Simple approach in understanding interzeolite transformations using ring building units

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Abstract. Recently, there are two general approaches used in understanding interzeolite transformations, thermodynamically represented by framework density (FD) and kinetically by structural building units. Two types of structural building units are composite building units (CBU’s) and secondary building units (SBU’s). This study aims to examine the approaches by using interzeolite transformation data available in literature and propose a possible alternative approach. From a number of cases of zeolite transformation, the FD and CBU approach are not suitable for use. The FD approach fails in cases involving zeolite parents that have moderate or high FD’s, while CBU approach fails because of CBU’s unavailability in parent zeolites compared with CBU’s in their transformation products. The SBU approach is most likely to fit because SBU’s are units that have basic form of ring structures and closer to the state and shape of oligomeric fragments present in zeolite synthesis or dissolution cases. Thus, a new approach can be considered in understanding the interzeolite transformation, namely the ring building unit (RBU) approach. The advantage of RBU approach is RBU’s can be easily derived from all framework types, but in SBU approach there are several types of frameworks that cannot be expressed in SBU forms.

1. Introduction

The interzeolite transformation is an interesting phenomenon to be studied because it is potentially developed for more efficient synthesis of zeolites, can be performed faster and/or lower temperatures than conventional synthesis \cite{1} \cite{2}. This phenomenon can be utilized to add variety of values to natural sources of abundant natural aluminosilicates. Although the phenomenon of inter-zeolite transformation has long been emerging and studied, to date this phenomenon is still not fully understood. Due to the metastability of the zeolite framework, the constraint in understanding the transformation comes from understanding the structural relationship between the parent zeolite and its product transformation. The difficulty to fully understand the phenomenon of interzeolite transformation involves many variables that affect it, such as reaction conditions (pH, temperature, and time) and other chemical involvements such as the presence of templates, seeds, organic directing agents, and the presence of ionic types and concentrations.

To solve the problem of understanding interzeolit transformation, several approaches can be done. To date there are two common approaches considered for understanding the inter-zeolite transformation, i.e. the framework density (FD) and the building unit relationships involved in the transformation. The
two most commonly used framework building units are composite building units (CBUs) [1] [3] and secondary building units (SBU’s) [2] [4]. Since each of these approaches is often shown as a separate case, it is interesting to examine its application for all transformation cases in the literature. In this study will be tested and discussed both approaches and possible approaches that may apply to zeolites in general, namely the ring-building unit (RBU) approach of the zeolite couples involved in transformation, as the parent and transformation product.

2. Evaluation of framework density approach in interzeolite transformations

Although zeolite has been recognized as a metastable material, the background of framework density has often been a major consideration in the zeolite transformation efforts, according to the majority of transformation cases using FAU parent zeolite as shown in Table 1, and the fact is FAU is one type of zeolite among the zeolites having the lowest FD’s. The consideration of framework density was proposed by Goel et al., although the zeolite-to-zeolite transformation is not a one-stage process because in equal system with time and temperature differences can produce a variety of zeolites and do not always produce zeolite types with higher FD’s [3]. Based on the data in Table 1 it is clear that by using zeolite types with high FD’s, the FD approach fails to understand the transformation from one to other zeolites.

| Parent zeolite Type | Transformation product Type | FD$^a$ / T-1000Å$^{-3}$ | Ref.$^b$ | suitability$^c$ |
|---------------------|-----------------------------|--------------------------|---------|-----------------|
| Using parent zeolite with low FD (< 15 T) |
| FAU 12.7            | CHA 14.5                    | [5]                      | +       |
| FAU 12.7            | GME 14.6                    | [6]                      | +       |
| FAU 12.7            | GIS 15.3                    | [7]                      | +       |
| FAU 12.7            | PHI 15.8                    | [6]                      | +       |
| FAU 12.7            | MER 16.0                    | [8]                      | +       |
| FAU 12.7            | LTL 16.3                    | [7]                      | +       |
| FAU 12.7            | HEU 17.1                    | [6]                      | +       |
| FAU 12.7            | MOR 17.2                    | [7]                      | +       |
| FAU 12.7            | BRE 17.3                    | [6]                      | +       |
| FAU 12.7            | STF 17.3                    | [1]                      | +       |
| FAU 12.7            | MFI 17.9                    | [1]                      | +       |
| FAU 12.7            | ANA 18.5                    | [4] [8] [6]              | +       |
| FAU 12.7            | ABW 19.0                    | [8]                      | +       |
| FAU 12.7            | MTW 19.4                    | [1]                      | +       |
| FAU+FER 12.7+(17.8) | GIS 15.3                    | [7]                      | +       |
| FAU+BEA 12.7+(15.1) | MFI 17.9                    | [1]                      | +       |
| LTA 12.9            | GIS 15.3                    | [9]                      | +       |
| LTA 12.9            | MWW 16.5                    | [10]                     | +       |
| LTA 12.9            | SOD 17.2                    | [11] [12] [13]           | +       |
| GME 14.6            | ANA 18.5                    | [14]                     | +       |

| Using parent zeolite with high FD (>15 T) |
| BEA 15.1            | MFI 17.9                    | [7]                      | +       |
| LEV 15.2            | CHA 14.5                    | [2]                      | -       |
| GIS 15.3            | ANA 18.5                    | [15]                     | +       |
| GIS 15.3            | CHA 14.5                    | [16]                     | -       |
| MWW 16.5            | FER 17.8                    | [17]                     | -       |
| SOD 17.2            | CAN 16.6                    | [18]                     | -       |
| MTW 19.4            | ITW 18.1                    | [19]                     | -       |
| TON 19.7            | ITW 18.1                    | [20]                     | -       |

$^a$FD obtained from reference [21], expressed by T, number of heteroatoms per 1000 Å$^3$.
$^b$Source data of the parent zeolite type and its transformation product.
$^c$ the suitability of framework density approach for the transformation, “+” and “-” are suitable and not suitable, respectively.
According to Maldonado et al. (2013) [3], the FD approach can only be used in a series of framework transformations in the reaction system that pass through the formation of some zeolites. Despite having the same framework type, the difference in Si and Al atomic composition of the parent zeolite can produce zeolite with increase or decrease in FD [3]. The failure of the FD approach is clear evidence that zeolite transformation involves not only thermochemical controls such as temperature, enthalpy, and entropy, but also the framework chemistry, dissolved fragments, basic concentrations, structure directing agents, and solvents.

3. Evaluation of composite and secondary building unit approaches in interzeolite transformations

Some research groups mentioned explicitly the phenomenon of transformation is the relationship of framework building units, both in general and in particular as composite building units (CBU’s) or secondary building units (SBU’s), between the parent zeolite and its transformation product [1] [2] [4] [7] [8] [13] [20]. The claims of the relationship of these building units are in fact still limited in their proofs, especially in the involvement of d4r and d6r CBU’s, or 4-4 and 6-6 SBU’s [1][2][7][14], which consecutively contain 8 and 12 units of TO$_{4/2}$. The CBU or SBU number correlated still limited in the number of existing CBU’s and SBU’s, of which at least 47 and 23 respectively [21]. The majority of CBU’s are fairly large blocks of the structure with a range of 5 - 48 units of TO$_{4/2}$, whereas SBU’s in 3 - 16 TO$_{4/2}$ [21].

If the parent zeolite has CBU/s or SBU/s are correlated to or correlated with its transformation product/s, the most feasible relationship can be expressed by "one of CBU/SBU constructing a transformed zeolite framework must be available in one of the CBU/SBU constructing its parent zeolite framework". By using the constraints of this building unit relationship, the most (at least 19 of 35 cases) of transformations have no CBU relationships as shown in Table 2, and little (at least 7 of 35 cases) of transformations still have no SBU relationships as shown in Table 3.

Based on Tables 2 and 3, SBU has more suitability than CBU in connecting the parent zeolite framework with its transformation product. We concluded that CBU approach could not be used in understanding transformation, the CBU fact is only a structural concept that connects large blocks between framework types [21], rarely match with dissolved fragments in zeolite or silica dissolution cases. Otherwise, the SBU has more compatibility to understand the transformation because the number of atoms of T involved in zeolite or silica dissolution cases is relatively small and has more resemblance to the fragments. In cases of zeolite or silica dissolutions, the dissolved fragments are more similar to SBU’s, such as ring 4, 5 and 6-membered T [22] [23] [24] [25] [26] [27]. Both CBU and SBU are basically composed of ring structure units, but the difference is that the rings in SBU’s are simpler and more likely to resemble the zeolite and silica dissolved fragments in basic solution.

4. Ring building unit (RBU) as an alternative approach

Basically, each SBU consists of one or a combination of several rings. Table 4 presents some cases of zeolite transformations that have no SBU relationship, especially in cases of transformation with support of seed or SDA. To explain transformation cases that do not have SBU relationship in transformations using seed or organic directing agent (SDA) can be explained by ring building approach (RBU). There is the fact that the interzeolite transformation always yields parent zeolite dissolution which not all dissolved fragments produce new zeolite type crystals [2] [7] [28], with dissolution of Si tends greater than Al [29] [30] [31]. Based on the data in Table 4 it can be seen the role of seeds in the case of FAU transformation into HEU, MFI, MTW and STF, because the existence of seeds can facilitate the crystal nucleation of dissolved silicate fragments. FAU does not contain a 5-ring but still produces a framework that has a 5-ring like MFI, MTW, and STF. Ring 5T is characteristic of high silica zeolites, because the most stable 5-ring contains only Si heteroatoms (pentasil). This characteristic can be proven by RBU’s belong to high silica zeolite as shown in Table 5 and 6. The always larger dissolution of Si than Al has provided enough Si to form these 5-rings.
Table 2 Composite building unit relationships between parent zeolite and its transformation product

| Parent zeolite | Transformation product | Ref. | Availability |
|---------------|------------------------|------|--------------|
| **Framework type** | **CBU’s** | **Framework type** | **CBU’s** | **Ref.** | **Availability** |
| Without template, structure directing agent, or seed | | | | | |
| *BEA | *BEA | MOF | *BEA | MOF | [7] | + |
| FAU | d6r, sod | ABW | d6r, sod | ABW | [8] | - |
| FAU | d6r, sod | ANA | d6r, sod | ANA | [8] | - |
| FAU | d6r, sod | BRE | d6r, sod | BRE | [6] | - |
| FAU | d6r, sod | CAN | d6r, sod | CAN | [33] | - |
| FAU | d6r, sod | CHAR | d6r, sod | CHAR | [1] | - |
| SOD | sod | CAN | sod | CAN | [18] | - |
| Supported with template, structure directing agent, or seed | | | | | |
| *BEA | *BEA | MOR | *BEA | MOR | [32] | + |
| FAU | d6r, sod | ABW | d6r, sod | ABW | [8] | - |
| FAU | d6r, sod | ANA | d6r, sod | ANA | [8] | - |
| FAU | d6r, sod | BRE | d6r, sod | BRE | [6] | - |
| FAU | d6r, sod | CHAR | d6r, sod | CHAR | [1] | - |
| FAU | d6r, sod | GME | d6r, sod | GME | [6] | - |
| FAU | d6r, sod | HEU | d6r, sod | HEU | [6] | - |
| FAU | d6r, sod | MBI | d6r, sod | MBI | [8] | - |
| FAU | d6r, sod | MOF | d6r, sod | MOF | [1] | - |
| FAU | d6r, sod | MTW | d6r, sod | MTW | [1] | - |
| FAU | d6r, sod | MWW | d6r, sod | MWW | [35] | + |
| FAU | d6r, sod | PH | d6r, sod | PH | [6] | - |
| FAU | d6r, sod | SOD | d6r, sod | SOD | [33] | + |
| FAU | d6r, sod | STF | d6r, sod | STF | [1] | - |
| LTA | d4r, sod, lla | MWW | d6r, sod, lla | MWW | [10] | - |
| GME | d6r, sod, gme | ANA | d6r, sod, gme | ANA | [14] | - |
| GIS | d6r, sod | CHAR | d6r, sod | CHAR | [36] | - |
| MTW | d6r, sod, lla | ITW | d6r, sod, lla | ITW | [19] | - |
| MWW | d6r, sod, lla | ITW | d6r, sod, lla | ITW | [17] | - |
| TON | d6r, sod, lla | ITW | d6r, sod, lla | ITW | [20] | - |

a CBU’s obtained from reference [21]. ANA have no specific CBU’s; b source data of the parent zeolite type and its transformation product; c Availability of CBU’s in parent zeolite, signs of “+” and “-” are available and not available, respectively, in one, some, or all of CBU’s, whereas “?” is not specified yet in reference [21].

The case of FAU can be transformed into HEU because the HEU zeolite type contains 4 and 6 rings available in the FAU framework. The first number on the SBU codes can represent the ownership of the RBU from a zeolite framework type, such as FAU with SBU 6-6, 6-2, 6, 4-2, 1-4-1, and 4 can be simplified into RBU 6 and 4, while in HEU 4-4=1 can be simplified into SPC 4. However, SBU codes does not always represent all existing RBU, as in HEU, besides containing RBU 4 also contains RBU 6. RBU can be easily determined directly from the structure framework image available in literature, while specifying the SBU requires sufficient time, unless it is stated in the framework type data. Thus, beside the transformation of FAU into HEU is supported by seed, it is also supported by the relationship of both RBU’s.
Table 3 Secondary building unit relationships between parent zeolit and its transformation product

| Parent zeolite | Transformation product | SBU’s<sup>a</sup> | SBU’s<sup>a</sup> | Ref.<sup>b</sup> | availability<sup>c</sup> |
|----------------|------------------------|------------------|------------------|----------------|------------------------|
| **Framework type** | **SBU’s<sup>a</sup>** | **Framework type** | **SBU’s<sup>a</sup>** |               |                       |
| *BEA* | 5-1 | MFI | 5-1 | [7] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | ANA | 6-2 / 6 / 4[1,1] / 1-4-1 / 4 | [4] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | GIS | 8 / 4 | [7] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | LTL | 6 / 4-2 | [7] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | MOR | 5-1 | [7] | + |
| FAU+*BEA | (6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4)+ (5-1) | MFI | 5-1 | [1] | + |
| FAU+FER | (6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4)+ (5-1) | GIS | 8 / 4 | [7] | + |
| GIS | 8 / 4 | ANA | 6-2 / 6 / 4[1,1] / 1-4-1 / 4 | [15] | + |
| LEV | 6 | CHA | 6-6 / 6 / 4-2 / 4 | [2] | + |
| LTA | 8 / 4-4 / 6-2 / 6 / 1-4-1 / 4 | FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | [3] | + |
| LTA | 8 / 4-4 / 6-2 / 6 / 1-4-1 / 4 | GIS | 8 / 4 | [9] | + |
| LTA | 8 / 4-4 / 6-2 / 6 / 1-4-1 / 4 | SOD | 6 | [11] [12] [3] | + |
| SOD | 6 | CAN | 12 / 6 / 4 | [18] | + |

**Without template, structure directing agent, or seed**

**Supported with template, structure directing agent, or seed**

| *BEA* | 5-1 | MOR | 5-1 | [32] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | ABW | 8 / 4 | [8] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | ANA | 6-2 / 6 / 4[1,1] / 1-4-1 / 4 | [8] [6] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | BRE | 4 | [6] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | CAN | 12 / 6 / 4 | [33] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | CHA | 6-6 / 6 / 4-2 / 4 | [1] [8] [28] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | GME | 12 / 6-6 / 8 / 6 / 4-2 / 4 | [6] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | HEU | 4-4=1 | [6] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | MER | 8-8 / 8 / 4 | [8] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | MFI | 5-1 | [1] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | MTW | 5[1,1] | [1] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | MWW | ? | [35] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | PHI | 8 / 4 | [6] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | SOD | 6 | [33] | + |
| FAU | 6-6 / 6-2 / 6 / 4-2 / 1-4-1 / 4 | STF | 5-3 | [1] | + |
| GIS | 8 / 4 | CHA | 6-6 / 6 / 4-2 / 4 | [36] [16] | + |
| GME | 12 / 6-6 / 8 / 6 / 4-2 / 4 | ANA | 6-2 / 6 / 4[1,1] / 1-4-1 / 4 | [14] | + |
| LTA | 8 / 4-4 / 6-2 / 6 / 1-4-1 / 4 | MWW | ? | [10] | + |
| MTW | 5[1,1] | ITW | 1-4-1 / 4-[1,1] | [19] | + |
| MWW | ? | FER | 5-1 | [17] | + |
| TON | 5-1 | ITW | 1-4-1 / 4-[1,1] | [20] | + |

<sup>a</sup> SBU’s obtained from reference [21]. The ”/” sign separating SBU’s states the alternative use of SBU, SBU’s constructing MWW type is not specified yet in the reference [37].

<sup>b</sup> source data of the parent zeolite type and its transformation product,

<sup>c</sup> Availability of SBU’s alternatives in parent zeolite, the "+" and "-" marks state that one of them is available and not available in the parent zeolite, respectively.

In Table 4 there is also a case of FAU transformation into a MOR that can be explained by RBU relationship. The MOR framework not only has RBU 5 (representation of SBU 5-1), but also has RBU 4 and 6. The RBU 5 which is not available in the FAU can be explained from the characteristics of RBU 5 that can be identified with high-silica zeolites. Honda et al. (2013) succeeded in transforming FAU into MOR without the aid of template or SDA due to using high-silica FAU (Si/Al ratio = 76), while using lower silica FAU, with Si/Al = 25 only produced GIS (containing only RBU 4) and LTL (containing RBU 4 and 6) [7], but RBUs are both available in FAU. Sufficient silicate fragments of FAU dissolution allow formed MOR transformation products containing RBU 5 as well.
Table 4 Some cases of transformation that have no SBU relationship

| Parent zeolite | Transformation product | Ref. | Support |
|---------------|------------------------|------|---------|
| FAU           | MOR 5-1                | [7]  | –       |
| FAU           | HEU 4-4=1              | [6]  | seed    |
| FAU           | MFI 5-1                | [1]  | seed    |
| FAU           | MTW 5-[1,1]            | [1]  | seed    |
| FAU           | STF 5-3                | [1]  | seed    |
| MTW           | ITW 1-4-1, 4-[1,1]     | [19] | SDA     |
| TON           | ITW 1-4-1, 4-[1,1]     | [20] | SDA     |

a source data SBU of zeolite type from reference [21].
b source data of the parent zeolite type and its transformation products.
c support in the transformation.

Table 5 Types of aluminosilicate and silica zeolites framework with SBU or RBU having 5-membered ring.

| Type | Si/Al ratio | SBU | RBU       | 5.0 | 5 and 6 |
|------|-------------|-----|-----------|-----|---------|
| BIK  | 2.0         | 5-1 | 5 and 6   | TON | 11.0 infinite |
| MAZ  | 2.6         | 5-1 / 4-2 | 4 and 5 | CDO | silica 5-1 |
| STI  | 2.6         | 4-4=1 | 4 and 5 | IME | silica 5-1 |
| DAC  | 3.8         | 5-1  | 4, 5 and 6 | NSI | silica 5-1 |
| BOG  | 4.3         | 6 / 5-1 / 4 | 4, 5 and 6 | DON | silica 5-3 |
| CAS  | 5.0         | 5-1  | 5 and 6   | GON | silica 5-3 |
| FER  | 5.0         | 5-1  | 5 and 6   | SFF | silica 5-3 |
| MOR  | 5.0         | 5-1  | 4, 5 and 6 | SGT | silica 5-3 |
| ESV  | 8.37        | 5-1  | 4 and 5   | STF | silica 5-3 |
| *BEA | 8.14        | ?    | 4, 5 and 6 | STT | silica 5-3 |
| EON  | 4.26 - 15.67| 5-1 | 4 and 5   | RTE | silica 6 / 5-1 |
| MFI  | 2.5         | infinite | 4, 5 and 6 | ISV | silica 6-2 |
| EUO  | 4.89 - infinite | 1-5-1 | 4, 5 and 6 | IFR | silica 6-2 |
| MEL  | 5.0         | infinite | 4, 5 and 6 | RWR | silica 6-2 |
| MTW  | 10.2 - infinite | 5-[1,1] | 4, 5 and 6 | RRO | silica 4=1=1 |
| MTT  | 11.0 - infinite | 5-1 | 5 and 6   | DOH | silica ? |

a and b source data taken from reference [21], *BEA and DOH are not specified yet in the reference

The transformation of MTW or TON into ITW can be explained also by the RBU relationship. MTW contains RBU 4, 5 and 6, while TON contains RBU 5 and 6. ITW itself consists only of RBU 4 and 6. TON which is a high-silica zeolite will have a considerable dissolution of silicates allowing the RBU 4 available to construct ITW framework. ITW is a bit of an exceptional silica zeolite that does not have RBU 5.

5. Relationship evidence of ring building units in zeolite classification based on silicon to aluminum molar ratio

Until now there has been no approach to understand framework types based on RBU relationships. Although SBU has basic ring forms, but not all rings within the zeolite framework can be represented in SBUs. Although there are 3 to 20 T-rings [21], only 4, 5, and 6 rings are most commonly found in all zeolites, as well as those found in the zeolite and silica dissolved fragments [22] [23] [24] [25] [26] [27].
The existence of 5-ring becomes the characteristic of high-silica aluminosilicate or silica zeolites, it is not surprising that the use of the term "pentasil" is often associated with rings 5 of high-silica zeolites, which means that the 5-ring tend to have only Si atoms, as in MFI, MEL, and *BEA [37]. In addition to having a single SBU 5-1, the three framework types are also dominated by RBU 5. From Table 5 and 6 we can compare the RBU approach with and without RBU 5.

| Tabel 6 Types of aluminosilicate and silica zeolites without 5-membered ring |
|-----------------------------|---------------------|---------------------------|------------------------|---------------------|
| **Tipe** | Si/Al | **SBU** | **RBU** | **Tipe** | Si/Al | **SBU** | **RBU** |
| GIS | 1.0 | 4 | GME | 2.0 | 12/6-6/8/6-4-2/4 | 4 and 6 |
| LIO | 1.0 | 6/4 | 4 and 6 | LAU | 2.0 | 6/1-4-1 | 4 and 6 |
| GIU | 1.0 | 6/4 | 4 and 6 | KFI | 2.2 | 6-6-2/8/6-4-2/4 | 4 and 6 |
| FRA | 1.0 | 6/4 | 4 and 6 | FAU | 2.3 | 6-6-2/6/4-2/1-4-1/4 | 4 and 6 |
| FAR | 1.0 | 6 | 4 and 6 | OFF | 2.6 | 6/4-2 | 4 and 6 |
| CAN | 1.0 | 12/6/4 | 4 and 6 | LTL | 3.0 | 6/4-2 | 4 and 6 |
| TSC | 1.0 | 8-8/6-6/6-4-2/4 | 4 and 6 | ERI | 3.0 | 6/4 | 4 and 6 |
| SOD | 1.0 | 6 | 4 and 6 | EAB | 3.0 | 6/4 | 4 and 6 |
| MAR | 1.0 | 8/4 | 4 and 6 | MOZ | 3.5 | 6-4-2 | 4 and 6 |
| LOS | 1.0 | 6-2/6/4 | 4 and 6 | HEU | 3.5 | 4-4=1 | 4 and 6 |
| AFG | 1.0 | 6/4 | 4 and 6 | EMT | 3.57 | 6-6-2/6/4-2/1-4-1/4 | 4 and 6 |
| LTA | 1.0 | 8-4-4/6-2/6-1-4-1/4 | 4 and 6 | TER | 5.5 | 2-6-2/4-1 | 4 and 6 |
| LTN | 1.0 | 6/4-2 | 4 and 6 | MSO | 13.3 | 2-6-2/4-1 | 4 and 6 |
| ANA | 2.0 | 6-2/6/4-[1,1]/1-4-1/4 | 4 and 6 | ITW silica | 1-4-1/4-[1,1] | 4 and 6 |
| CHA | 2.0 | 6-6/6/4-2/4 | 4 and 6 | |

a and b obtained from reference [21]

From Table 5 it can be seen that most SBU's that have 5-rings are high-silica zeolites. However, there are low Si/Al framework types although they contain SBU 5-1 or RBU 5 as presented in Table 7. In Table 7, there are framework types that have RBU 5 but are classified as having low to moderate Si/Al, i.e. BIK, MAZ, DAC, BOG, CAS, FER, MOR, and STI. For FER and MOR, the presence of 5-rings assumed to be possessed only by zeolites that have a moderate to high Si/Al can be proven because both of these have recently been shown to be synthesized with high Si/Al [38]. Furthermore, in Table 7 it is seen that STI have only SPS 4-4=1, but the zeolite can be synthesized with high-silica [39] because STI has RBU 5. There is a possibility of BIK, MAZ, DAC, BOG, and CAS can be found in medium or high Si/Al as it does on FER, MOR, and STI.

As shown in Table 6, MSO and ITW are two types of high-silica zeolites among zeolite types that do not have RBU 5. However, siliceous zeolites or high-silica zeolites without 5-ring can be produced from synthesis using HF mineralizer and SDA, such as ITW [40] and LTA A [41], even in the lower H2O/SiO2 ratio indicate more 4-ring zeolites [40]. The tendency of fragmentation in the fluoride solution media is analogous to fragmentation in the base medium, a concentrated base concentration causes silicate fragmentation tends to be in ring forms 4 rather than 5 and 6, or more containing smaller rings [2] [42].

The cases of aluminosilicate and silica zeolite transformation generally employed in an alkaline solution medium. There are few cases of transformation studies using fluoride solution media so there is still difficulty in understanding the role of CBU, SBU, and RBU in these cases. To date, there have been at least two cases of transformation using fluoride solution media, i.e., MTW to ITW [19], and TON to ITW [20], both using SDA (see Table 4). The use fluoride media tends to be able synthesized...
siliceous zeolites easier than hydroxide media [40] [41], but always using SDA [19] [40] [41] [43] [44]. These facts suggested that zeolite transformation in fluoride media occur by parent zeolite dissolution completely. Thus the RBU approach in understanding the transformation in fluoride media cannot be used. Transformations in the fluoride solution media tend to be determined by the SDA. Because of the total dissolution, the process of forming a new zeolite in the fluoride solution medium takes a relatively long time and the temperature is relatively high [19] [20] [40] [41] [43] [44].

In Table 8, it can be seen that the RBU is better able to distinguish zeolite classification than SBU approach based on Si/Al, i.e. on zeolite types with non-SBU 5-ring (STI, DOH, IFR, ISV, RRO, and RWR). However, there are still some cases of RBU incompatibilities that also occur in their SBU, especially in MSO and ITW, both of which are high-silica but do not have 5-ring. The opposite of the case is on BIK, MAZ, DAC, BOG, and CAS, are low-silica but have 5-ring.

| Type | Si/Al ratio | SBU ownership | RBU ownership |
|------|-------------|---------------|---------------|
| BIK  | 2.0 n.a.    | 5-1           | ? 5 and 6 ?   |
| MAZ  | 2.6 n.a.    | 5-1 / 4-2     | ? 4 and 5 ?   |
| DAC  | 3.8 n.a.    | 5-1           | ? 4, 5 and 6 |
| BOG  | 4.3 n.a.    | 6 / 5-1 / 4   | ? 4, 5 and 6 |
| CAS  | 5.0 n.a.    | 5-1           | ? 5 and 6 ?   |
| FER  | 5.0 46 [39] | 5-1           | + 5 and 6 +   |
| MOR  | 5.0 60 [38] | 5-1           | + 4, 5 and 6 +|
| STI  | 2.6 45 [39] | 4-4=1         | + 4 and 5 +   |

*Si/Al value based on reference [21]; ¹ reference of recent findings in Si/Al ratio; ² a "+" sign matching the Si/Al mole ratio, "-" states that the match is not certain yet.

Based on the ratio of Si/Al mole ratios, zeolite classification is divided into three categories, namely low (Si/Al = 1.0 ~ 1.5), medium (Si/Al = 2 ~ 5), and high (Si/Al = 10 ~ 100) siliceous zeolites [37]. This
categorization is actually still rough but quite useful in tracing the relationship of the chemical composition of zeolite and its framework with its ring structure units. Using the RBU 5 limits, there is a fairly wide slice of the Si/Al ratio between medium- and low- or high-silica zeolites. Based on the facts in RBU 4, 5, and 6, the following provisions can be made:

1. Under Lowenstein's rule, the lowest Si/Al ratio in RBU 4 and 6 only allows the ratio of Si/Al = 1, this corresponds to the fact that all zeolites with Si/Al = 1 can be found in zeolite frameworks having 4 and 6-ring only,
2. RBU 5 is the most common feature present in high-silica aluminosilicate zeolites, while the ownership of RBU 5 allows Si/Al> 1,
3. The characteristic of zeolites having RBU 5 extends to a range of 1 < Si/Al < infinite, so that the majority of siliceous zeolites will have the distinctive features of RBU 5 ownership as well,
4. Lowenstein's rule allows the formation of silica zeolites without having SPC 5,
5. The combined repeat of RBU 4 and 6 will have T = 6n (n = repetition), as shown in the following scheme,

MCM-61 (MSO), having the chemical formula $[\text{K}_{2.1}\text{C}_{12}\text{H}_{24}\text{O}_{6}] [\text{Al}_{2.1}\text{Si}_{27.9}\text{O}_{60}]$ [21], with T = 30 per unit of formula (with Si/Al = 13.29), has a population ratio of RBU 4 relatively equal to RBU 6 (directly calculated from the framework description available in literature). The amount of T = 30 per unit of the formula represents the repetition of RBU 4 and 6 combinations by 5 times, so that some possible Si/Al mole ratios are $29/1 = 29, 28/2 = 14, ..., 15/15 = 1$. If MCM-61 is an aluminosilicate zeolite having the highest Si/Al ratio among zeolites without RBU 5, the Si/Al = 14 ratios can be considered as the highest Si/Al limit of the medium-silica zeolite category. Based on the assumptions above, zeolites can be categorized based on Si/Al ratio as follows:

| Criteria | Zeolite category |
|----------|------------------|
|          | Low-silica zeolites | Medium-silica zeolites | High-silica zeolites | Siliceous zeolites |
| RBU      | 4 or 6 | 4, 5, or 6 | Always contains RBU 5 | 4, 5, or 6 |
| Chemical framework | Si/Al = 1 | $2 \leq \text{Si/Al} \leq 14$ or Si/Al > 14 | Si/Al > 29 | Infinite Si/Al, the majority always contain RBU 5, except ITW only contains RBU 4 and 6 |
|          | $2 \leq \text{Si/Al} \leq 29$ | |

Based on the above categorization, it can be explained why FAU (RBU 4 and 6) can be transformed to MOR (RBU 4, 5, and 6) without the aid of SDA, template, or seed (see Table 3). According to Honda et al. (2013), the dealuminated FAU reaches Si/Al = 76 transformed to MOR, whereas with FAU on Si / Al = 25 produces a mixture of MOR and GIS (containing only SPC 4), only GIS or LTL (RBU 6 and 4) [7]. This proves that RBU 5 is the characteristics of high-silica zeolite, RBU 5 can obtain from dealuminated-FAU dissolution and can build a MOR framework zeolite.

The presence of 5-ring-SBU and RBU 5 are generally identical with high-silica zeolites and can correlate the structure between the parent zeolite and its transformation product. However, the RBU has more suitability with the Si/Al ratio than the SBU approaches. In addition, the RBU is more suitable than SBU approaches for early consideration in choosing parent zeolites and predicting several transformation products, based on the facts as follows:

1. In general, the transformation product may be attributed to the availability of its RBUs in the parent zeolite, either do not change or reduced in RBU numbers, of both its type and its dominance,
2. The attributable RBUs are mainly 4, 5, and 6,
3. The higher the Si/Al ratio in parent zeolites the higher chance of producing transformation products that have RBU 5 without the aid of templates, SDAs, or seeds,

4. The process of transformation by using an alkaline solution will always decrease the Si/Al ratio, the higher alkaline concentration the less chances of obtaining RBU 5 in its transformation product if there is no template or SDA aid, and

5. An increase in concentration of base will increasingly provide an opportunity to produce a product with RBU 4 more dominance than RBU 6 on the framework because an increase in base concentration tends to produce smaller fragments.

6. Conclusion
Understanding the transformation between zeolites can be performed by using the ring building units (RBUs) approach as an alternative to using existing approaches, such as framework density (FD), composite building unit (CBU) and secondary building unit (SBU). The FD approach has many discrepancies because the zeolite is metastable material so that the transformation is more affected by the type and population of soluble oligomers partially or completely. The SBU approach has more suitability than CBU approaches because the basic forms of SBU have more resemblance to the basic ring forms in zeolite dissolution cases and in conventional zeolite synthesis. The RBU approach can overcome the shortcomings of the SBU approach in transformation cases involving 5-ring contained zeolites. The RBU approach has been shown to distinguish zeolite classification based on its Si/Al molar ratio, namely low-silica, medium-silica, high-silica, and siliceous zeolites. The RBU approach can be a simple and easy preliminary consideration in selecting zeolite parent and predicting zeolite types based on RBU’s ownership of the parent's zeolite, with or without the aid of a template, structure directing agent, or seed. Thus, the success of transformation can be considered as the success of keeping the type and population of RBU’s available in the parent zeolite required to construct transformation product framework.

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