89.84 [1] | 0.1131 | 14.58 [5] | 85.42 [5] | 0.1707 |
| | 8.15 [2] | 91.85 [2] | 0.0887 | 16.98 [6] | 83.02 [6] | 0.2045 |
| | 9.02 [3] | 90.98 [3] | 0.0991 | 15.18 [7] | 84.82 [7] | 0.1790 |
| | 6.93 [4] | 93.07 [4] | 0.0745 | 14.61 [8] | 85.39 [8] | 0.1711 |

* The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

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. The size of a foreign body is important and there is an evidence to suggest that the most active particle (heteronuclei) in liquid solution lie in the range 0.1 to 1 μm (Mullin, 2001). 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 (Mullin, 2001). 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 are correlated as a function of the number of particles and the supersaturation in the solution (Funakoshi *et al.*, 2001). 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. That is because the higher number of primary nuclei can generate the higher number of secondary nuclei in the system. After the secondary nucleation, these nuclei start to agglomerate and grow (Mullin, 2001). Hence, the purity of agglomerates decreases with the increase of the number of elementary crystals constituting agglomerates. Moreover, the purity decrease is more substantial when the agglomerate size is smaller. This can be explained that the number of elementary crystals significantly affects the purity decrease since the higher number of nuclei, the greater contact probabilities and collision of nuclei in the system leads to the entrainment of mother liquor during agglomeration (Funakoshi *et al.*, 2001). 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.

To see the tendency of precipitate compositions clearly, the CNB precipitate compositions from Run#1 in the feed solution below the eutectic composition with 5 and 10 grains of zeolites were calculated in terms of *m*-/*p*-CNB ratio, as seen in Figures 4.3 and 4.4, respectively. Moreover, crystallization temperatures of the solution with the presence of each zeolite at 5 and 10 grains are shown in Table 4.8. From Figure 4.3, the result shows 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 increases at the locations far from the zeolite except BaX, which provides the similar ratio in both areas. The m/p -CNB ratio of the precipitates near the zeolite seems to be independent on a type of zeolite. With 10 grains of zeolites, as shown in Figure 4.4, the results revealed that a type of zeolite significantly affects the ratio of the precipitates far from the zeolite. Nevertheless, that has very little effect on the ratio of the precipitates near the zeolite. Furthermore, the presence of zeolites can induce nucleation at a temperature lower than that requires for crystallization without any zeolite, as seen in Table 4.8. The tendency of crystallization temperature in the feed with 5 grains of zeolites is higher than that in the feed with 10 grains of zeolites.

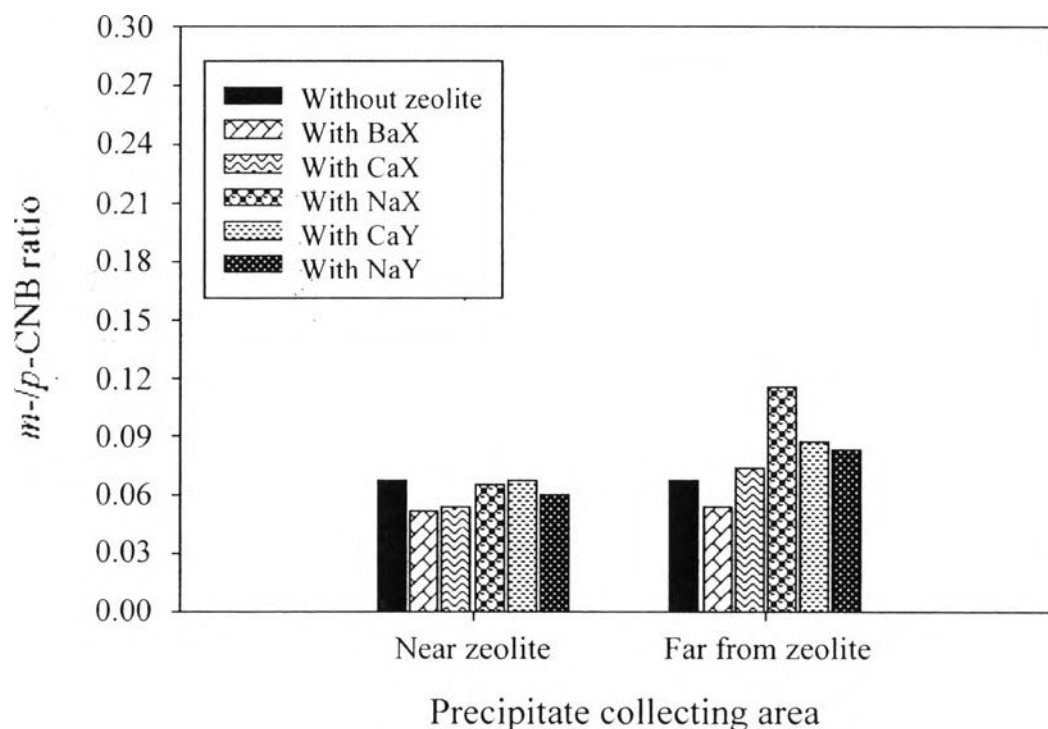


Figure 4.3 Comparison of m/p -CNB ratio of the precipitates with 61 wt% of m -CNB in the feed and 5 grains of zeolites (BaX, CaX, NaX, CaY, and NaY).

Table 4.8 Crystallization temperatures at 61 wt% of *m*-CNB in the feed with 5 and 10 grains of zeolites

| Type of zeolite | Crystallization Temperature (°C) | |
|-----------------|----------------------------------|----------------------|
| | 5 grains of zeolite | 10 grains of zeolite |
| Without zeolite | 23 | 23 |
| BaX | 22 | 20 |
| CaX | 21 | 21 |
| NaX | 21 | 21 |
| CaY | 22 | 20 |
| NaY | 22 | 21 |

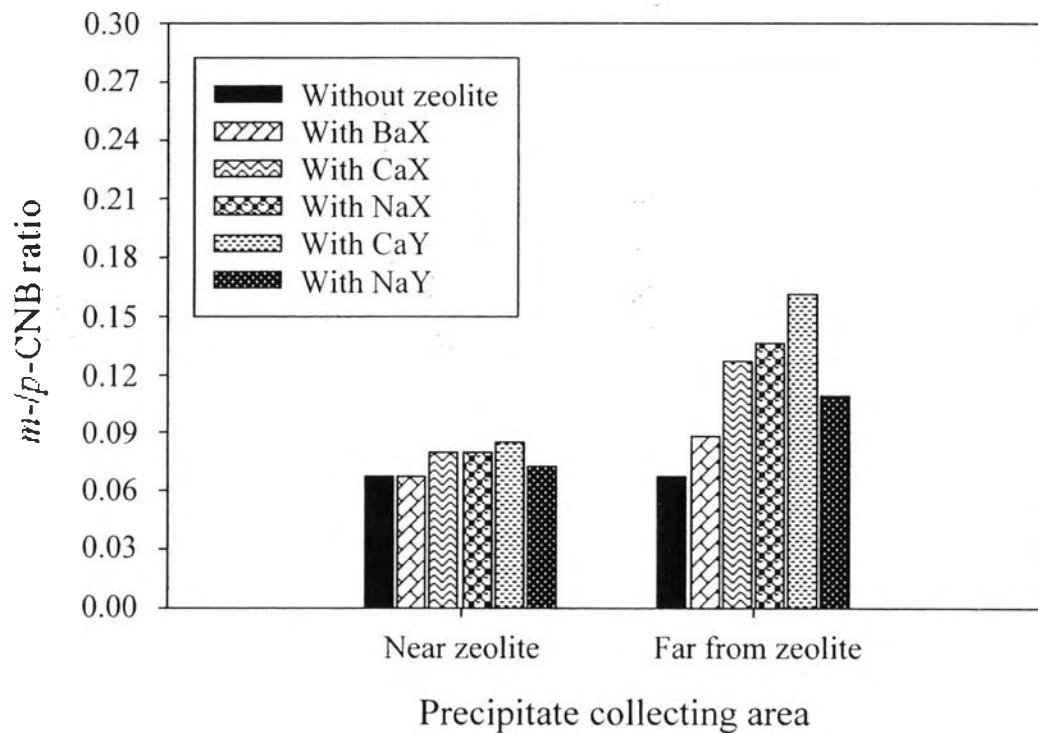


Figure 4.4 Comparison of *m-p*-CNB ratio of the precipitates with 61 wt% of *m*-CNB in the feed and 10 grains of zeolites (BaX, CaX, NaX, CaY, and NaY).

From Figures 4.3 and 4.4, 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 crystallization temperatures from 10 grains of zeolites are lower than those from the 5 grains. That may be due to high supersaturation resulting in fast nucleation and creation of large number of very small crystal (Mullin, 2001). 10 grains of the zeolites may accelerate the system into nucleation step faster than 5 grains of zeolites, and precipitates from the 10 grains will have the longer time in agglomeration and growth than the 5 grains. Agglomeration in the bulk can occur more than in the area of zeolites because of higher number of nuclei so the m/p -CNB ratio of precipitates near and far from 10 grains of zeolites is clearly different. The rate of nucleation of a solution can be affected considerably by the presence of mere trace impurities in the system. However, impurities that act as a nucleation inhibitor in one case may not necessarily be effective in another; indeed, it may even act as an accelerator. No general rule applies and each case must be considered separately (Mullin, 2001).

In order to compare compositions of CNB precipitates from the feed below the eutectic composition with 5 and 10 grains of zeolites, all precipitates in the crystallizer after Run#2 were collected and the results are shown in Table 4.9 and Figure 4.5. Table 4.9 shows that precipitates from the feed with 5 grains of zeolites have higher p -CNB purity than those from the feed with 10 grains of zeolites, and it is true in all tested zeolites. This result confirms the result of the precipitates collected from the positions 1 to 8 in the two areas as shown in Figure 4.2.

Table 4.9 *m*- and *p*-CNB compositions of all precipitates collected from 61 wt% *m*-CNB in the feed with 5 and 10 grains of zeolites

| Zeolite | 5 grains of zeolites | | | 10 grains of zeolites | | |
|---------|-------------------------------|---------------|---------------------------------|-------------------------------|---------------|---------------------------------|
| | Precipitate composition (wt%) | | <i>m</i> -/ <i>p</i> -CNB ratio | Precipitate composition (wt%) | | <i>m</i> -/ <i>p</i> -CNB ratio |
| | <i>m</i> -CNB | <i>p</i> -CNB | | <i>m</i> -CNB | <i>p</i> -CNB | |
| NaX | 10.38 | 89.62 | 0.1158 | 13.79 | 86.21 | 0.1600 |
| CaX | 9.44 | 90.56 | 0.1042 | 12.96 | 87.04 | 0.1489 |
| BaX | 9.19 | 90.81 | 0.1012 | 9.69 | 90.31 | 0.1073 |
| NaY | 8.67 | 91.33 | 0.0949 | 11.35 | 88.65 | 0.1280 |
| CaY | 9.71 | 90.29 | 0.1075 | 16.45 | 83.55 | 0.1969 |

Figure 4.5 indicates that a type of zeolite has a great influence on the *m*-/*p*-CNB ratio in the feed with 10 grains of zeolites, but has a very little effect on the ratio in the feed with 5 grains of zeolites. BaX provides the lowest *m*-/*p*-CNB ratio or the highest *p*-CNB composition at 10 grains of zeolites. A possible reason why the purity of *p*-CNB in Figure 4.5 is not as high as that in Figures 4.3 and 4.4 may be from the contamination with residual solvent or other impurities that have not been removed by washing.

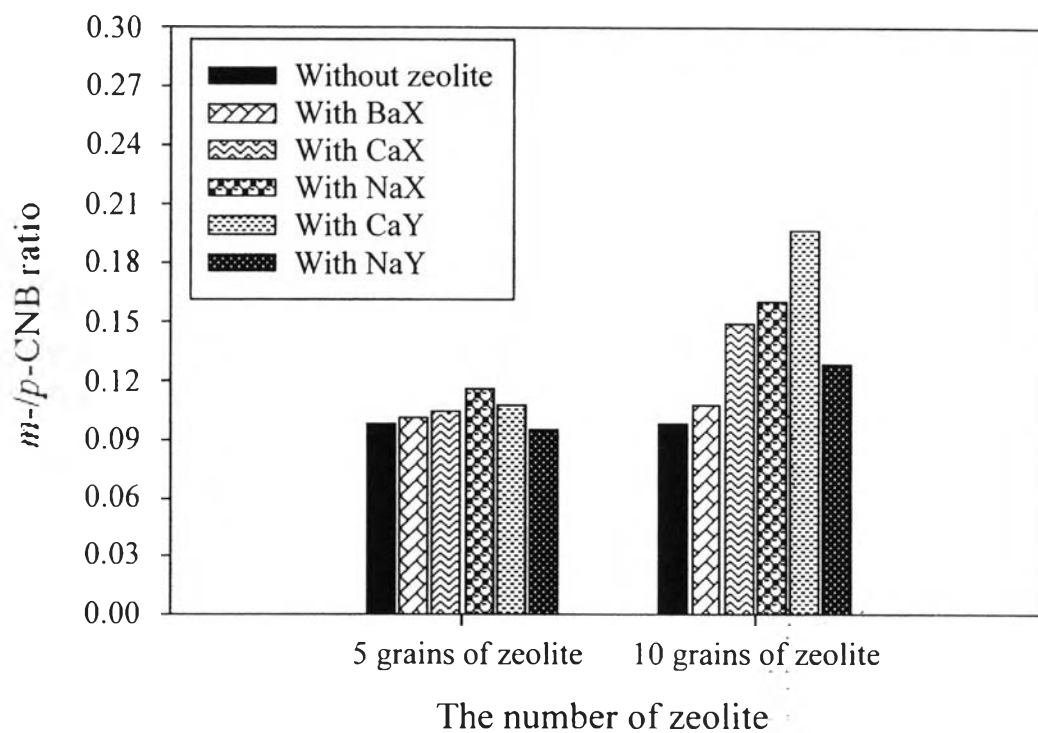


Figure 4.5 Effect of the number of zeolite on $m-/p$ -CNB ratio of the precipitates at 61 wt% m -CNB in the feed.

4.2.3 Effect of FAU Zeolites on the CNB Precipitate Compositions

In addition, to investigate the effects of the zeolites on precipitates from the feed above the eutectic composition, experiments were carried out at 65 wt% m -CNB in the feed with 5 grains of zeolites. The experiment was done in the same procedure as that below the eutectic composition. The precipitates were taken from 8 positions in two areas; the 1-4 positions near the zeolites (area (a)) and the 5-8 position far from the zeolites (area (b)). The results are shown in Tables 4.10 and 4.11.

Table 4.10 Composition of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#1) with 65 wt% *m*-CNB in the feed and 5 grains of zeolites

| Zeolite | Precipitate near zeolite | | | Precipitate far from zeolite | | |
|---------|--------------------------|---------------|--------------------------|------------------------------|---------------|--------------------------|
| | Composition (wt%) | | | Composition (wt%) | | |
| | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> / <i>p</i> -CNB | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> / <i>p</i> -CNB |
| NaX | 4.90 [1] | 95.10 [1] | 0.0515 | 6.36 [5] | 93.64 [5] | 0.0679 |
| | 5.62 [2] | 94.38 [2] | 0.0595 | 7.59 [6] | 92.41 [6] | 0.0821 |
| | 4.95 [3] | 95.05 [3] | 0.0521 | 7.98 [7] | 92.02 [7] | 0.0867 |
| | 4.65 [4] | 95.35 [4] | 0.0488 | 6.97 [8] | 93.03 [8] | 0.0749 |
| CaX | 4.94 [1] | 95.06 [1] | 0.0520 | 5.65 [5] | 94.35 [5] | 0.0599 |
| | 5.25 [2] | 94.75 [2] | 0.0554 | 5.49 [6] | 94.51 [6] | 0.0581 |
| | 4.69 [3] | 95.31 [3] | 0.0492 | 6.28 [7] | 93.72 [7] | 0.0670 |
| | 4.42 [4] | 95.58 [4] | 0.0462 | 7.87 [8] | 92.13 [8] | 0.0854 |
| BaX | 5.02 [1] | 94.98 [1] | 0.0529 | 8.40 [5] | 91.60 [5] | 0.0917 |
| | 6.31 [2] | 93.69 [2] | 0.0673 | 9.20 [6] | 90.80 [6] | 0.1013 |
| | 4.10 [3] | 95.90 [3] | 0.0428 | 10.98 [7] | 89.02 [7] | 0.1233 |
| | 4.92 [4] | 95.08 [4] | 0.0517 | 8.61 [8] | 91.39 [8] | 0.0942 |
| NaY | 5.01 [1] | 94.99 [1] | 0.0527 | 5.80 [5] | 94.20 [5] | 0.0616 |
| | 4.56 [2] | 95.44 [2] | 0.0478 | 6.09 [6] | 93.91 [6] | 0.0648 |
| | 4.80 [3] | 95.20 [3] | 0.0504 | 5.75 [7] | 94.25 [7] | 0.0610 |
| | 5.26 [4] | 94.74 [4] | 0.0555 | 7.39 [8] | 92.61 [8] | 0.0798 |
| CaY | 4.72 [1] | 95.28 [1] | 0.0495 | 6.10 [5] | 93.90 [5] | 0.0650 |
| | 4.65 [2] | 95.35 [2] | 0.0488 | 6.71 [6] | 93.29 [6] | 0.0719 |
| | 4.57 [3] | 95.43 [3] | 0.0479 | 7.25 [7] | 92.75 [7] | 0.0782 |
| | 4.41 [4] | 95.59 [4] | 0.0461 | 5.74 [8] | 94.26 [8] | 0.0609 |

* The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

Table 4.11 Composition of *m*- and *p*-CNB in the precipitates located near and far from zeolites (Run#2) with 65 wt% *m*-CNB in the feed and 5 grains of zeolites

| Zeolite | Precipitate near zeolite | | | Precipitate far from zeolite | | |
|---------|--------------------------|---------------|---------------------------|------------------------------|---------------|---------------------------|
| | Composition (wt%) | | | Composition (wt%) | | |
| | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> -/ <i>p</i> -CNB | <i>m</i> -CNB | <i>p</i> -CNB | <i>m</i> -/ <i>p</i> -CNB |
| NaX | 4.68 [1] | 95.32 [1] | 0.0491 | 8.66 [5] | 91.34 [5] | 0.0948 |
| | 5.12 [2] | 94.88 [2] | 0.0540 | 6.46 [6] | 93.54 [6] | 0.0691 |
| | 5.09 [3] | 94.91 [3] | 0.0536 | 6.84 [7] | 93.16 [7] | 0.0734 |
| | 5.24 [4] | 94.76 [4] | 0.0553 | 7.13 [8] | 92.87 [8] | 0.0768 |
| CaX | 5.60 [1] | 94.40 [1] | 0.0593 | 7.31 [5] | 92.69 [5] | 0.0789 |
| | 5.92 [2] | 94.08 [2] | 0.0629 | 6.16 [6] | 93.84 [6] | 0.0656 |
| | 6.36 [3] | 93.64 [3] | 0.0679 | 8.94 [7] | 91.06 [7] | 0.0982 |
| | 6.09 [4] | 93.91 [4] | 0.0648 | 8.53 [8] | 91.47 [8] | 0.0933 |
| BaX | 5.58 [1] | 94.42 [1] | 0.0591 | 9.13 [5] | 90.87 [5] | 0.1005 |
| | 5.69 [2] | 94.31 [2] | 0.0603 | 8.77 [6] | 91.23 [6] | 0.0961 |
| | 5.97 [3] | 94.03 [3] | 0.0635 | 9.29 [7] | 90.71 [7] | 0.1024 |
| | 4.77 [4] | 95.23 [4] | 0.0501 | 11.35 [8] | 88.65 [8] | 0.1280 |
| NaY | 5.68 [1] | 94.32 [1] | 0.0602 | 6.93 [5] | 93.07 [5] | 0.0745 |
| | 5.23 [2] | 94.77 [2] | 0.0552 | 7.76 [6] | 92.24 [6] | 0.0841 |
| | 4.47 [3] | 95.53 [3] | 0.0468 | 6.42 [7] | 93.58 [7] | 0.0686 |
| | 5.92 [4] | 94.08 [4] | 0.0629 | 6.06 [8] | 93.94 [8] | 0.0645 |
| CaY | 5.27 [1] | 94.73 [1] | 0.0556 | 7.06 [5] | 92.94 [5] | 0.0760 |
| | 6.15 [2] | 93.85 [2] | 0.0655 | 6.83 [6] | 93.17 [6] | 0.0733 |
| | 5.61 [3] | 94.39 [3] | 0.0594 | 6.44 [7] | 93.56 [7] | 0.0688 |
| | 4.32 [4] | 95.68 [4] | 0.0452 | 8.18 [8] | 91.82 [8] | 0.0891 |

* The number in the parenthesis refers to the position where precipitates were collected as shown in Figure 4.2.

The results show that the presence of zeolites in the feed above the eutectic composition can shift the precipitate composition from being rich in *m*-CNB to rich in *p*-CNB, and the precipitates near the zeolites have purity of *p*-CNB higher than those far from the zeolites. Furthermore, the precipitate composition from Run#2 is about the same as that from Run#1. The precipitates from the feed with a zeolite form at 18°C, which is lower than the crystallization temperature in the feed without any zeolite. The *m*-/*p*-CNB ratio of the precipitates with 65 wt% *m*-CNB in the feed and 5 grains of zeolites is shown Figure 4.6. The *m*-/*p*-CNB ratio of precipitates near the zeolites is lower than that far from the zeolites. The *m*-/*p*-CNB ratio near the zeolites seems to be independent on a type of a zeolite, whereas, far from the zeolites, the ratio slightly increases in the presence of BaX and NaX.

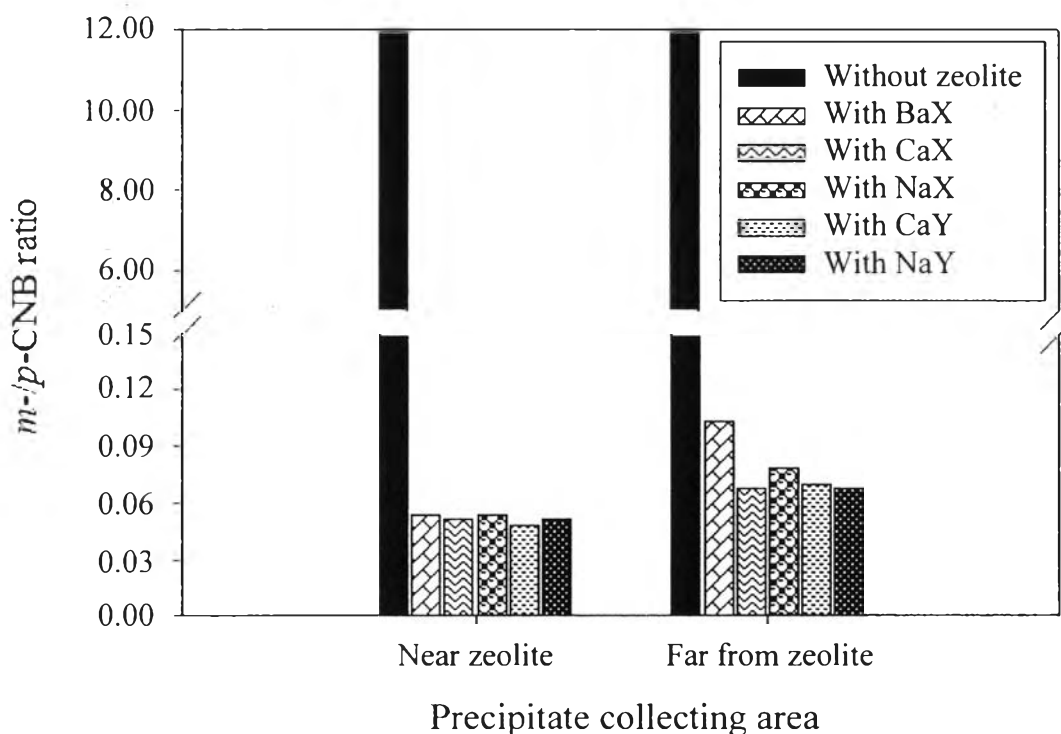


Figure 4.6 Comparison of *m*-/*p*-CNB ratio of the precipitates with 65 wt% *m*-CNB in the feed and 5 grains of zeolites (BaX, CaX, NaX, CaY, and NaY).

The m/p -CNB ratios of the precipitates with 61 and 65 wt% m -CNB in the feed and 5 grains of zeolites collected from all precipitates after Run#2 are presented in Figure 4.7. Comparison between the m/p -CNB ratios of all precipitates received from the feed below and above the eutectic composition with 5 grains of zeolites shows that, at the feed below the eutectic composition, most ratios from the crystallization with the zeolites have the m/p -CNB ratio higher than that from the crystallization without any zeolite. Again, the figure reiterates that for the feed above the eutectic composition, the precipitate compositions are shifted from being rich in m -CNB to rich in p -CNB. The m/p -CNB ratio of the precipitates in the feed below and above the eutectic composition seem to be independent on a type of the zeolites.

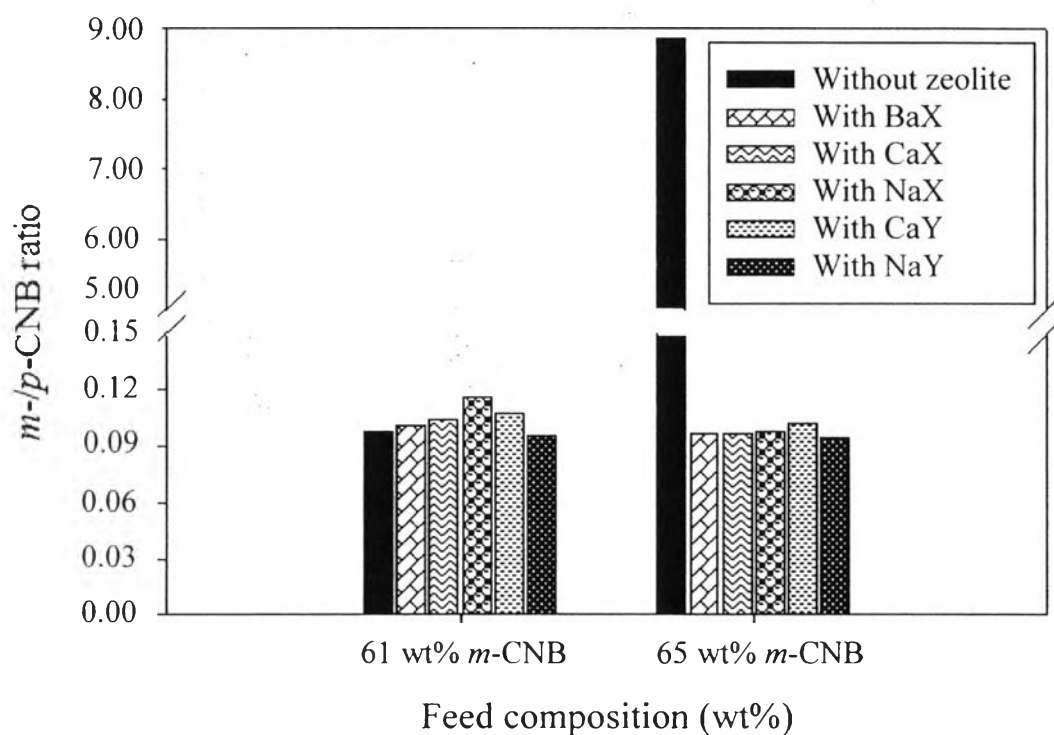


Figure 4.7 Comparison of m/p -CNB ratio of the precipitates with 61 and 65 wt% m -CNB in the feed and 5 grains of zeolites (BaX, CaX, NaX, CaY, and NaY).

From the results, a type of a zeolite affects the CNB precipitate compositions obtained from the feed below the eutectic composition with 10 grains of the zeolites. It might be because the difference of the crystallization condition or the amount of impurity in each experiment. Therefore, crystallization of the CNB mixtures below and above the eutectic composition with two grains of each zeolite (BaX, CaX, NaX, CaY, and NaY) was carried out, and the precipitates were collected above the zeolites in the five positions as shown in Figure 4.8.

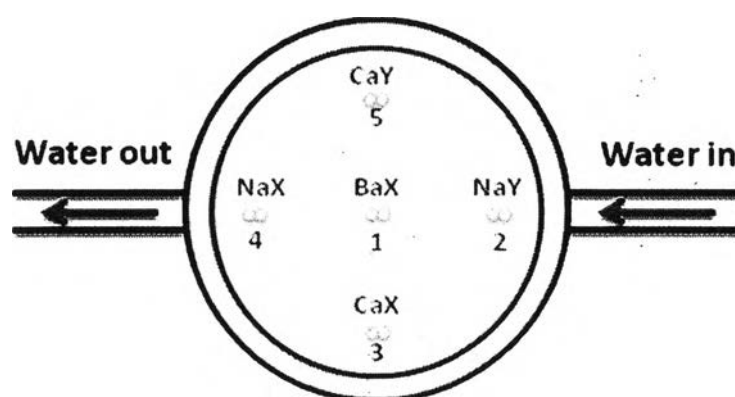


Figure 4.8 Experimental set up to study effects of two grains of each zeolites (BaX, CaX, NaX, CaY, and NaY) in 61 and 65 wt% of *m*-CNB in the feed.

The *m*-/*p*-CNB ratio of the precipitates at different feed compositions are presented in Figure 4.9. In the feed below the eutectic composition or 61 wt% *m*-CNB, the precipitates form at 22°C, which is higher than in the case with 10 grains but it is still lower than that without a zeolite. A type of zeolite considerably affects the *m*-/*p*-CNB ratio of the precipitates at 61 wt% *m*-CNB, while it is hardly so for the feed above the eutectic composition or 65 wt% *m*-CNB where the precipitates form at 18°C. Moreover, NaY provides the lowest *m*-/*p*-CNB ratio of the precipitates for both feed compositions. However, as a whole, when precipitate compositions from all precipitates were analyzed, the *m*-/*p*-CNB ratio of all precipitates collected from 61 wt% *m*-CNB in the feed with two grains of each zeolite is lower than that without a zeolite but higher than that collected from 65 wt% *m*-CNB in the feed. It means that the feed above the eutectic composition provides higher *p*-CNB purity than the

feed below the eutectic composition. Moreover, the m/p -CNB ratios of all precipitates from 61 wt% m -CNB in this case is lower than that from 61 wt% m -CNB with 5 and 10 grains of the zeolites in every type of zeolite.

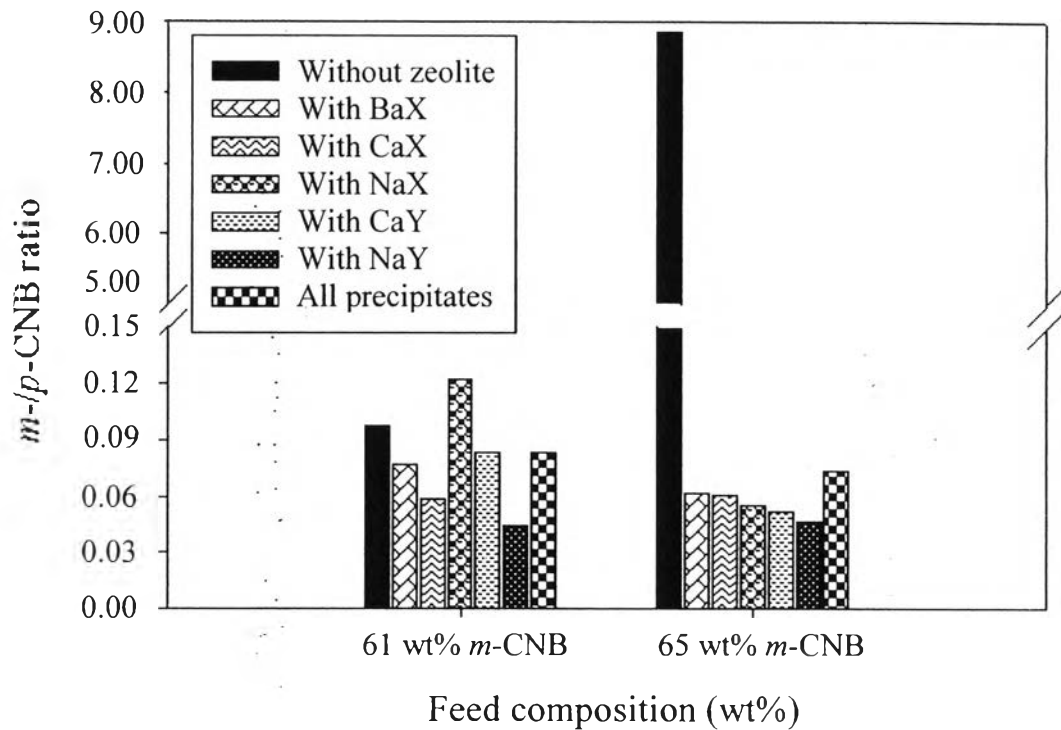


Figure 4.9 Comparison of m/p -CNB ratio of the precipitates with 61 wt% and 65 wt% m -CNB in the feed and two grains of each zeolites (BaX, CaX, NaX, CaY, and NaY).

The 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. Due to the presence of a zeolite in the CNB mixture, the crystallization temperature is lower than that in the system without any zeolite. The metastable zone width is explained by the solubility-supersolubility diagram (Figure 4.10) as for interfacial tension associates with the overall free energy change under heterogeneous conditions $\Delta G'_{\text{crit}}$ and the overall free energy change under homogeneous nucleation ΔG_{crit} .

The relationship between supersaturation and spontaneous crystallization led to a diagrammatic representation of the metastable zone on a solubility-supersolubility diagram as shown in Figure 4.10. The lower continuous solubility curve can be located with precision. The upper broken supersolubility curve, which represents temperatures and concentrations, at which uncontrolled spontaneous crystallization occurs, is not as well defined as that of the solubility curve. Its position in the diagram is considerably affected by, amongst other things, the rate at which supersaturation is generated, the intensity of agitation, the presence of trace impurities and the thermal history of the solution. The diagram is divided into three zone (Mullin, 2001):

1. The stable (unsaturated) zone, where crystallization is impossible.
2. The metastable (supersaturated) zone, between the solubility and supersolubility curve, where spontaneous crystallization is impossible. However, if a crystal seed were placed in such a metastable solution, growth would occur on it.
3. The unstable or labile (supersaturated) zone, where spontaneous crystallization is possible, but not inevitable.

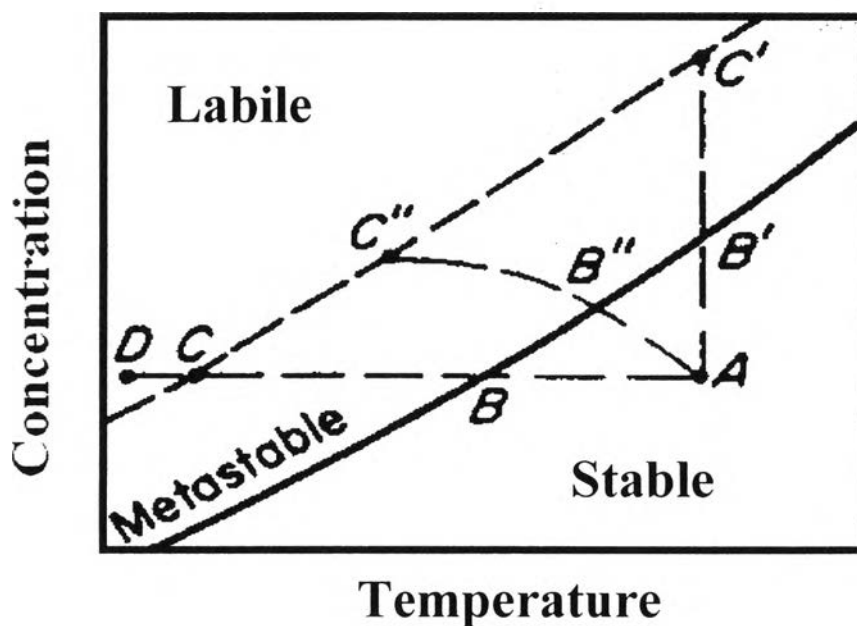


Figure 4.10 Solubility-supersolubility diagram (Mullin, 2001).

If a solution represented by point *A* in Figure 4.10 is cooled without loss of solvent (line *ABC*), spontaneous crystallization cannot occur until conditions represented by point *C* are reached. At this point, crystallization may be spontaneous or it may be induced by seeding, agitation or mechanical shock. Further cooling to some point *D* may be necessary before crystallization can be induced (Mullin, 2001). The position in the diagram is considerably effected by the presence of trace impurities (Mullin, 2001) so that the presence of zeolite in the CNB mixture may change the position in the diagram as well.

The maximum allowable supersaturation, Δc_{\max} , may be expressed in terms of the maximum allowable undercooling, $\Delta\theta_{\max}$:

$$\Delta c_{\max} = \left(\frac{dc^*}{d\theta} \right) \Delta\theta_{\max} \quad (4.1)$$

As the presence of a suitable foreign body or ‘sympathic’ surface can induce nucleation at degree of supercooling lower than those required for spontaneous nucleation (Mullin, 2001). This sentence conforms with crystallization temperature in the presence of zeolite, which is lower than in the absence of a zeolite. When the degree of supercooling decreases, $\Delta\theta_{\max}$ and Δc_{\max} increase according to the relationship between $\Delta\theta_{\max}$ and Δc_{\max} in Equation (4.1). Increasing $\Delta\theta_{\max}$ and Δc_{\max} results in a broader metastable zone width.

The overall free energy change associated with the formation of a critical nucleus under heterogeneous conditions, $\Delta G'_{\text{crit}}$, must be less than the corresponding free energy change, ΔG_{crit} , associated with homogeneous nucleation, i.e. (Mullin, 2001).

$$\Delta G'_{\text{crit}} = \phi \Delta G_{\text{crit}} \quad (4.2)$$

where the factor ϕ is less than unity.

The interfacial tension, γ , is one of the important factors controlling the nucleation process. Figure 4.11 shows an interfacial energy diagram for three

phases in contact; in this case, however, the three phases are not the more familiar solid, liquid, and gas, but two solids and a liquid. The three interfacial tensions are denoted by γ_{cl} (between the solid crystalline phase, c, and the liquid l), γ_{sl} (between another foreign solid surface, s, and the liquid) and γ_{cs} (between the solid crystalline phase and foreign solid surface) (Mullin, 2001). Resolving these forces in a horizontal direction

$$\gamma_{sl} = \gamma_{cs} + \gamma_{cl} \cos\theta \quad (4.3)$$

or

$$\cos\theta = \frac{\gamma_{sl} - \gamma_{cs}}{\gamma_{cl}} \quad (4.4)$$

The angle, θ , of contact between the crystalline deposit and foreign solid surface, corresponds to the angle of wetting in liquid-solid system (Mullin, 2001).

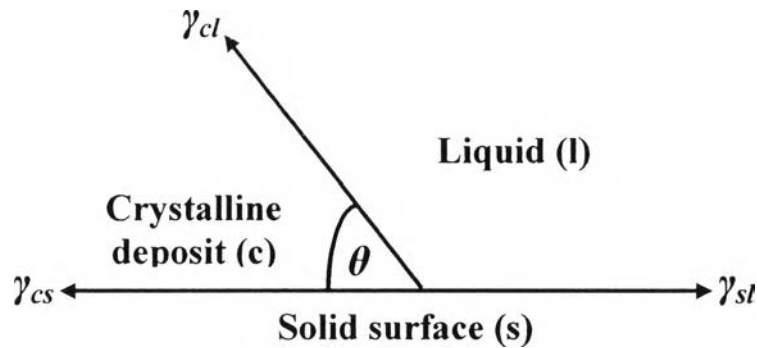


Figure 4.11 Interfacial tension at the boundaries between three phases (two solids, one liquid) (Mullin, 2001).

The factor ϕ in Equation 4.2 can be express as

$$\phi = \frac{(2 + \cos\theta)(1 - \cos\theta)^2}{4} \quad (4.5)$$

Thus, when $\theta=180^\circ$, $\cos \theta = -1$ and $\phi = 1$, Equation 4.2 becomes

$$\Delta G'_{\text{crit}} = \Delta G_{\text{crit}} \quad (4.6)$$

When θ lies between 0 and 180° , $\phi < 1$; therefore,

$$\Delta G'_{\text{crit}} < \Delta G_{\text{crit}} \quad (4.7)$$

When $\theta = 0$, $\phi = 0$, and

$$\Delta G'_{\text{crit}} = 0 \quad (4.8)$$

This is illustrated in Figure 4.12, which shows a foreign particle in a supersaturated solution (Mersmann, 2001).

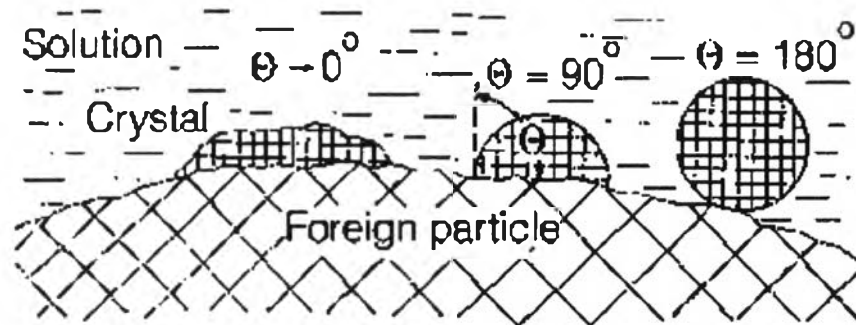


Figure 4.12 Nucleation on a foreign particle for different wetting angles (Mersmann, 2001).

For the cases of complete non-affinity between the crystalline solid and the foreign solid surface (corresponding to that of complete non-wetting in liquid-solid system), $\theta=180^\circ$, and Equation (4.6) applies, i.e. the overall free energy of nucleation is the same as that required for homogeneous or spontaneous nucleation. For the case partial affinity (cf. the partial wetting of a solid with a

liquid), $0 < \theta < 180^\circ$, and Equation (4.7) applies, which indicates that nucleation is easier to achieve because the overall excess free energy required is less than that for homogeneous nucleation. For the case of complete affinity (cf. complete wetting) $\theta=0$, and the free energy of nucleation of zero. This case corresponds to the seeding of a supersaturation solution with crystals of the required crystalline product, i.e. no nuclei have to be formed in the solution (Mullin, 2001).

The presence of a zeolite may be in the case of the partial wetting of a solid with a liquid which is described by Equation (4.7), and ΔG_{crit} relate to $(\Delta T)^{-2}$ as indicated in Equation (4.9).

$$\Delta G_{\text{crit}} \propto (\Delta T)^{-2} \quad (4.9)$$

where $\Delta T = T^* - T$ is the supercooling, T^* is the solid-liquid equilibrium temperature, and T is degree of supersaturation (Mullin, 2001).

From Equation (4.2), (4.7) and (4.9), the value of $\Delta G'_{\text{crit}}$ will be less than ΔG_{crit} when the value of ΔT is high that means the value of T or degree of supersaturation must be low. This relates to “The presence of a suitable foreign body or ‘sympathic’ surface can induce nucleation at degree of supercooling lower than those require for spontaneous nucleation (Mullin, 2001).” The metastable zone width may become broader. Thus, the crystallization temperature of the feed with a zeolites decreases from the crystallization temperature of the feed without any zeolite. From this hypothesis, the binary phase diagram of *m*- and *p*-CNB may be changed with the presence of a zeolite. The reason why the precipitate composition in the feed above the eutectic composition is shifted from being rich in *m*-CNB to *p*-CNB might come from the change of the phase diagram, which has to be further studied.

4.3 Influences of Seeds on the Crystallization

To study influence of seeds on the crystallization, experiments were conducted by using the starting liquid mixtures at 61.0 and 65.0 wt% *m*-CNB. The mixture was cooled by the cooling water from 30°C to 24°C with a 1°C/hr cooling rate. Seeds were added in the crystallizer as shown in Figure 3.3. Two types of crystal were used as the seed, *m*- and *p*-CNB. After a given time, all precipitates in the crystallizer were collected, washed, and dissolved with hexane. The dissolved precipitates were measured for the CNB compositions by using the GC.

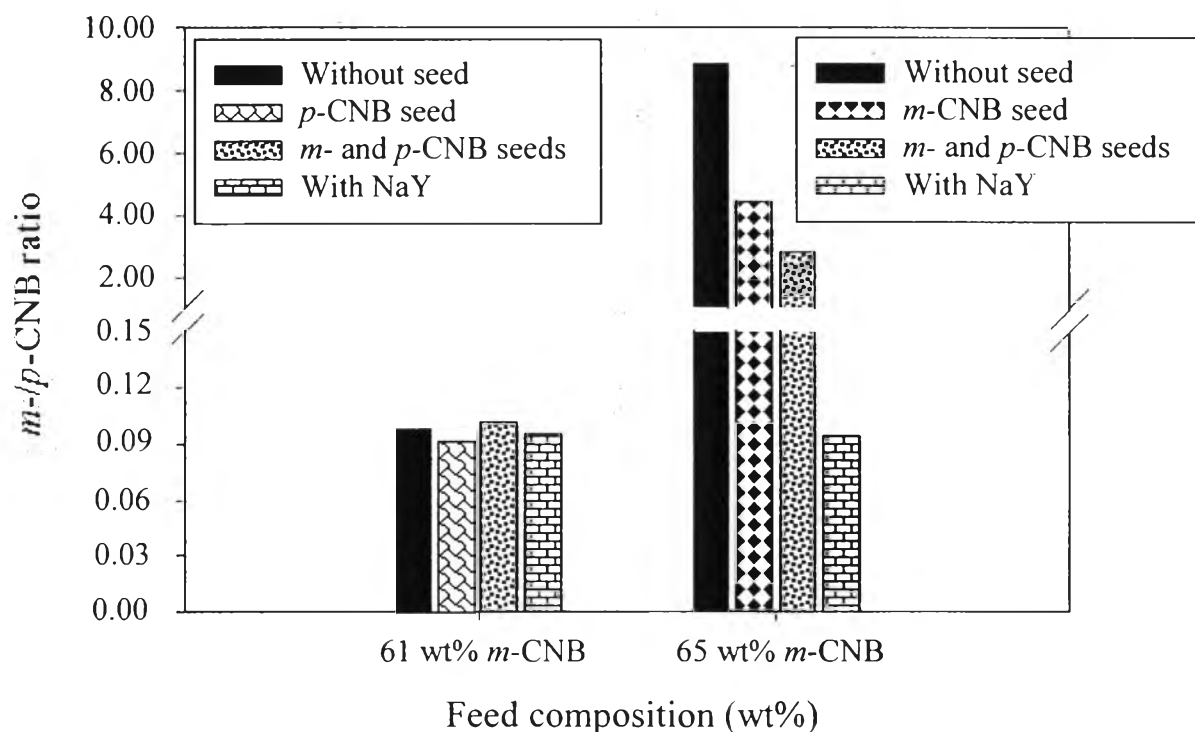


Figure 4.13 Effects of the seeds on the *m*-/*p*-CNB ratio of the precipitates at 61 wt% and 65 wt% *m*-CNB in the feed.

Figure 4.13 shows the *m*-/*p*-CNB ratio of all precipitates obtained with different seed types. It was found that the presence of seeds of the material to be crystallized can induce the crystallization of precipitates following the phase diagram at that feed composition. At the feed below the eutectic composition, the precipitates

from the feed without any zeolite have the m/p -CNB ratio lower than one. In other words, the precipitates are rich in p -CNB. With a p -CNB seed, p -CNB precipitates form. However, m -CNB precipitates form with a m -CNB seed. At the feed above the eutectic composition, the precipitates in the feed without any zeolite have m/p -CNB ratio higher than one or rich in m -CNB. Moreover, crystallization without any seed provides the highest m/p -CNB ratio of the precipitates or the highest purity of m -CNB. When both of m - and p -CNB seeds are present in the CNB mixture, the results show that the p -CNB seeds induce crystallization of p -CNB precipitates at the feed below the eutectic composition and the m -CNB seeds induce the m -CNB precipitates at the feed above the eutectic composition. The precipitate purity decreases with the increase in the number of seed crystals for both feed compositions.

The reason why the precipitates can occur and grow at 24°C can be explained by the general phenomenon of nucleation in the bulk and on the surface of seed crystals in a batch crystallization processes as shown Figure 4.14. In the supersaturated solutions, there are three periods in relation to elapsed time: (1) seeding period, (2) surface nucleation period, and (3) growth period (agglomeration and crystal growth). Homogeneous/heterogeneous nuclei occur in the time period (1) within the metastable zone width (MZW). Secondary nucleation in the bulk can take place in time period (2) due to presence of the seeds. This means that the width of metastable zone becomes narrower. At the same time, surface nucleation takes place on the surface of the seed crystals. However, the number of surface nuclei is lower than those in the supersaturated bulk. After the secondary nucleation and surface nucleation, these nuclei start to agglomerate and grow in the time period (3) on the surface of seed particles simultaneously (Kim and Ulrich, 2003). With the presence of seed crystal at 24°C, the precipitates can occur and grow at this temperature, which is higher than crystallization temperature of that feed composition, because the width of metastable zone is narrower.

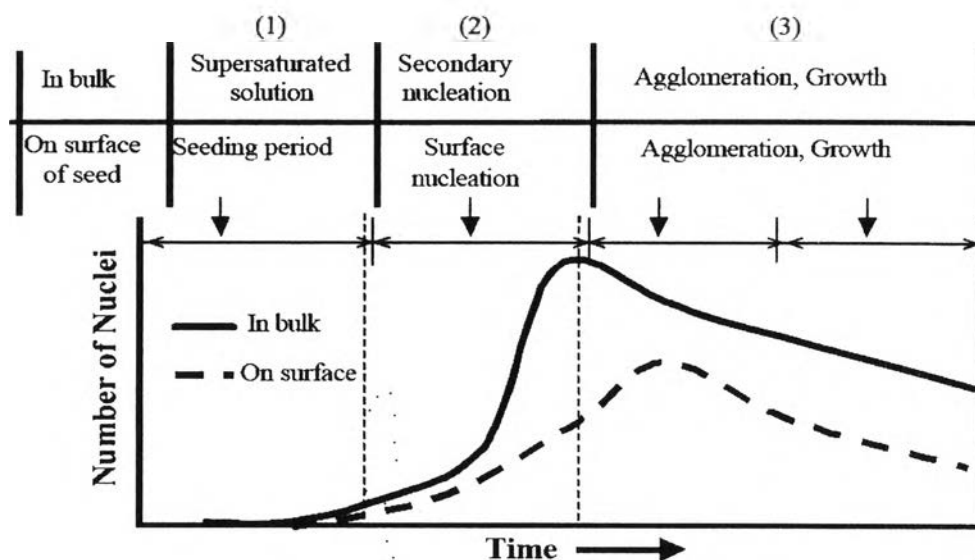


Figure 4.14 Typical phenomenon of nucleation in bulk and surface of seeds (Kim and Ulrich, 2003).

Based on the phenomenon of nucleation in bulk and surface of seeds, if the number of nuclei in the primary nucleation is larger, the number of nuclei in the secondary nucleation will be larger leading to agglomeration. When the number of seed particles is larger, primary nuclei are larger. Thus, the product purity decreases with the increase in the number of the particles. Agglomeration in the bulk takes place at a higher pace seed particle area because of higher number of nuclei, which, in turn, increases the chance in the nuclei collision. When two particles collide, they can entrain mother liquor during the agglomeration leading to low product purity. This result of the seed particles may be a cause of lower purity of precipitates near the zeolites than those far from the zeolites.