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Comparison between template assisted and OSDA-free synthesis of ZSM-12 and Zeolite Beta

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Abstract: Ever since the discovery of Stilbite by Cronstedt a class of minerals namely zeolites came into existence. Owing to their unique characteristics like cation exchange property, presence of channels like pore system approaching molecular size and extreme thermal stability made them attractive for variety of industrial applications as adsorbents, molecular sieves, catalysts etc. The early work in zeolite synthesis involved only inorganic reagents namely sources of silicon, aluminium and alkali and alkali earth metals resulted in the discovery of zeolite A, X, Y, L and Mordenite. Ever since the introduction of organic reagents in zeolite synthesis especially quaternary ammonium cations by R.M.Barrer et al revolutionized the zeolite synthesis resulted in new, novel and silicon rich zeolites such as zeolite Beta, ZSM-5, ZSM-12 etc. They are now used in the several industrial processes such as in Fluidized Catalytic Cracking (FCC) as catalysts and as adsorbents in Xylene separation etc. Any commercial process, cost is the major determinant parameter and hence the application of these novel zeolites is restricted owing to the usage of expensive organic structure directing agents (OSDA) in their synthesis. Thus the cost reduction in the synthesis of these novel zeolites by using seed assisted OSDA free synthesis, constitute an important area of research currently. This paper critically analyses the OSDA assisted and OSDA free seed assisted synthesis of two important novel and large pore twelve membered ring containing high silica zeolites namely Zeolite Beta and ZSM-12. The various parameters affecting the crystallization kinetics and crystal size of Zeolite Beta and ZSM-12 involving OSDA assisted and OSDA free seed assisted synthesis will be presented in detail.

Keywords—Organic-structure directing agents (OSDA), Seed assisted synthesis, OSDA assisted, Zeolite-Beta, ZSM-12.

I. INTRODUCTION

The synthesis of zeolites, crystalline aluminosilicate framework type materials, has been extensively investigated for a long time. To date, 206 types of zeolite and related structures have been identified [1] and this number keeps increasing. Aluminosilicate Zeolites are

crystalline microporous materials with 3-D framework structure consisting of tetrahedrally coordinated SiO₄ and AlO₄ units. They are widely used as catalysts, cation-exchangers, and adsorbents in many industrial processes owing to their well-defined channels, good ion-exchange capabilities and solid-acid properties of their H-form. [2-5]

Conventionally zeolites such as A (LTA), X, Y (FAU), L (LTL) and mordenite (MOR) have been synthesized by aluminosilicate gels without the use of Organic Structure Directing Agents (OSDAs).[6-8] These zeolites have played important role in various industrial fields. More recently synthesized zeolites depend on the use of various OSDAs, fluoride ions and introduction of metal atoms other than aluminium to the framework. [9-16]. These structure directing agents affect the nucleation process and ultimately affect the crystal structure. OSDAs are bulky organics such as tetraethylammonium hydroxide (TEAOH). One major advantage of these OSDA is that aluminosilicate zeolite with higher SiO₂/Al₂O₃ ratio, such as ZSM-5, ZSM-11, ZSM-12, Theta-1, and beta, have been synthesized. Few of these materials have high potential use in catalysis and adsorption and thus have new catalytic applications in oil-refining and petrochemical industry.

However the cost of OSDAs accounts for a larger part of the total cost of the starting materials. From an economic point of view, the amount of OSDA has to be reduced to as minimum as possible due to the high cost, complex synthesis processes involved, consumption of energy for removal of OSDA in the zeolite by calcinations, and the burden on environment by the release of the waste gas. Thus synthesis of zeolites without using OSDAs has been one of the most important topics for commercialization of zeolites based processes. [16-20]

This paper compares the synthesis of zeolites ZSM-12 and Zeolite-beta by OSDA assisted and OSDA free seed assisted synthesis in terms of synthesis procedures, factors



Fig. 1: Hydrothermal Zeolite synthesis (With the use of OSDAs). The starting materials (Si-O-Si and Al-O bonds) are converted by an aqueous mineralizing medium (OH- and/or F-) into the crystalline product (Si-O-Al bonds) whose micro-porosity is defined by the crystal structure

affecting the crystallization time, the size of the crystal etc.

II. SYNTHESIS PROCESS/ PROCEDURE:

A. Synthesis with the use of OSDAs:

S.Gopal et.al. synthesized ZSM-12 (MTW type zeolite) using colloidal Silica, LUDOX HS-40 (40% wt. DuPont) as silica source, Sodium aluminate as the aluminum and sodium source and TEAOH as the OSDA.[21] The gel composition used was:

$\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 80 \text{ SiO}_2 : 12.7 \text{ TEAOH} : 1040 \text{ H}_2\text{O}$

The crystallization was carried out at 160°C for 5.5 days and the calcination for removing the template was carried out at 520°C for 4h.

M.J. Eapen et.al. were able to synthesize zeolite beta with a molar composition of the initial gel :

$3.1 \text{ Na}_2\text{O} : 15(\text{NH}_4)_2\text{O} : 5.0 (\text{TEA})_2\text{O} : 35 \text{ SiO}_2 : \text{Al}_2\text{O}_3 : 656 \text{ H}_2\text{O}$

using TEABr as the OSDA and the crystallization temperature was varied from 373-413 K.

B. Seed-assisted OSDA-free synthesis process:

Majano et. al. reported the seed-assisted synthesis of aluminum rich zeolite beta (Si/Al ratio as low as 3.9:1)

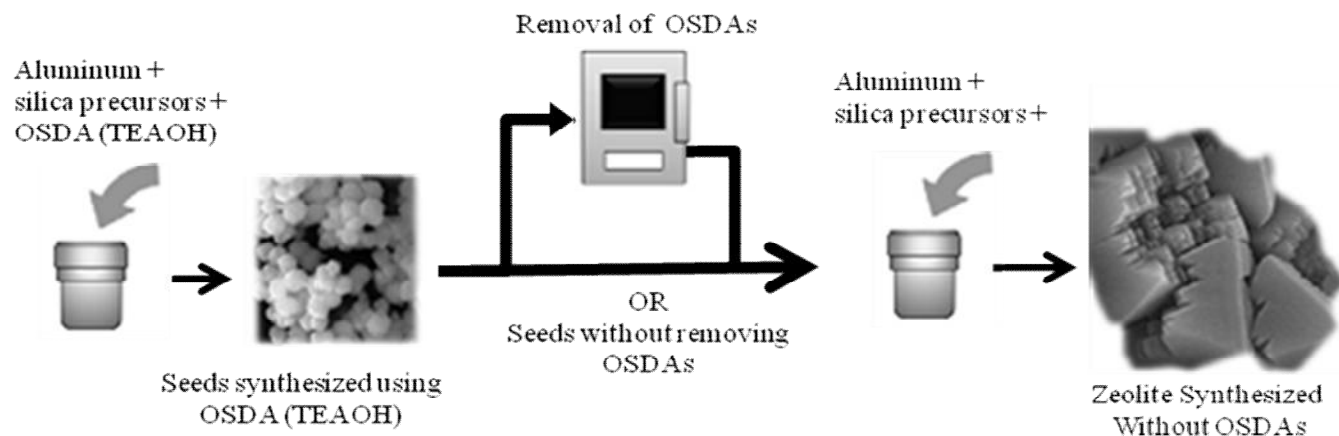


Fig. 2: Schematic illustration of seed-assisted, OSDA-free synthesis of zeolites [30]

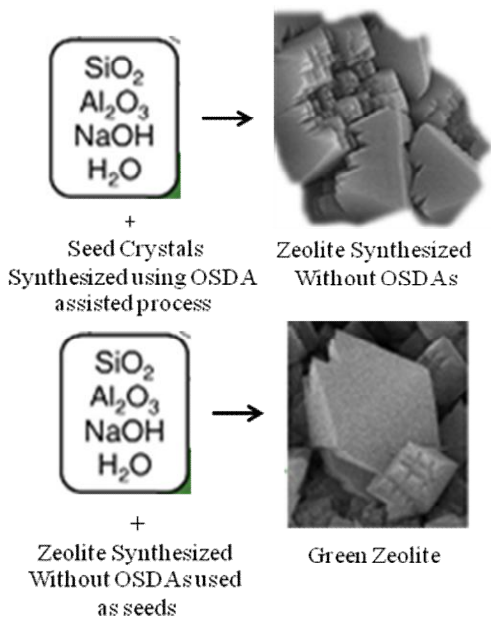
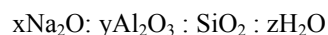


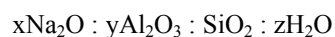
Fig. 3: The concept of “Green Beta”: Completely OSDA-free process^[30]

by adding uncalcined, zeolite beta containing TEA⁺ as seeds with Si/Al ratio 26:1 and 50 nm size to Sodium aluminosilicate gel with the composition of:



Where $x=0.3$, $y=0.01-0.03$ and $z=15$. [22]

Y. Kamimura et. al. were able to synthesize zeolite beta using recycled seeds i.e. seeds produced using seed-assisted OSDA-free synthesis process. This zeolite was given a special name by the authors as “Green Beta” as this provides the basis for completely OSDA-free synthesis of zeolite beta which is economically favorable. The gel composition used in both the first generation and Green Beta synthesis was:



Where $x=0.225-0.35$, $y=0.01-0.025$ and $z=20-25$, while the Si/Al ratio of the seeds were 14-24 and 11-13 respectively.

III. FACTORS AFFECTING THE CRYSTALLIZATION KINETICS

A. Synthesis with the use of OSDAs:

It is observed that the gel SiO₂/Al₂O₃ ratio affects to some extent the crystallization kinetics of the beta zeolite. As the concentration of Al₂O₃ was increased in the gel, the nucleation and crystallization time was marginally increased. It may be noted that, as the aluminum concentration in the gel increases, the incorporation of the silicon in the zeolite framework is more efficient, resulting in a higher yield of zeolite beta. [23] No zeolite beta was obtained in the absence of aluminum.

Most studies may not have employed sufficiently long crystallization time but Gies and Marler reported crystallization time as long as 6 months. [24] OSDA introduced have no effect if the crystallization time is significantly increased. Gies and Marler synthesized pure-silica ZSM-12 using alkali-metal cations in addition to the Silica and organic species. When the ratio of SiO₂/Na₂O = 5, ZSM-12 was crystallized in 7 days at 150°C. If sodium is not added, pure-silica ZSM-12 can be synthesized in 84 days. [25] They also showed that increasing alkali-metal concentration at constant concentrations of OSDA and hydroxide ion shortens the crystallization time necessary for obtaining pure-silica ZSM-12. Thus alkali metal concentration affects the crystallization rate in synthesis process using OSDAs.

B. Seed-assisted OSDA-free synthesis process:

In the seed-assisted OSDA free synthesis of beta, the crystallization rate strongly depends on the SiO₂/Al₂O₃ and Na₂O/SiO₂ ratios in the starting Sodium aluminosilicate gel, although the Si/Al ratio and the quantity of beta seeds are also important factors. Crystallization rate of zeolite Beta rises as the SiO₂/Al₂O₃ and Na₂O/SiO₂ ratios increases. [26] This is mainly due to the increase in concentration of NaOH in the initial reactant gel. At higher SiO₂/Al₂O₃ and Na₂O/SiO₂ ratios, a more –concentrated NaOH solution would accelerate the dissolution of silica sources and as a result, the formation of aluminosilicate precursors and the subsequent crystallization of the beta phase would be facilitated. On the other hand it is also important to mention that with the increasing SiO₂/Al₂O₃ and Na₂O/SiO₂ ratios, the yield of OSDA free beta product decreases. H₂O/SiO₂ ratio has no significant impact on the crystallization of beta phase.

The Si/Al ratio of the seeds also affects the crystallization rate. Longer crystallization time is required as the Si/Al ratio of the seeds decreased. Majano et.al. reported that samples seeded with calcined beta with Si/Al=26 does not yield any crystalline phase. Possible reason theorized is deactivation of crystalline surface by additional condensation of the high silica seeds upon calcination. The amount of TEA⁺ in the seeds and its liberation into the synthesis mixture is negligible to have any impact on the crystallization process.

Quantity of seeds is the factor that affects the crystallization kinetics. With increase in quantity of seeds calculated in terms of wt% of SiO₂ in the initial gel, the crystallization rate increases. The probable reason is highly

active and well-defined crystal surface of the zeolite has better nucleation ability than the OSDA. Similar observations were observed with MTW type zeolites too as reported by Y. Kamimura et. al. [27]

Majano et.al. reported that faster crystallization was achieved by using more reactive, freshly prepared, freeze-dried silica whereas the precursor suspensions prepared with the colloidal silica solution required 3 days more to reach a similar degree of crystallinity.

IV. FACTORS AFFECTING THE SIZE OF CRYSTALS:

A. Synthesis with the use of OSDAs:

Gel H₂O/ SiO₂ ratio affect the size of crystal synthesized. When H₂O/ SiO₂ ratio is increased, the nucleation period and crystallization period increases but larger crystal sizes are obtained. It is interesting to note that dilution level has no effect on the crystal shape.

As the ratio of TEAOH to Al₂O₃ increases from 10 to 30, the crystal size of zeolite beta reduces from about 500 to about 30 nm. [29]

B. Seed-assisted OSDA-free synthesis:

SEM images show that the crystals of seed-assisted OSDA-free synthesis with 1 wt% of seeds were larger and had clearer crystals habits than those synthesized with 10 wt% seeds. [26]. This is possibly because with higher amount of seeds more nucleation sites and as the result the gel mass is distributed to many nuclei and hence donot grow larger.

Y. Kamimura et.al. even reported that the “Green MTW” crystal size was larger than that of the MTW seeds used to prepare them.

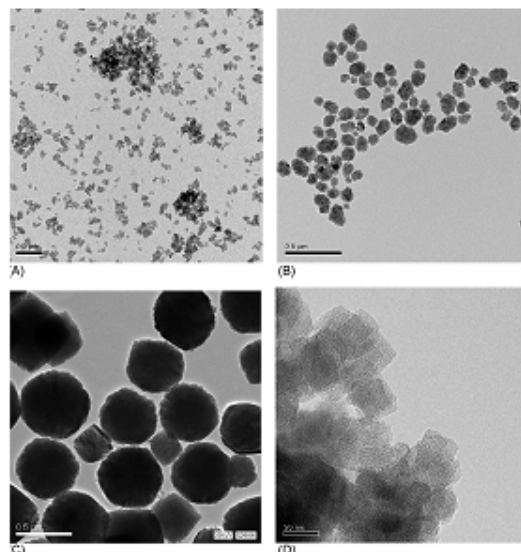


Fig. 4: TEM micrographs of zeolite beta at (A) TEAOH/Al₂O₃= 30; (B) TEAOH/Al₂O₃ = 20; (C) TEAOH/Al₂O₃= 10 (NB-21); (D) amplified clusters of (A). [29]

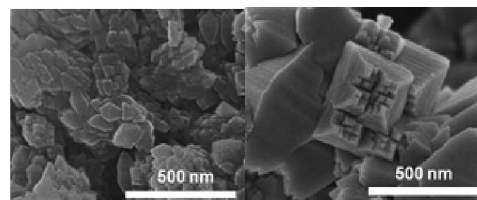


Fig. 5: (a) OSDA-free beta synthesized with 10wt% seeds. (b) OSDA-free beta synthesized with 1% seeds.

V. EFFECTS OF STARTING GEL COMPOSITION:

A. Synthesis with the use of OSDAs:

The gel composition that is the Si/Al, TEA⁺/SiO₂, OH⁻/SiO₂ and Na⁺/SiO₂ ratios have a very important role and have been studied in great depths. S. Gopal et. al. studied the effect of these ratios in the synthesis of ZSM-12 using TEAOH as the OSDA.[20] It was noted that with the ratio of TEA/SiO₂ = 0.245, ZSM-12 crystallized out readily at high Si/Al ratios. But for the gel with Si/Al >= 55, small amounts of zeolite beta impurities appeared. The OH⁻/SiO₂ ratio was varied by addition of sulfuric acid.

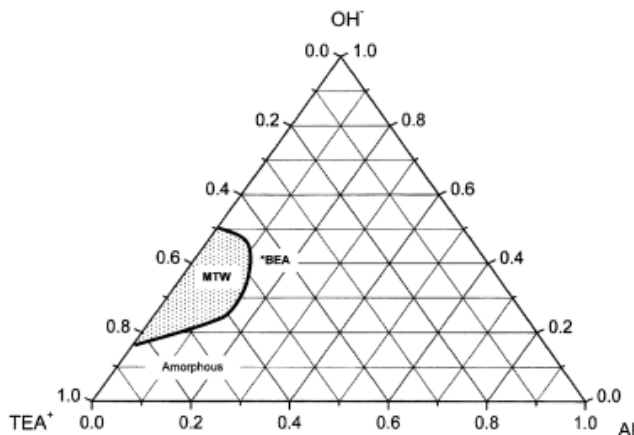


Fig. 6: Ternary phase diagram describing the crystallization domain of ZSM-12 (MTW) as a function of Al, TEA⁺ and OH⁻ concentrations at 160 °C (Na/Al=1; H₂O/SiO₂=13) [20]

With the addition of sulfuric acid, the decrease in pH of the gel was monitored. For OH⁻/SiO₂ of 0.06 pure ZSM-12 phase was obtained. A variation in the gel viscosity with the pH of the gel was also reported by them. A gel with Si/Al ratio of 44 was thick initially and had a pH of 13.9. With the addition of sulfuric acid, the viscosity gradually decreased with the pH around 13.3. Gel properties remained more or less the same on further addition of sulfuric acid till the pH of the gel reached 12.8 after which the viscosity of the gel again started increasing. The optimum range pH for the synthesis was determined to be 13.3. It was even reported that low OSDA concentrations were more favorable for the ZSM-12 formations and that higher TEA⁺/SiO₂ ratios favored formation of zeolite beta. Decreasing the template concentration resulted in the formation of aluminum rich zeolite. Fig.6. Identifies the crystallization domain of ZSM-12 as a function of the Al, OH⁻ and TEA⁺ content of the gel, where the shaded area represents the crystallization of ZSM-12.

S. Gopal et. al. also reported the synthesis of ZSM-12 using TEABr as the template. It was observed that OH⁻/SiO₂ ratio played a critical role in determining the crystallization of the zeolite. The OH⁻/SiO₂ ratio range in which ZSM-12 crystallized using TEABr as the OSDA was narrower as compared to that of synthesis using TEAOH. At low Si/Al ratio and TEA⁺/SiO₂ = 0.245, OH⁻/SiO₂ ratio had to be fixed at very close to 0.07 and slightest variation in yielded amorphous materials. This sensitivity to the OH⁻/SiO₂ ratio was reduced on reducing the TEA⁺/SiO₂ ratio to 0.125 but it still had to be in the region of 0.07. On increasing the Si/Al ratio to 60, the OH⁻/SiO₂ ratio range widened and ZSM-12 crystals were able to crystallize at OH⁻/SiO₂ = 0.11. However at OH⁻/SiO₂ = 0.1, with Si/Al ratio further

increased to higher than 60 resulted in the formation of Cristobalite impurities, which did not appear when the OH⁻/SiO₂ ratio was decreased to 0.08.

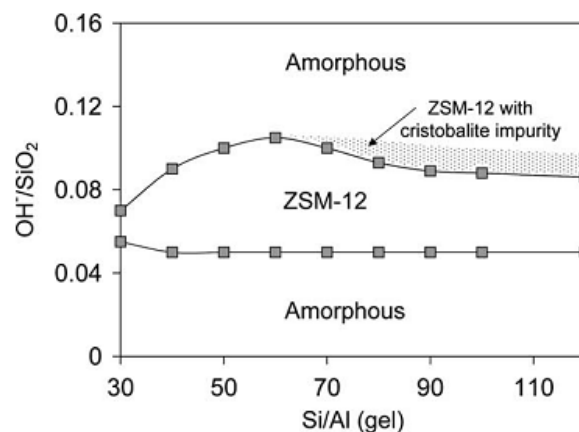


Fig. 7: Phase diagram showing the variation of the boundary for crystallization of pure ZSM-12 phase at different OH⁻/SiO₂ ratios versus gel Si/Al ratios. [31]

The shaded region in Fig.7, just above the boundary for ZSM-12 formation indicates the region in which Cristobalite co-crystallizes in amounts greater than 10% along with ZSM-12. This behavior was uniquely observed only in synthesis using TEABr whereas with TEAOH pure ZSM-12 was obtained at high Si/Al ratios even from gels having OH⁻/SiO₂ ratio of 0.25.

The effect of pH of the gel is very well explained by M.J. Eapen et. al. for the hydrothermal synthesis of zeolite beta [28]

The effect of alkalinity in the synthesis of zeolite beta is shown in Fig.7. At lower $\text{OH}^-/\text{SiO}_2 = 0.6$ as described by the curve 3, the rate of crystallization is very low. Hydroxyl ion concentration is responsible for the dissolution of silicate and aluminate species. A gel with $\text{OH}^-/\text{SiO}_2 = 0.6$ has very low concentration of hydroxyl ions to provide

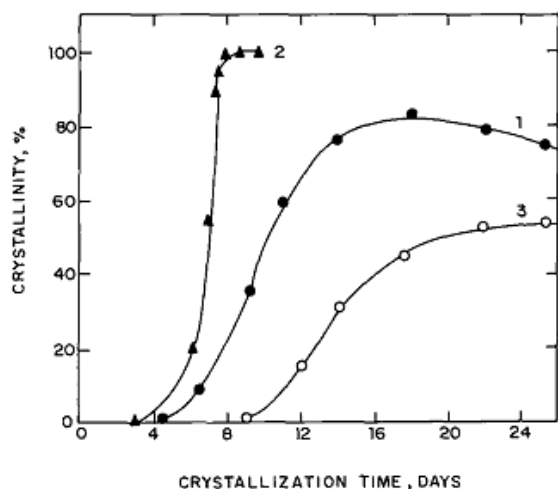


Fig. 8: The influence of OH^-/SiO_2 ratio on crystallization kinetics of zeolite beta: (1) 1.5; (2) 1.0; (3) 0.6. $\text{SiO}_2/\text{Al}_2\text{O}_3 = 35$, $\text{TEA}^+/\text{SiO}_2 = 0.25$ and $\text{H}_2\text{O}/\text{SiO}_2 = 19$ at 413K. [28]

solubilization of silicate and aluminate species to accelerate the rate of crystallization. At $\text{OH}^-/\text{SiO}_2 = 1.0$ (Curve 2), the induction period is shortened and enough solubilized aluminosilicate species available which form nuclei and accelerate the nucleation and hence the crystallization process. However, at a higher alkalinity ($\text{OH}^-/\text{SiO}_2 = 1.5$, curve 1), the hydroxyl concentration is much higher than required. It is theorized that excess OH^- ions probably dissolve the nuclei formed and therefore decrease the rate of nucleation and hence the rate of crystallization at a given temperature (413K).

Thus it is clear that an optimum OH^- concentration in the required for the depolymerization of silica source and to initiate the nucleation process, but not too high to dissolve the nuclei and retard the crystallization.

It is also reported the influence of Na^+ concentration on the rate of crystallization and the product yield. It was stated that gels with Na^+ concentration higher than $\text{Na}_2\text{O}/\text{SiO}_2 = 0.12$ yielded product rich in zeolite beta but also containing ZSM-5 and Mordenite in 13 days, whereas hydrogel with $\text{Na}_2\text{O}/\text{SiO}_2 = 0.08$ yielded pure zeolite beta within 8 days at 413K.

$\text{H}_2\text{O}/\text{SiO}_2$ ratio does not affect the nucleation rate but affects the crystallization rate which has been discussed in detail earlier. The gel Si/Al ratio and the product Si/Al ratio discussion is done later in the paper.

B. Seed-assisted OSDA-free synthesis:

Y Kamimura et.al. synthesized crystalline MTW-type zeolite in a wide range of initial OSDA free sodium aluminosilicate gel compositions: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 60-120$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.1-0.2$ and $\text{H}_2\text{O}/\text{SiO}_2 = 8.25-13.3$ which was wider than the previously reported Lithium, Sodium aluminosilicate gel system. [32-33] It was reported that a high Si/Al ratio (>30) when lithium cation was introduced to the aluminosilicate gels never yielded ZSM-12 but resulted in the co-crystallization of lithium silicates. [32] Suzuki et. al. have elucidated the co-operative effect of sodium and potassium cations on the crystallization of ferrierite in the non-seeded, OSDA-free aluminosilicate system. [34] It was reported that potassium contributed to the formation of building units of ferrierite, while sodium played an important role to complete the crystallization by ordering the building unit of ferrierite. Sodium and lithium cations might have a similar role in the present seeded, OSDA-free sodium aluminosilicate and (lithium, sodium) aluminosilicate gel systems as suggested by Y. Kamimura. [33] The Si/Al ratio of the pure MTW-type zeolite synthesized using the OSDA-free seed assisted synthesis are in the range of 11.7-16.2, and interestingly these values were much lower than OSDA assisted synthesis of ZSM-12 reported earlier. [20,29,31,35] The crystallinity of MTW-type zeolite prepared using the composition of $\text{SiO}_2/\text{Al}_2\text{O}_3 < 40$ and $\text{Na}_2\text{O}/\text{SiO}_2 < 0.15$ led to decrease in crystallinity of the product. For example when the seeded gel composition was $\text{SiO}_2/\text{Al}_2\text{O}_3 = 20$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.1$ and $\text{H}_2\text{O}/\text{SiO}_2 = 10$, the crystallinity of ZSM-12 obtained was only 10%. It was also reported that increase in initial $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the gel resulted in ZSM-12 containing Cristobalite. Ernst et. al. [36] also reported the similar observation for the preparation of ZSM-12 by the hydrothermal treatment at 160°C of sodium aluminosilicate gel containing Methyltriethylammonium bromide (MTEABr) with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 120$, $\text{Na}_2\text{O}/\text{SiO}_2 = 0.1$. Suzuki

TABLE I
Si/Al MOLAR RATIO IN INITIAL GEL, CRYSTALLIZATION TEMPERATURE
AND CRYSTAL SIZE OF ZEOLITE BETA SYNTHESIZED SAMPLE

Sample	Si/Al Ratio	Crystallization Temp. (°C)	Phase obtained	Crystal size (by P-XRD) (nm)
S1	25	80	Amorphous	-
S2	25	100	Amorphous	-
S3	25	120	Amorphous	-
S4	25	140	Crystalline	43.7
S5	25	160	Crystalline	88.4
S6	25	180	Crystalline	119.5
S7	100	80	Amorphous	-
S8	100	100	Amorphous	-
S9	100	120	Amorphous	-
S10	100	140	Crystalline	63.3
S11	100	160	Crystalline	113.6
S12	100	180	Crystalline	145.1

And Hayakawa [37] also reported the occurrence of Cristobalite as impurity when the initial gel is at high SiO₂/Al₂O₃, lower Na₂O/SiO₂ ratios and at higher crystallization temperatures. Ernst et. al. have also suggested that lowering the crystallisation temperature could prevent the formation of Cristobalite. It was also reported that Si/Al ratio of MTW type zeolite with Cristobalite as impurity were in the range of 23.4-33, higher than those of pure MTW type zeolite (Si/Al= 11.7-16.2).

VI. EFFECT OF TEMPERATURE AND CRYSTALLIZATION TIME:

A. Synthesis with the use of OSDAs:

B. Modhera et. al. made a detailed analysis on the effect of temperature on the crystallization of zeolite beta. Fig. 8a and 8b shows the powder XRD patterns of the samples synthesized with Si/Al ratio of 25 and 100. The sharp and broad peaks (fig. 8a) correspond to zeolite beta synthesized at 140°C and higher. The absence of sharp peaks suggests amorphous phase of samples synthesized at temperatures below 140°C i.e. 80°C, 100°C and 120°C. Figure 8b shows the XRD patterns for the samples with Si/Al ratio of 100. The figure again suggests that with crystallization temperatures below 140°C, only amorphous product is obtained. It was further reported by them that the surface area exhibited by the materials synthesized at lower crystallization temperature (lower than 140°C) was much lower and it was typical to the amorphous phase. Whereas

crystals obtained at 140°C and 160 °C had much higher surface areas.

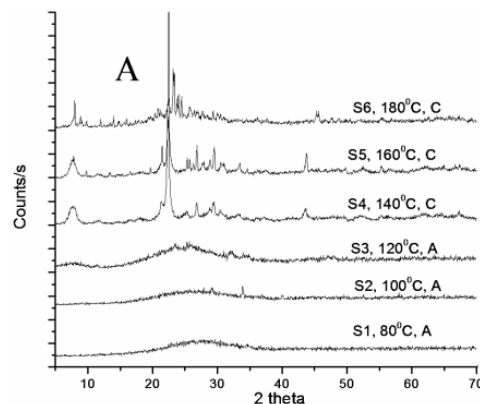


Fig. 9a: XRD patterns of samples with Si/Al= 25

Further, table 1 shows that at constant Si/Al ratio, crystal size increased with increase in crystallization temperature.. Another observation made is that the pore opening increases with crystallization temperature.

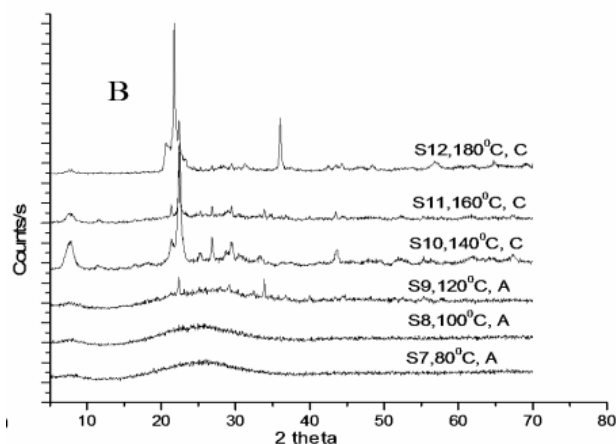


Fig. 9b. XRD pattern of samples with Si/Al=100

B) OSDA free seed assisted synthesis:

H. Zhang et. al. demonstrated synthesis of Beta in the absence of OSDAs, with improved quality at low temperature. Synthesis of Beta crystals with high crystallinity, good thermal stability and large textural parameters at 120°C compared to Beta Zeolite synthesized at 140°C. Further it was reported that synthesis of Beta zeolite at 140°C required 10.3% seeds (with respect to silica content of the initial gel). Y. Kamimura were able to show that lowering the crystallization temperature yielded MTW-type-zeolite but it required longer crystallization period. Product obtained with the initial gel composition of

SiO₂/Al₂O₃=80, Na₂O/SiO₂=0.175 and H₂O/ SiO₂= 11.7 yielded crystalline ZSM-12 crystals in 96 h when the crystallization temperature used was 165°C but, when the crystallization temperature was decreased to 140°C, the crystallization required 20 days to complete.

CONCLUSION

With increase in Al₂O₃ concentration in the gel crystallization time decreases marginally in OSDA-assisted synthesis whereas it increases in the case of OSDA free seed assisted synthesis. Increasing the hydroxide composition favors the dissolution of silica subsequently favors crystallization and reduces the crystallization time. The H₂O/ SiO₂ ratio does not have any significant impact on the crystallization time. In OSDA free seed assisted synthesis, the increase in Si/Al ratio of seeds and the quantity of seeds increases the crystallization rate. In OSDA assisted synthesis, with the increase in the H₂O/SiO₂ ratio crystal size increases while increase in the ratio of TEA⁺/Al₂O₃ reduces the crystal size. In OSDA free synthesis the decrease in amount of seeds produced clearer and larger crystals. Crystal size of Green-Beta and Green-MTW are larger than their seeds. In OSDA-assisted Zeolite beta could not be synthesized below 140°C and at constant Si/Al ratio, with increase in crystallization temperature the crystal size increased. Whereas in OSDA-free seed assisted synthesis Beta crystals with high crystallinity, good thermal stability and large textural parameters are obtained at 120°C compared to Beta Zeolite synthesized at 140°C.

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