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Review article

# Hydrothermally synthesized zeolites based on kaolinite: A review

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ABSTRACT

Many types of zeolites have been developed based on kaolinite in previous years. This review focuses on the current reports of kaolinite-based zeolites and the important factors in their synthesis. Among the factors discussed in this review are the effect of $SiO_2/Al_2O_3$ (Si/Al) molar ratio of the gel mixture, metakaolinization time and temperature, aging condition, alkalinity, and crystallization time and temperature. This review only covers the most recent kaolinite-based zeolite papers published from 2005 to present. A brief discussion on the evolution of zeolites is also included.

## 1. Introduction

The first zeolite mineral, stilbite, was found by a Swedish mineralogist, Cronstedt in 1756. The mineral was named after the property of a mineral that exhibits intumescence when heated in a blowpipe flame. *Zeolite* is derived from two Greek words, *zeo* and *lithos*, meaning “to boil” and “stone”, respectively (Cronstedt, 1756). Until the 1880s, the properties of zeolite, such as adsorption properties, reversible cation exchange, and dehydration have been described by various authors. The first hydrothermal synthesis of zeolite, levynite, was reported by de St Claire Deville (1862). Friedel (1896) has developed the thought that the structure of dehydrated zeolite consists of spongy framework. McBain (1932) established the term “molecular sieve” to define porous solid material that acts as sieves on a molecular scale. Between 1949 and 1954, a number of commercially significant zeolites, types A, X, and Y were discovered by Milton and Donald W. Breck (Reed and Breck, 1956).

According to International Zeolite Association (2014), until now, there are 218 zeolite framework type codes that have been discovered. Back in 2006, only about 170 molecular sieve structures were registered under the Structure Commission of the International Zeolite Association, and only 17 of them have commercial interest (Theo, 2007). The annual market for synthetic zeolites and molecular sieves was developed vastly to 1,800,000 ton worldwide in 2008 (Davis and Inoguchi, 2009). Zeolite role as ion exchangers in detergents has been the largest single market by volume, however, by market value, zeolites as catalysts have the highest market value. LTA-type zeolite is popular as an ion exchanger in industry, while FAU-type is popular as a catalyst (Maesen and Marcus, 2001).

Molecular sieve materials have no systematic nomenclature. When the first synthetic materials were discovered by Milton, Breck and coworker at Union Carbide, they used the modern Latin alphabet such as zeolites A, B, X, Y, and L to name the zeolites. After that, Mobil and Union Carbide initiated the usage of the Greek alphabet, for example, zeolites alpha, beta, and omega. Synthetic zeolites with a structural topology of mineral zeolites were allotted the name of mineral, for example chabazite, erionite, mordenite, and offretite (Barrer, 1979). A three-letter code has been assigned by IZA Structure Commission to be used for known framework topology irrespective of composition. For example, LTA for Linde Type A zeolite and FAU for zeolite with a faujasite topology 1 (Baerlocher et al., 2007). Over the past decade, the term “zeolite” has evolved and changed, which includes non-aluminosilicate compositions and structures (Meier and Olson, 1988). In 2008, the term “nanoporous” material was applied to zeolites and related molecular during the Nanoporous Material Gordon Research Conference (Flanigen et al., 2010).

This review attempts to summarize the important factors that affect the hydrothermal synthesis of kaolinite-based zeolite. According to Youssef et al. (2008) kaolinite-based zeolites were using cheap natural materials compared to conventional system, where pure sodium silicate and sodium aluminate were used. Hence, kaolinite-based system is more cost efficient. Beginning with a brief introduction on zeolites and the evolution of synthetic zeolites, it is then followed by kaolinite, which is the raw material to synthesize zeolite. The hydrothermal synthesis technique is also described, which is the main technique used to synthesize all of the zeolites discussed in this review. Furthermore, the factors affecting the zeolite synthesis in hydrothermal

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synthesis are being discussed. Finally, the optimum condition for the zeolite synthesis is summarized.

### 1.1. Zeolites

Zeolites are porous material with a three-dimensional framework structure of crystalline aluminosilicate that forms uniformly sized pores and commonly referred as molecular sieves (Theo, 2007). Examples of two different types of zeolite framework, LTA type framework and FAU type framework are shown in Figs. 1 and 2, respectively. Carbons, glasses, and oxides are molecular sieves, but most of the molecular sieves in practice today are zeolites (Flanigen et al., 2010). Crystalline aluminosilicate zeolites are made of group IA and group IIA elements such as sodium, potassium, magnesium and calcium (Breck, 1974). The empirical formula for zeolite is $M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot wH_2O$, where $y$ is 2–200, $n$ is the cation valence, and $w$ represents the water contained in the intracrystalline channels of zeolite (Flanigen et al., 2010). By sharing of oxygen ions, zeolite framework, which consists of four connected framework of $AlO_4$ and $SiO_4$ tetrahedra, are joined together. In the framework, each $AlO_4$ tetrahedron carries a net negative charge, which is balanced by an extra framework cation. The intracrystalline channels in the zeolite framework structure are occupied by water molecules and cations. The cations are mobile and generally undergo ion exchange. The water molecules may be removed reversibly, generally by the application of heat and pass through the micropores and voids, which made up to 50% of the crystal volume. The crystalline host structure remains intact despite the removal of water molecules. The intracrystalline channels can be one, two, or three-dimensional. However, in facilitating the intracrystalline diffusion in adsorption and catalytic applications, two or three dimensions are preferred. Somehow, zeolite framework should be viewed as slightly flexible because of the size and shape of the framework and pores that corresponds to the changes in temperature and guest species (Flanigen et al., 2010).

### 1.2. Evolution of zeolites

The evolution trends in synthetic zeolites are summarized in Table 1.

The period of 1980s was considered as the period of explosion in the discovery of new composition and structure types of zeolites. The discoveries of new zeolites can be seen from the various editions of *Atlas of Zeolite Structure Types* (Baerlocher et al., 2007). The first edition (1978) comprised 38 structure types, the second edition (1987) listed 64 types, the third edition (1992) listed 85, the fourth edition (2007) listed 176, and according to the most recent from the Structure Commission of International Zeolite Association of www.iza-structure.org in 2014, in total, there are 218 framework types. However, not all of the structure types are truly molecular sieve materials, since some of them are not stable for the removal of as-synthesized guest species (Flanigen et al., 2010).

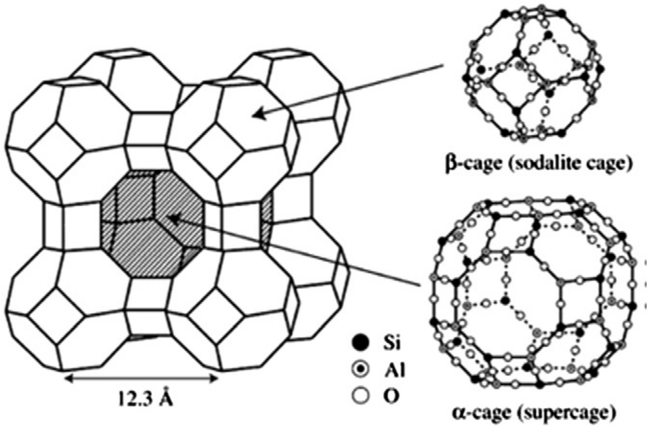

**Fig. 1.** The framework structure of the LTA (Nam et al., 2007).

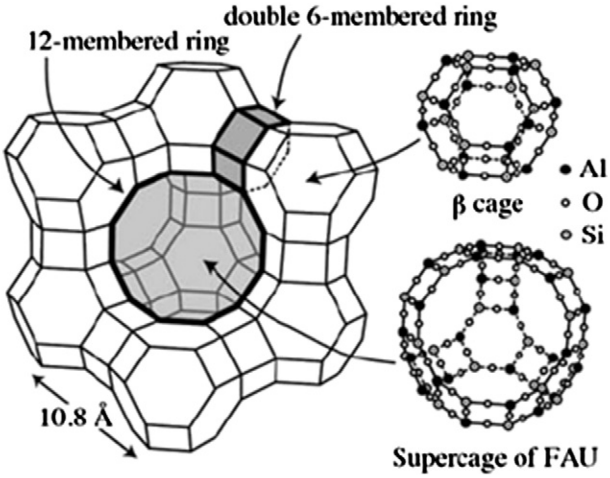

**Fig. 2.** The framework structure of FAU type zeolite (Nozue et al., 2012).

### 1.3. Kaolinite for zeolitization

Kaolinite is the main component of kaolin. The material is formed mainly by the decomposition of feldspars, granite, and aluminum silicates, or generally by weathering process. The process of kaolin formation is called kaolinization. Kaolinite can exist in white, grayish-white, or slightly colored. Kaolinite structure consists of a tetrahedral silica sheet alternating with an octahedral alumina sheet (Brigatti et al., 2013), which forms the 1:1 clay mineral layer, as shown in Fig. 3. The repeating 1:1 layer is attached to each other by hydrogen bonds (Brigatti et al., 2013). Kaolinite is non-expanding and as a result of its high molecular stability, isomorphous substitution is limited or non-existent (Brigatti et al., 2013). Change in the chemical structure and physicochemical properties of kaolinite could be observed when static pressures or grinding is applied to kaolinite (Iglesia, 1993; Kristof et al., 1993). The usage of kaolinite as the source of alumina and silica in the zeolite synthesis has been reported previously by Barrer (1982), where it was calcined between 700 °C and 1000 °C to produce metakaolin by dehydroxylation process. Since then, a lot of kaolinite related papers have been produced (Bosch et al., 1983; Costa et al., 1988; Madani et al., 1990; Basaldella et al., 1993; de Lucas et al., 1993; Chandrasekhar and Pramada, 2001). Some of the zeolites produced from natural aluminosilicate minerals also show outstanding catalytic cracking performance as reported by Li et al. (2012). The reaction (1) involved in metakaolinization process is:

$$\underset{\text{Kaolinite}}{Si_2Al_2O_5(OH)_4} \xrightarrow[\Delta]{550^\circ} \underset{\text{Metakaolinite}}{Al_2O_3 \cdot 2SiO_2} + 2H_2O. \tag{1}$$

The reaction transforms four hydroxyl groups into two water molecules, which then leaves two oxygen anions in the material, as shown in this reaction: $4(OH^-) \rightarrow 2H_2O + 2O^{2-}$ (Wardle and Brindley, 1972). According to Dion et al. (1998) the dehydroxylation occurs according to two elementary processes, diffusion and first order. First order process is responsible for the formation of water from two adjacent hydroxyl groups, meanwhile, the transport of water is via a diffusion process. The metakaolin then undergoes hydrothermal treatment in NaOH to produce zeolite. The general conversion reaction of reactants, such as polymeric silica and alumina, to a microporous zeolite crystalline framework, is shown as below:

$$T\text{–}OH + {}^{-}O\text{–}T \leftrightarrow T\text{–}O\text{–}T + OH^{-} \tag{2}$$