Simple approach in understanding interzeolite transformations using ring building units

IOP Conf. Series: Materials Science and Engineering **349** (2018) 012016 doi:10.1088/1757-899X/349/1/012016

Simple approach in understanding interzeolite transformations using ring building units

D Suhendar[1,2], Buchari[1], R R Mukti[1], Ismunandar[1]

[1] Program Studi Kimia, Fakultas Matematika dan Ilmu Pengetahuan Alam, Institut Teknologi Bandung, Jl. Ganesha no. 10 Bandung 40132, Indonesia,
[2] Program Studi Kimia, Fakultas Sains dan Teknologi, Universitas Islam Negeri Sunan Gunung Djati, Jl. A. H. Nasution no. 105 Bandung 40614, Indonesia

dede.suhendar@uinsgd.ac.id

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 [1] [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.

Table 1 Framework density data in selected interzeolite transformation cases

Parent zeolite		Transformation product		Ref.[b]	suitability[c]
Type	FD[a] / T·1000A^{-3}	Type	FD[a] / T·1000 Å^{-3}		
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 couldnot 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 SBUs, 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.[b]	Availability[c]
Framework type	CBU's[a]	Framework type	CBU's[a]		
Without template, structure directing agent, or seed					
*BEA	*mor, bea*	MFI	*mor, cas, mel, mfi*	[7]	+
FAU	*d6r, sod*	ANA	?	[4]	?
FAU	*d6r, sod*	GIS	*dcc, gis*	[7]	–
FAU	*d6r, sod*	MOR	*mor*	[7]	–
FAU	*d6r, sod*	LTL	*dsc, d6r, can, ltl*	[7]	+
FAU+*BEA	*(d6r, sod) + (mor, bea, mtw)*	MFI	*mor, cas, mel, mfi.*	[1]	+
FAU+FER	*(d6r, sod) + (fer)*	GIS	*dcc, gis*	[7]	–
GIS	*dcc, gis*	ANA	*?*	[15]	?
LEV	*d6r*	CHA	*d6r, cha*	[2]	+
LTA	*d4r, sod, lta*	FAU	*d6r, sod*	[3]	+
LTA	*d4r, sod, lta*	GIS	*dcc, gis*	[9]	–
LTA	*d4r, sod, lta*	SOD	*sod*	[11] [12] [13] [3]	+
SOD	*sod*	CAN	*dzc, can*	[18]	–
supported with template, structure directing agent, or seed					
*BEA	*mor, bea, mtw*	MOR	*mor*	[32]	+
FAU	*d6r, sod*	ABW	*dzc, abw*	[8]	–
FAU	*d6r, sod*	ANA	?	[8] [6]	?
FAU	*d6r, sod*	BRE	*bre*	[6]	–
FAU	*d6r, sod*	CAN	*dzc, can*	[33]	–
FAU	*d6r, sod*	CHA	*d6r, cha*	[1] [8] [28] [6] [5] [34]	+
FAU	*d6r, sod*	GME	*dcc, d6r, gme*	[6]	+
FAU	*d6r, sod*	HEU	*bre*	[6]	–
FAU	*d6r, sod*	MER	*dcc, d8r, pau*	[8]	–
FAU	*d6r, sod*	MFI	*mor, cas, mel, mfi*	[1]	–
FAU	*d6r, sod*	MTW	*jbw, cas, bik, mtw*	[1]	–
FAU	*d6r, sod*	MWW	*d6r, mel*	[35]	+
FAU	*d6r, sod*	PHI	*dcc double crankshaft chain*	[6]	–
FAU	*d6r, sod*	SOD	*sod*	[33]	+
FAU	*d6r, sod*	STF	*cas, stf*	[1]	–
LTA	*d4r, sod, lta*	MWW	*d6r, mel*	[10]	–
GME	*dcc, d6r, gme*	ANA	?	[14]	?
GIS	*dcc, gis*	CHA	*d6r, cha*	[36] [16]	–
MTW	*jbw, cas, bik, mtw*	ITW	*d4r*	[19]	–
MWW	*d6r, mel*	FER	*fer*	[17]	–
TON	*jbw, mtt, bik, ton*	ITW	*d4r*	[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		Ref.[b]	availability[c]
Framework type	SBU's[a]	Framework type	SBU's[a]		
Without template, structure directing agent, or seed					
*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]	+
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] [6] [5] [34]	+
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]	–

[a] 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].
[b] source data of the parent zeolite type and its transformation product,
[c]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.[b]	Support[c]
Type	SBU[a]	Type	SBU[a]		
FAU	6-6, 6-2, 6, 4-2, 1-4-1, 4	MOR	5-1	[7]	–
FAU	6-6, 6-2, 6, 4-2, 1-4-1, 4	HEU	4-4=1	[6]	seed
FAU	6-6, 6-2, 6, 4-2, 1-4-1, 4	MFI	5-1	[1]	seed
FAU	6-6, 6-2, 6, 4-2, 1-4-1, 4	MTW	5-[1,1]	[1]	seed
FAU	6-6, 6-2, 6, 4-2, 1-4-1, 4	STF	5-3	[1]	seed
MTW	5-[1,1]	ITW	1-4-1, 4-[1,1]	[19]	SDA
TON	5-1	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[a]	SBU[b]	RBU				
BIK	2.0	5-1	5 and 6	TON	11.0 - infinite	5-1	5 and 6
MAZ	2.6	5-1 / 4-2	4 and 5	CDO	silica	5-1	5 and 6
STI	2.6	4-4=1	4 and 5	IMF	silica	5-1	4, 5 and 6
DAC	3.8	5-1	4, 5 and 6	NSI	silica	5-1	5 and 6
BOG	4.3	6 / 5-1 / 4	4, 5 and 6	DON	silica	5-3	4, 5 and 6
CAS	5.0	5-1	5 and 6	GON	silica	5-3	4, 5 and 6
FER	5.0	5-1	5 and 6	SFF	silica	5-3	4, 5 and 6
MOR	5.0	5-1	4, 5 and 6	SGT	silica	5-3	5 and 6
ESV	8.37	5-1	4 and 5	STF	silica	5-3	4, 5 and 6
*BEA	8.14	?	4, 5 and 6	STT	silica	5-3	4, 5 and 6
EON	4.26 - 15.67	5-1	4 and 5	RTE	silica	6 / 5-1	4, 5 and 6
MFI	2.5 - infinite	5-1	4, 5 and 6	ISV	silica	6-2	4, 5 and 6
EUO	4.89 - infinite	1-5-1	4, 5 and 6	IFR	silica	6-2	4, 5 and 6
MEL	5.0 - infinite	5-1	4, 5 and 6	RWR	silica	6-2	5 and 6
MTW	10.2 - infinite	5-[1,1]	4, 5 and 6	RRO	silica	4-1=1	4, 5 and 6
MTT	11.0 - infinite	5-1	5 and 6	DOH	silica	?	4, 5 and 6

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[a]	SBU[b]	RBU	Tipe	Si/Al[a]	SBU[b]	RBU
GIS	1.0	4	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 / 6-2 / 8 / 6 / 4-2 / 4	4 and 6
FRA	1.0	6 / 4	4 and 6	FAU	2.3	6-6 / 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 / 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 / 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 H_2O/SiO_2 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].

Table 7 The relationship between SBU and RBU with low-silica zeolites but has 5-ring

Type	Si/Al ratio			SBU ownership		RBU ownership	
	Previous findings[a]	Recent findings	Ref.[b]	SBU	suitability[c]	RBU	suitability[c]
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	+

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

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.

Table 8 The comparison between the SBU and RBU approaches in less common Si/Al ratio zeolites

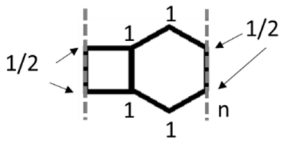
Tipe	Si/Al[a]	SBU approach		RBU approach	
		SBU[b]	suitability[c]	RBU	suitability[c]
MSO	13.3	2-6-2 / 4-1	–	4 and 6	–
STI	2.6 or 45	4-4=1	+	4 and 5	+
ITW	silica	1-4-1 / 4-[1,1]	–	4 and 6	–
DOH	silica	?	?	4, 5 and 6	+
IFR	silica	6-2	–	4, 5 and 6	+
ISV	silica	6-2	–	4, 5 and 6	+
RRO	silica	4-1=1	–	4, 5 and 6	+
RWR	silica	6-2	–	5 and 6	+

[a] Si/Al value based on reference [21]; [b] SBU data obtained from reference [21], "?" states it is not be ascertained yet; [c] "+" and "-" marks express suitable or not suitable with the Si/Al mole ratio, "?"states can not be ascertained suitability.

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 $|K_{2.1}C_{12}H_{24}O_6|$ $[Al_{2.1}Si_{27.9}O_{60}]$ [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	$2 \leq Si/Al \leq 14$ or $2 \leq Si/Al \leq 29$	Si/Al > 14 or Si/Al > 29	Infinite Si/Al, the majority always contain RBU 5, except ITW only contains RBU 4 and 6

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.

Acknowledgement

Financial support by Ministry of Religious Affairs (Bantuan Biaya Penyelesaian Studi Pascasarjana 2016) is gratefully acknowledged.

References

[1] S. Goel, S. I. Zones dan E. Iglesia, "Synthesis of zeolites via interzeolite transformations without organic structure-directing agents," *Chemistry of Materials,* vol. 27, no. 6, pp. 2056-2066, 2015.

[2] I. Goto, M. Itakura, S. Shibata, K. Honda, Y. Ide, M. Sadakane and T. Sano, "Transformation of LEV-type zeolite into less dense CHA-type zeolite," *Microporous and Mesoporous Materials,* vol. 158, p. 117–122, 2012.

[3] M. Maldonado, M. D. Oleksiak, S. Chinta dan J. D. Rimer, "Controlling crystal polymorphism in organic-free synthesis of Na-zeolites," *Journal of the American Chemical Society,* vol. 135, pp. 2641-2652, 2013.

[4] Y. Wang, X. Li, Z. Xue, L. Dai, S. Xie dan Q. Li, "Preparation of zeolite ANA crystal from zeolite Y by in situ solid phase iso-structure transformation," *Journal of Physical Chemistry B,* vol. 114, p. 5747–5754, 2010.

[5] T. Takata, N. Tsunoji, Y. Takamitsu, M. Sadakane dan T. Sano, "Nanosized CHA zeolites with high thermal and hydrothermal stability derived from the hydrothermal conversion of FAU zeolite," *Microporous and Mesoporous Materials,* vol. 225, pp. 524-533, 2016.

[6] O. Chiyoda dan M. E. Davis, "Hydrothermal conversion of Y-zeolite using alkaline-earth cations," *Microporous and Mesoporous Materials,* vol. 32, pp. 257-264, 1999.

[7] K. Honda, M. Itakura, Y. Matsuura, A. Onda, Y. Ide, M. Sadakane dan T. Sano, "Role of structural similarity between starting zeolite and product zeolite in the interzeolite conversion process," *Journal of Nanoscience and Nanotechnology,* vol. 13, pp. 3020-3026, 2013.

[8] L. V. Tendeloo, E. Gobechiya, E. Breynaert, J. A. Martens and C. E. Kirschhock, "Alkaline cations directing the transformation of FAU zeolite into five different framework types," *Chemical Communications,* vol. 49, pp. 11737-11739, 2013.

[9] B. Subotic, I. Smit, O. Madzija dan L. Sekovanic, "Kinetic study of the transformation of zeolite A into zeolite P," *Zeolites,* vol. 2, pp. 135-142, 1982.

[10] E. Xing, Y. Shi, A. Zheng, J. Zhang, X. Gao, D. Liu, M. Xin, W. Xie, F. Zhang, X. Mu dan X. Shu, "Transformation from NaA to MCM-49 zeolite and its catalytic alkylation performance," *Industrial and Engineering Chemistry Research,* vol. 54, no. 12, pp. 3123-3135, 2015.

[11] B. Subotic, D. Skrtic, I. Smit and L. Sekovanic, "Transformation of zeolite A into hydroxysodalite: I. An approach to the mechanism of transformationa nd its experimental evaluation," *Journal of Crystal Growth,* vol. 50, pp. 498-508, 1980.

[12] R. I. Walton, F. Millange, D. O'Hare, A. T. Davies, G. Sankar dan C. R. A. Catlow, "An in situ energy-dispersive X-ray diffraction study of the hydrothermal crystallization of zeolite A. 1. Influence of reaction conditions and transformation into sodalite," *Journal of Physical Chemistry B,* vol. 105, no. 1, pp. 83-90, 2001.

[13] L. Ding, H. Yang, P. Rahimi, O. Omotoso, W. Friesen, C. Fairbridge, Y. Shi dan S. Ng, "Solid transformation of zeolite NaA to sodalite," *Microporous and Mesoporous Materials,* vol. 130, pp. 303-308, 2010.

[14] P. N. Joshi, A. Thangaraj and P. V. Shiralkar, "Studies on zeolite transformation of high-silica gmelinite into analcime," *Zeolite,* vol. 11, pp. 164-168, 1991.

[15] S. N. Azizi, A. A. Daghigh dan M. Abrishamkar, "Phase Transformation of Zeolite P to Y and Analcime Zeolites due to changing the time and temperature," *Journal of Spectroscopy,* vol. 2013, 2013.

[16] S. I. Zones, "Direct Hydrothermal Conversion of Cubic P Zeolite to Organozeolite SSZ-13," *Journal of the Chemical Society, Faraday Transactions,* vol. 86, no. 20, pp. 3467-3472, 1990.

[17] S. Xie, S. Liu, N. Gao, X. Li, Y. Gao, K. Liu and L. Xu, "Interzeolite conversion of zeolite MCM-49 into zeolite ZSM-35 in cyclohexylamine–hexamethyleneimine–Na2O–H2O containing systems," *New Journal of Chemistry,* vol. 38, pp. 2514-2521, 2014.

[18] M. C. Barnes, J. Addai-Mensah and A. R. Gerson, "The mechanism of the sodalite-to-cancrinite phase transformation in synthetic spent Bayer liquor," *Microporous and Mesoporous Materials,* vol. 31, p. 287–302, 1999.

[19] A. Rojas, M. L. San-Roman, C. M. Zicovich-Wilson dan M. A. Camblor, "Host-guest stabilization of a zeolite strained framework: In situ transformation of zeolite MTW into the less dense and more strained ITW," *Chemistry of Materials,* vol. 25, pp. 729-738, 2013.

[20] C. M. Zicovich-Wilson, F. Gandara, A. Monge dan M. A. Camblor, "In Situ Transformation of TON Silica Zeolite into the Less Dense ITW: Structure-Direction Overcoming Framework Instability in the Synthesis of SiO2 Zeolites," *Journal of American Chemical Society,* vol. 132, pp. 3461-3471, 2010.

[21] C. Baerlocher, L. B. McCusker dan D. H. Olson, Atlas of zeolite framework types, 6th penyunt., Amsterdam: Elsevier, 2007.

[22] I. H. Lim, W. Schrader dan F. Schüth, "The formation of zeolites from solution – Analysis by mass spectrometry," *Microporous and Mesoporous Materials,* vol. 166, pp. 20-36, 2013.

[23] M. Castro, M. Haouas, I. Lim, H. J. Bongard, F. Schuth, F. Taulelle, G. Karlsson, V. Alfredsson, E. Breyneart, C. E. Kirschhock dan W. Schmidt, "Zeolite beta formation from clear sols: silicate

speciation, particle formation and crystallization monitored by complementary analysis methods," *European Journal of Chemistry,* vol. 22, pp. 1-14, 2016.

[24] L. I. Meza, M. W. Anderson, B. Slater dan J. R. Agger, "In situ atomic force microscopy of zeolite A dissolution," *Physical Chemistry Chemical Physics,* vol. 10, pp. 5066-5076, 2008.

[25] B. B. Schaack, W. Schrader dan F. Schuth, "Detection of structural elements of different zeolites in nucleating solutions by electrospray ionization mass spectrometry," *Angewandte Chemie International Edition,* vol. 47, pp. 9092-9095, 2008.

[26] L. Ren, C. Li, F. Fan, Q. Guo, D. Liang, Z. Feng, C. Li, S. Li dan F.-S. Xiao, "UV–raman and NMR spectroscopic studies on the crystallization of zeolite A and a new synthetic route," *Chemistry: A European Journal,* vol. 17, pp. 6162-6169, 2011.

[27] Y. Xiao, N. Sheng, Y. Chu, Y. Wang, Q. Wu, X. Liu, F. Deng, X. Meng dan Z. Feng, "Mechanism on solvent-free crystallization of NaA zeolite," *Microporous and Mesoporous Materials,* vol. 237, pp. 201-209, 2017.

[28] M. Itakura, I. Goto, A. Takahashi, T. Fujitani, Y. Ide, M. Sadakane and T. Sano, "Synthesis of high-silica CHA type zeolite by interzeolite conversion of FAU type zeolite in the presence of seed crystals," *Microporous and Mesoporous Materials,* no. 144, pp. 91-96, 2011.

[29] A. Cizmek, B. Subotic, R. Aiello, F. Crea, A. Nastro dan C. Tuoto, "Dissolution of high-silica zeolites in alkaline solutions I. Dissolution of silicalite-1 and ZSM-5 with different aluminum content," *Microporous Materials,* vol. 4, pp. 159-168, 1995.

[30] A. Cizmek, B. Subotic, I. Smit, A. Tonejc, R. Aiello, F. Crea dan A. Nastro, "Dissolution of high-silica zeolites in alkali solutions II. Dissolution of 'activated' silicalite-1 and zsm-5 with different aluminum content," *Microporous Materials,* vol. 8, pp. 159-169, 1997.

[31] A. Petushkov, J. Freeman dan S. C. Larsen, "Framework stability of nanocrystalline NaY in aqueous solution at varying pH," *Langmuir,* vol. 26, no. 9, pp. 6695-6701, 2010.

[32] H. Zhang, H. Zhang, P. Wang, Y. Zhao, Z. Shi, Y. Zhang dan Y. Tang, "Organic template-free synthesis of zeolite mordenite nanocrystals through exotic seed assisted conversion," *RSC Advances,* vol. 6, pp. 47623-47631, 2016.

[33] J.-C. Buhl, "Enhanced methods of crystallization: The crossover synthesis from gel to melt flow - A case study on sodalites," *Microporous and Mesoporous Materials,* vol. 236, pp. 13-20, 2016.

[34] X. Xiong, D. Yuan, Q. Wu, F. Chen, X. Meng, R. Lv, D. Dai, S. Maurer, R. McGuire, M. Feyen, U. Müller, W. Zhang, T. Yokoi, X. Bao, H. Gies, B. Marler, D. E. De Vos, U. Kolb, A. Moini dan F.-S. Xiao, "Efficient and rapid transformation of high silica CHA zeolite from FAU zeolite in the absence of water solvent," *Journal of Materials Chemistry A,* vol. 5, no. 19, pp. 9076-9080 , 2017.

[35] E. Xing, Y. Shi, W. Xie, F. Zhang, X. Mu dan X. Shu, "Size-controlled synthesis of MCM-49 zeolite from NaX for liquid phase alkylation of benzene with ethylene," *Microporous and Mesoporous Materials,* vol. 236, pp. 54-62, 2016.

[36] S. I. Zones dan R. v. Nordstrand, "Novel zeolite transformations: The template-mediated conversion of cubic P zeolite to SSZ-13," *Zeolites,* vol. 8, pp. 166-174, 1988.

[37] R. Xu, W. Pang, J. Yu, Q. Huo dan J. Chen, Chemistry of Zeolites and Related Porous Materials: Synthesis and Structure, Singapore: John Wiley & Sons (Asia) Pte Ltd, 2007.

[38] A. Lv, H. Xu, H. Wu, Y. Liu and P. Wu, "Hydrothermal synthesis of high-silica mordenite by dual-templating method," *Microporous and Mesoporous Materials,* vol. 145, pp. 80-86, 2011.

[39] T. M. Davis, C.-Y. Chen, N. Zilková, D. Vitvarová-Procházková, J. Cejka and S. I. Zones, "The importance of channel intersections in the catalytic performance of high silica stilbite," *Journal of Catalysis,* vol. 298, pp. 84-93, 2013.

[40] S. I. Zones, S.-J. Hwang, S. Elomari, I. Ogino, M. E. Davis and A. W. Burton, "The fluoride-based route to all-silica molecular sieves; a strategy for synthesis of new materials based upon close-packing of guest–host products," *C. R. Chimie,* vol. 8, pp. 267-282, 2005.

[41] T. Moteki and R. F. Lobo, "A General Method for Aluminum Incorporation into High-Silica Zeolites Prepared in Fluoride Media," *Chemistry of Materials,* vol. 28, no. 2, pp. 638-649, 2016.

[42] M. D. Oleksiak, J. A. Soltis, M. T. Conato, R. L. Penn dan J. D. Rimer, "Nucleation of FAU and LTA zeolites from heterogeneous aluminosilicate precursors," *Chemistry of Materials,* vol. 28, no. 14, pp. 4906-4916, 2016.

[43] D. F. Shantz, A. Burton and R. F. Lobo, "Synthesis, structure solution, and characterization of the aluminosilicate MCM-61: the first aluminosilicate clathrate with 18-membered rings," *Microporous and Mesoporous Materials,* vol. 31, pp. 61-73, 1999.

[44] C. Jo, W. Park and R. Ryoo, "Synthesis of mesoporous zeolites in fluoride media with structure-directing multiammonium surfactants," *Microporous and Mesoporous Materials,* vol. 239, pp. 19-27, 2017.