

## CHAPTER II

### LITERATURE REVIEWS

Beta zeolite is developing into a major catalyst in organic chemicals conversion, contribution to low waste technology. Beta zeolite was first synthesized by Wadlinger et al. [2] from alkaline aluminosilicate gels in the presence of sodium and tetraethylammonium cations in the range of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio from 10 to 200 in 1967. Then beta zeolite was studied continuously.

Zeolites are generally synthesized by a hydrothermal process from a source of alumina (e.g., sodium aluminate or aluminium sulfate) and of silica (e.g., a silica sol, fumed silica, or water glass) and an alkali such as NaOH, and/or a quaternary ammonium compound. An inhomogeneous gel is produced which gradually crystallizes, in some cases forming more than one type of zeolite in succession. Nucleation effects can be important, and an initial induction period at near ambient temperature may be followed by crystallization temperature that may range up to 200°C or higher. The pressure is equal to the saturated vapor pressure of the water present.

After synthesis the zeolite are washed, dried, heated to remove water of crystallization, and calcined in air, e.g., at about 550 °C. Organic species are also thus removed. For most catalytic purpose, the zeolite is converted into acidic form. For some zeolites this can be achieved by treatment with aqueous HCl without significantly altering the framework structure. For other zeolites  $\text{Na}^+$  is replaced with  $\text{NH}_4^+$  via an ammonium compound such as  $\text{NH}_4\text{OH}$ ,  $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{NO}_3$ . Upon heating  $\text{NH}_3$  is driven off, leaving the zeolite in the acid form. For some reaction a hydrogenation component such as platinum or nickel is introduced by impregnation or ion exchange

The final product depends on a complex interplay between many variables including  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio in the starting medium, nucleating agents, temperature, pH, water content, aging, stirring, and the presence of various inorganic and organic

cations. Much remains to be learned about how the initial reaction mixture forms the precursor species and how these arrange into the final crystalline products. A key concept is that the cations present give rise to a templating action, but clearly the process is more complex.

The mechanism of action of the organic species is still controversial. It was originally thought to be primarily a templating effect, but later it was found that at least some of zeolites could be synthesized without an organic template. Further, organic species other than quaternary ammonium compounds had directing effects not readily ascribed to their size or shape. However, an important result was the zeolites of higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio than before could be synthesized. Previously, only structures with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios of about 10 or less could be directly forms, but with organic additives, zeolites with ratio of 20 to 100 or more can be directly prepared [12].

Beta zeolite is generally synthesized by hydrothermal method using tetraethylammonium hydroxide (TEAOH), tetraethylammonium bromide-diethanolamine or tetraethylammonium hydroxide-tetraethylammonium bromide triethanolamine as the organic template and using excess water [13, 14], which always has a low product yield and could not be synthesized with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio above 250.

Perez Pariente et al. [15] studied the efficiency of the synthesis of beta zeolite by hydrothermal method and the chemical composition of crystals. It was very difficult to effectively synthesize siliceous crystal of beta zeolite. From aluminum-rich gels ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ ), high yield of beta zeolite could easily be obtained, whereas from siliceous gels ( $\text{SiO}_2/\text{Al}_2\text{O}_3 = 900$ ), beta zeolite was found in small amount. The crystals were enriched in aluminium. This synthesis insufficiency was due to the inefficiency use of silicon, the mother liquor always being exhausted in aluminium at the end of the crystallization. The incorporation of silicon in beta zeolite could be improved by several means. When ethanol was kept in the system, when aluminium was excluded from the gel particles, or when the synthesis temperature was increased from 100 to 120°C, reasonable yields of siliceous beta zeolite crystals were obtained.

On the other hand, Bibby and Dale first reported the crystallization of silica sodalite in an ethylene glycol media in 1985 [16]. It has been reported that various types of zeolites including ZSM-5 and FFR were synthesized in organic solvents without additional water [17]. They suggest that water is not always essential as a media for zeolite synthesis.

In 1990, Xu et al. reported that a dry aluminosilicate gel could be transformed to ZSM-5 by contact with vapors of water and volatile amines such as ethylenediamine (EDA) [4]. Since then, such methods to transform dry gel to zeolite in vapor have extensively been developed and found a lot of applications for synthesizing microporous crystals with new compositions and structures.

Recently, zeolite with beta zeolite structure was prepared using a new crystallization method called 'Dry Gel Conversion technique', where a hydrogel is dried and the resultant dry gel is converted into microporous crystals in steam or in a mixed vapor of steam and organic template, has been developed by Hari Prasad Rao and M. Matsukata [5]. This dry gel conversion technique is a convenient method to prepare zeolites and enables one to synthesize beta zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios from 30 to infinity using tetraethylammonium hydroxide (TEAOH) as an organic template, which higher  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio than beta zeolite synthesized by the conventional hydrothermal method. Beta zeolite crystallized by this method had uniform particles of about 60 nm.

Hari Prasad Rao et al. [6] studied the synthesis of beta zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios ranging from 30 to 740 were crystallized at 140 and 180°C by the dry gel conversion. They found that the particle size of the products increased with increasing  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio as well as with increasing crystallization temperature and high silica beta zeolite could be crystallized at a lower temperature of 140°C, though a crystallization time more than six days was required. Furthermore, they investigated the thermal stabilities of beta zeolite. They found that the framework of H-beta zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios ranging from 400 to 740 were stable even after calcinations at 1100°C and had higher thermal stabilities than those with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio 30, its was stable only up to 900°C and became amorphous when calcined at

1100°C. Beta zeolite crystallized at 140°C and 180°C obtained similar thermal stabilities.

Matsukata et al. [18] studied the crystallization behavior of beta zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratios ranging from 30 to 730 by dry gel conversion method. They found that the crystallized product obtained within 24 h were characterized by means of XRD, SEM,  $^{29}\text{Si}$ -MAS NMR, TPD of TEA for confirmed the formation of highly crystalline beta zeolite. They are shown that agglomerates of nano-particles were from a dry gel before the development of beta crystals in a long-range order, which can be detected by XRD. After several hours of crystallization, morphological changes in nano-particle agglomerates proceeded to give highly crystalline beta zeolite.

Furthermore, a wide varied of microporous crystals, pure silica microporous crystals, aluminosilicates and metasilicates can be synthesized using the dry gel conversion method [19].

Xia and Tatsumi [20] studied the nucleation and crystallization kinetic of  $\text{Ti}\beta$  zeolite with tetraethylammonium hydroxide as the template and fumed silica as the source of silica by the dry gel conversion technique. They found that a low temperature in the initial stage favors the nucleation of  $\text{Ti}\beta$  zeolite and that the subsequent high temperature is beneficial to the crystal growth. Furthermore, Influents of various synthesis parameters such as temperature program, silica and alumina sources and gel composition on the formation of  $\text{Ti}\beta$  zeolite were investigated. It was found that nanosized  $\text{Ti}\beta$  zeolite (20-50 nm) depended on kind of silica sources (Aerosil-200) and the optimal composition ( $\text{Si}/\text{Al}$  of 120-130,  $\text{Si}/\text{Na}$  of 90,  $\text{Si}/\text{Ti}$  of 30-40,  $\text{TEAOH}/\text{Si}$  of 0.4-0.6) and these condition obtained high activity in oxidation reactions with  $\text{H}_2\text{O}_2$ .

Arnold et al. [7] studied the dry gel conversion method for synthesis of EU-1 zeolite using HMBR as template with  $\text{Si}/\text{Al}$  ratio of 18-142. They found that the most critical parameters of the dry gel synthesis of EU-1 zeolite are the amount of water present in the autoclave during the crystallization process and the contents of sodium

cations and template molecules in the dry gel. EU-1 zeolites with a high crystallinity were obtained with the optimum water content in the autoclave.

Tatsumi and Jappar [21] studied properties of Ti-beta zeolite has been synthesized by dry gel conversion technique. The obtained Ti-beta zeolites were compared with hydrothermal synthesized Ti-beta zeolites. It was found that Ti-beta zeolites with synthesized by dry gel conversion adsorbed less water than Ti-beta zeolites with synthesized by hydrothermal. These results indicated that Ti-beta zeolites with synthesized by dry gel conversion was more hydrophobic than Ti-beta zeolites with synthesized by hydrothermal.

Beta zeolite has been found to be a much attentive catalyst, because it has a unique structure, acidity, and activity as a solid acid catalyst [22]. In addition, beta zeolite has been studied in a large range of reaction, and it is a potential catalyst in several processes [23,24]. Thus, beta zeolite is the interest of many researchers.

For several reaction, the activity and product selectivity of acidic zeolite catalysts depend strongly on the number, strength and nature of the acid sites present [25,26], and on the shape and size of the micropores which can induce different shape-selectivity effects on the product distribution [27]. In addition, the crystal/particle size and morphology can also influence their catalytic performance.

Camiloti et al. [28] studied acidity of zeolite beta with Si /Al ratios ranging from 18 to 33 by temperature programmed desorption (TPD) of ammonia and its catalytic behavior was evaluated by disproportionation of ethylbenzene. The acid strength of zeolite beta determined by TPD of ammonia increased as the Si /Al ratio was increased from 18 to 33. Despite of carrying out TPD measurements under very careful condition, the  $\text{NH}_3/\text{Al}$  ratios were always higher than unity and this result was probably a consequence of Lewis acid sites formed by structural defects present in H-beta zeolite. The ammonia desorbed between 380 °C and 600 °C seemed to be very appropriate to quantify the number of Brönsted acid sites in this zeolite. The results correlated very well with the catalytic behavior of this zeolite: the catalysts with stronger acid sites, determined by  $\text{NH}_3$ -TPD, present also higher catalytic activity in

the disproportion of benzene. The induction period of this reaction had no dependence on zeolite Si/Al ratio.

The recent studies demonstrated that part of aluminium atom disconnected from the framework during calcination or steaming could reinsert by post-synthesis hydrothermal treatments [29,30]. The state of the aluminium atoms in actual catalysts would then strongly depend on the nature and severity of the activation treatments as well as on the composition and structure of parent solid. Careful characterization of the local environment of the aluminium atom was therefore essential for the understanding of the catalytic properties of zeolite.

The acid properties and resultant catalytic activity of zeolite material were known to be related to the degree of substitution of aluminum for silicon in the framework [31]. The concentration of acid sites in non-dealuminated (Si/Al = 10), and dealuminated (Si/Al = 20-90) H-beta zeolites has been studied by quantitative IR measurements of pyridine sorption [32]. The number of Brønsted sites was found to be less than that of Al atom. Most probably this was due to the presence of Al in extraframework position (Al-OH groups and Lewis acid sites were found). Some positively charged extraframework Al species may neutralize the charge of  $\text{AlO}_4^-$  and lower the concentration of protonic sites.

Cambor et al [33] studied characterization of beta zeolite with crystal sizes in the range of 200 to 10 nm by using a combination of physicochemical techniques ( $\text{N}_2$  adsorption, XRD,  $^{29}\text{Si}$ -MAS NMR, pyridine adsorption, Thermal analysis). They found that the macropore volume of the zeolite decreases as a function of the decreases in crystal size. This decrease is apparent below 100 nm. The nanocrystallinity does not affect much the thermal stability of the zeolite in terms of crystallinity as measured by X-ray diffraction, but severely reduces the stability of aluminium in the framework during calcinations in air and highly aluminium content also indicate that severe dealumination.

Dealumination decreased the amount of extraframework Al species and, hence, the difference between the amounts of Al and Brønsted sites. Dealumination also decreased the number of Lewis acid sites [34]. IR studies of pyridine desorption evidenced that, as well as strong Brønsted sites (Si-OH-Al), there were also weak Brønsted sites, not Si-OH-Al; their nature is not clear. The contribution of such weak Brønsted sites decreased with the extent of dealumination. Dealumination removed the less acidic hydroxy groups first.

Nakao et al. [35] studied performance and characterization of beta zeolite catalysts for catalytic cracking. They was found that beta zeolite prepared by a hydrothermal synthesis method had more Brønsted acid sites than commercial beta zeolite and exhibited much higher activity in catalytic cracking of hydrocarbons, especially *n*-heptane. The structure of beta zeolite prepared by a hydrothermal synthesis method was found to be partly changed and partly destroyed; however, beta zeolite prepared by a hydrothermal synthesis method gave high *n*-heptane conversion even after the regeneration treatment.

A variety of H-zeolites and zeolite material have been reported to catalyst the reaction where methanol converted into hydrocarbons [36-38]. Methanol converted to hydrocarbons has been well studied, since Chang and Silvestri reported this reaction using H-ZSM-5 as catalyst [39]. At the same time, the data on the catalysis properties of other type of zeolite and zeolite-like materials such as beta zeolite [37,39] and mesoporous molecular sieves [41] are still rather scarce. Although the industrial realization of the process have already been a matter of common knowledge, some topics concerning its mechanism are still of great interest.

Recently, Bjørgen and Kolboe [42] studied the conversion of methanol to hydrocarbons over beta zeolites with varying contents of aluminum, the obtained by dealumination of the parent sample with oxalic acid. They found that the dealumination leads to catalysts which are more resistant to deactivation. The total amount of methanol which might be converted to hydrocarbons before the catalyst becomes completely deactivated increased. The conversion capacity is higher at high reactant feed rates.

Aguayo et al. [43] studied the transformation of methanol into light olefins (C<sub>2</sub>–C<sub>4</sub>) on several acid catalysts prepared by agglomerating different microporous acid phases (SAPO-11, SAPO-18, SAPO-34 and beta-zeolites) with bentonite and inert alumina. Consequently, they have different porous structure, total acidity and site acid strength. They found that the influence of their properties (micropore diameter, total acidity, acid strength and site density on their surface) on the kinetic behaviour of the catalysts (initial conversion and selectivity to olefins and deactivation rate). The catalyst SAPO-18 has a lower deactivation rate than the SAPO-34 due to a slightly lower acid strength and to a lower density of strong acid sites on the surface. These behaviors of SAPO-18 an interesting alternative to SAPO-34, which is the one used in industry in the MTO. And they proven that the acid strength moderation obtained in the SAPO-11 and in the beta-zeolites, does not provide acceptable results. In the case of the SAPO-11s, the moderation of acid strenght gives way to an excessive decrease in total acidity and, consequently, in conversion. Their higher micropore size than SAPO-18 and SAPO-34 makes easier the deposition of heavy products and their evolution to coke. The moderation of acid strenght is also attained in the beta-zeolites, although the higher micropore size allows the formation of heavy paraffins, which are not crackeable due to the low acid strenght of the sites.

Most of the studies on the MTO process have mainly focused on the SAPO-34 catalyst (isomorphous to chabazite), which allows for carrying out different modifications in its preparation and composition [44-46]. The deactivation by coke of SAPO-34 is very fast [47-48].

The conversion of methanol to hydrocarbons over H-beta zeolite has briefly been investigated by Hutchings et al. [37]. The authors reported 30-50% isobutane in the product stream, but hardly any products above C<sub>6</sub>. This appeared surprising, since wide-pore zeolite like beta zeolite might allow the formation of aromatic products.

From the above literature reviews, a wide varied of microporous crystals, pure silica microporous crystals, aluminosilicates and metallocates can be synthesized using the dry gel conversion method. However, the synthesis of beta



zeolite by dry gel conversion has been not fully studied. Thus, we were studied the synthesis of beta zeolite by dry gel conversion in order to obtain the optimum beta zeolite synthesized by dry gel conversion. In addition, thus-obtained products synthesized by dry gel conversion were also tested with methanol conversion in order to determination of the relation between the catalyst performance and characterization.