

SYNTHESIS OF OMEGA ZEOLITE

Blagica Cekova*, Dragi Kocev and Elena Kolcakovska,
School of chemistry and technology “Maria Curie-Sklodovska”
III Makedonska Udarna Brigada, 1000 Skopje,
Republic of Macedonia

e-mail:cekovab@yahoo.com

ABSTRACT

A new way of synthesis of omega zeolite in absence of tetramethylammonium ions has been found. According to that way of synthesis glycerol is used as a solvent; waterfree aluminosilicate gel is prepared (10 Na₂O Al₂O₃ 13.9 SiO₂ 100 glycerol) and water is added only in small quantities in the prepared gel (11.9% water in the mixture for synthesis). The prepared mixture has crystallized on a temperature of 398K in static conditions for 45 days.

The obtained product has been examined with X-ray diffraction, IR-spectroscopy, SEM method and thermal analysis.

Also we have examined the crystallization curves and the effect of the water in the gel on the synthesized products and the role of the water in formation of the zeolite is also discussed.

INTRODUCTION

Although many zeolites, around seventy up to now, have been synthesized and/or found in nature, studies on framework topology have shown that more other types of structures could exist but have not yet been synthesized. So, the synthesis of zeolites continues to be an ongoing challenge. On the other hand, only a handful of the known zeolites are practically useful at present. They are among those with more open frameworks and larger accessible pores rather than those with dense frameworks. The porous zeolite structures are less stable than the compact ones in the process of zeolite formation, so the former zeolites are considered as kinetic products and the latter as thermodynamic products. Furthermore, it is well known that lower temperature favors the formation of kinetic products and higher temperature favors thermodynamic products. Therefore, synthesis of large porous zeolites seems more promising through low temperature crystallization methods.

I-MATERIALS AND METHODS

The water-free silicoaluminate glycerol gel was prepared as follows: (1) 8.29g of sodium aluminate (54.2% Al₂O₃, 38.5% Na₂O) was added to 405.0g glycerol (99.9%) in a 500 ml beaker at ~ 180°C by stirring the mixture, water vapor was expelled and a suspended mixture was obtained; (2) at ~ 180°C and under stirring, 31.49g of sodium hydroxide pellets(>99.0%;calculated as 100%) were added to the mixture prepared above; violent vaporization was observed at the beginning and a clear (light yellow) solution shortly appeared; (3) the hot solution was cooled down and kept at ~ 120°C; 39.63g of precipitated silica (extra pure, 92.8% SiO₂) was added to the solution little by little under slow stirring; a homogeneous water-free gel-like viscous mixture (10.0 Na₂O - 1.00 Al₂O₃ - 13.9 SiO₂ - 100.0 glycerol) was finally obtained after 25 minutes stirring.

The crystallization mixture was prepared ~ 50°C and under manual stirring by adding 27.00g of distilled water to 200.0g of the first prepared water-free silicoaluminate glycerol gel. The water content, $W_{\text{water}}/(W_{\text{water}}+W_{\text{water-free gel}})=11.9$ wt% in the final synthesis mixture, was used for standard synthesis; mixtures with water content of 0.0 wt%, 5.1 wt%, 9.1 wt%, 16.7 wt%, 33.3 wt% and 50.0 wt% were also tested in separate synthesis. Crystallization took place in sealed stainless steel reactors (~ 20.00 g synthesis mixtures in a ~ 40 ml reactor) at $125\pm 2^\circ\text{C}$, without stirring and under autogenous pressure. After the fixed period of crystallization, e.g. 45 days, the reactor was withdrawn from the oven. A light yellow clear solution appeared above white slurry when the crystallization process was stopped. The solid products were recovered from the crystallized mixtures by filtration, washed with distilled water (until PH~ 9.0) and dried in 180°C oven for one day.

Characterization

The synthesized products were examined by X-ray diffraction, scanning electron microscopy, infrared spectra and thermal analysis.

Results and discussion

Characterization of the synthesized omega zeolite

The X-ray powder diffraction (XRD) pattern of the product obtained from standard synthesis mixture after 45 days crystallization at 120°C is shown in Fig.1. By comparing this XRD pattern with those of known zeolites, the product was identified as omega zeolite, and found free from any other crystallized phases. The scanning electronic microscopy (SEM) photograph of the product is presented in Fig.2. It can be observed that the product is free from amorphous materials and its morphology appears to be spherulitic agglomerates of 30-40 μm diameters. The IR spectra of the product (Fig.3) indicate the same characteristic bands in the range of $1300\text{-}300\text{ cm}^{-1}$ as omega zeolite.

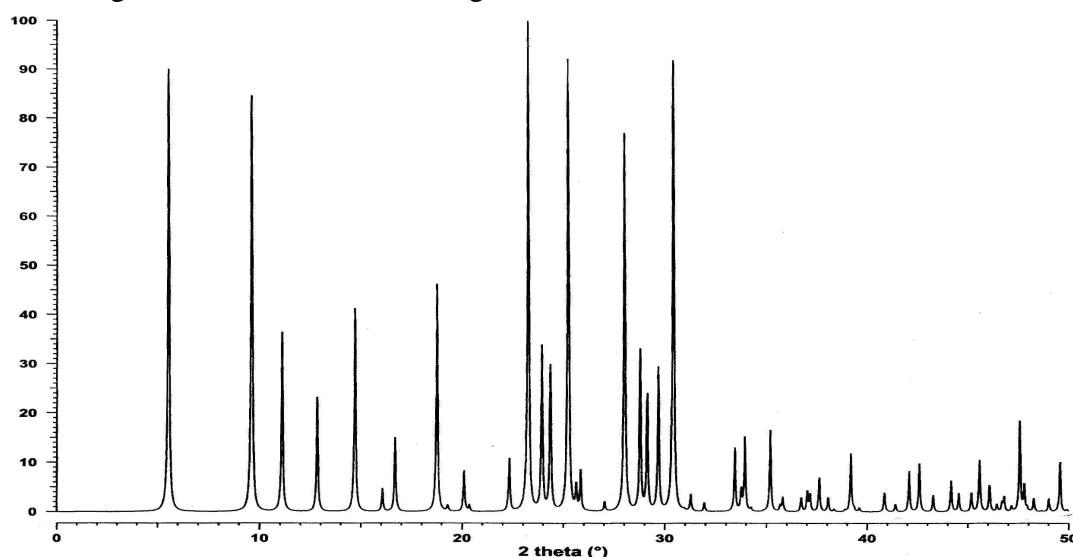


Fig.1 XRD pattern of omega zeolite crystallized from standard synthesis mixture (11.9 wt% of water) at 120°C and under static condition for 45 days

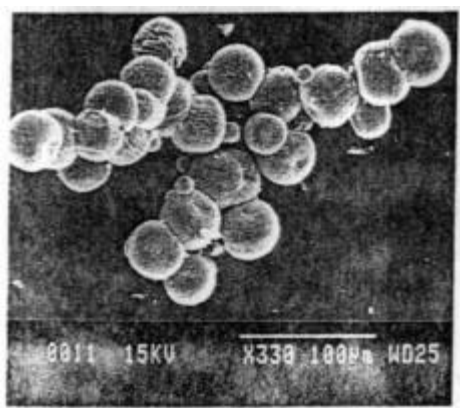


Fig.2 SEM of omega zeolite

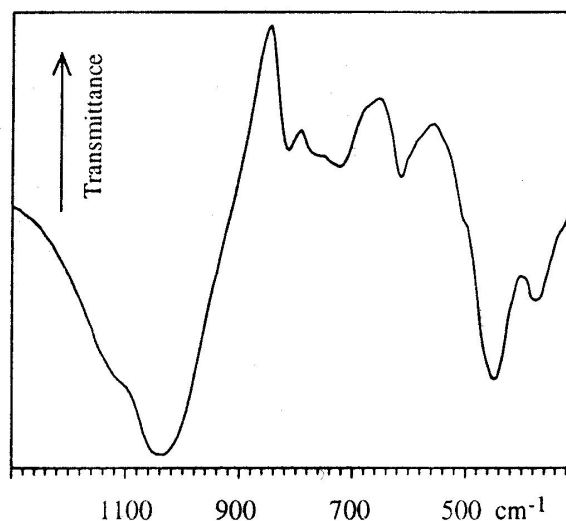


Fig.3 IR spectra of omega zeolite

The chemical composition of the solid product is: 58.1 wt% of SiO₂, 13.8 wt% of Al₂O₃, 9.2 wt% of Na₂O, 11.0 wt% of H₂O and 7.5 wt% of organic species; yield on SiO₂ is 46.5%, Al₂O₃ 60.2%; mole ratio of SiO₂/Al₂O₃ is 7.2 and Na₂O/Al₂O₃ 1.10. It was noticed that the mole ratio of Na₂O/Al₂O₃ was higher than the expected value, 1.00. By grinding and re-washing the product with hot water, 0.8 wt% of Na₂O was removed away from the product, and then the mole ratio of Na₂O/Al₂O₃ in the re-washed product became 1.00. In the re-washed product, 12.0 wt% of H₂O and 5.5 wt% of organic species were found. This may suggest: (1) some extra sodium ions which do not act as counter ions for the zeolitic framework are trapped in the agglomerates and could not be washed out easily before smashing the grain-like omega zeolite; (2) some organic species are removed also by re-washing the product.

The thermal analysis results of the re-washed product, see Fig.4, demonstrate: (1) the sample has two stages of weight loss; the first one (50-330°C) is likely due to the gradual loss of water while the second one (330-420°C) is due to the loss of glycerol-related organic species, (2) the combustion of the organic species takes place at ~380°C, (3) there is no heat uptake in the first stage of weight loss (a matter for further investigation).

It was claimed that the high temperature (~560°C) required for driving the trapped TMA out of omega zeolite was possibly responsible for destroying part of the zeolitic structure and thereby rendering fragile the whole of the structure. It is very interesting to notice that although the combustion temperature of the trapped organic species in the omega zeolite synthesized through this new route is rather low, the thermal stability shows no difference from that of TMA-omega zeolite. This may suggest that the low break-down temperature of omega zeolite may be due to other factors, such as its intrinsic framework topology, crystal size and crystal defects.

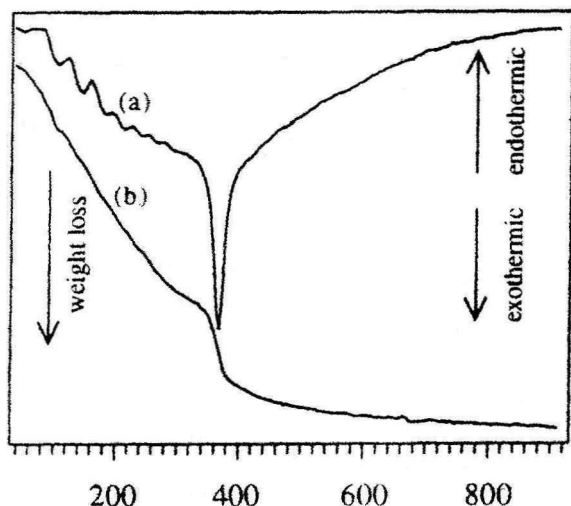


Fig.4 (a) TG and (b) DTA of omega zeolite (after being re-washed)

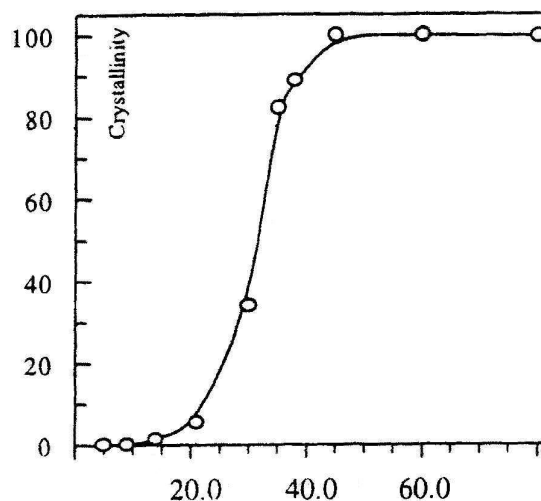


Fig.5 Crystallization curve of omega zeolite from standard synthesis mixture

The course of the crystallization

The crystallization course of the standard mixture is shown in Fig.5. After about 14 days of crystallization, omega zeolite appears in the product. From 21 to 40 days of crystallization, the crystallinity of the product increases sharply; the crystallinity approaches ~ 100% after about 45 days of crystallization. During the prolonged period of crystallization, up to 80 days, the crystallinity shows no change and no any other crystallized phases are found in the products, see Fig.5. This suggests that the omega zeolite in this synthesis is rather stable and its pure phase can be readily produced. The course of the crystallization shown in Fig.5 falls into the category of general crystallization pattern of zeolities, i.e. a fast growth of crystallinity follows an induction period and then the crystallinity reaches the maximum value, an “S” shape crystallization curve.

Synthesis with different water contents in the crystallization mixture

With water contents lower than 11.9 wt% (i.e. in the standard mixture), omega zeolite is not formed or it is formed very slowly; with water contents higher than 11.9 wt%, another zeolite phase, analcime, competes with omega zeolite and with higher water contents, analcime becomes the only phase in the products. Both higher water content in the synthesis mixture and longer crystallization time favor the larger portion of analcime phase in product. Omega zeolite which has a more porous framework structure than analcime is expected to be the metastable phase in synthesis, but apparently the metastability of omega zeolite over analcime can be observed only when the crystallization mixture contains high water content. It seems that in order to get pure omega zeolite the water content in the synthesis mixture needs to be controlled within the narrow region of 9.1 to 11.9 wt%. The repeated synthesis of the standard synthesis mixtures indicated that pure omega zeolite could be readily obtained through this new synthesis route but both the induction time and the crystallization time might be slightly different from time to time.

The effects of different water contents in the crystallization mixtures on the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of the products (around 6-7 except the 10.6 obtained from water-free

synthesis mixture) are not manifest. With increase of water contents from 5.1 wt% to 11.9 wt% in the crystallization mixture, the yields of the products have no significant change; but the yields decrease considerably with further increase of the water contents in the synthesis mixtures. Possibly this is because the significant increase of water contents (after 11.9 wt %) in the synthesis mixture leads to dissolve more aluminosilicate in liquid from gel.

CONCLUSION

During the formation of a zeolite the cations (inorganic and/or organic) in synthesis mixture not only play a role of providing counter charges for balancing the excess negative charges of the zeolite framework to be formed, but also have a structure-directing role as is well documented. Certain organic molecules, like various amines, alcohols and others were also considered to have a structure-directing role. However, the structure-directing mechanism in zeolite synthesis has not been well established yet. Within an as-synthesized zeolite, besides framework and cations (and organic molecules if used as template), the rest pore space of the zeolite is not free but occupied by solvent molecules, such as H₂O in hydrothermal synthesis. What draws our attention is the role of water in formation of zeolites.

In a sense water is not only acting as a solvent in hydrothermal synthesis but also can be considered as part of the as-synthesized zeolite because of its presence in the pores and channels. Compared with other parts of as-synthesized zeolite, water is less strongly held, but it does help stabilizing and therefore possibly structuring the synthesized zeolite. This follows from the following well-known facts: (1) dehydrated zeolite shows strong tendency to regain water, this indicates the removal of water from as-synthesized zeolite makes it less stable; (2) complete dehydration of a zeolite may cause collapse of its structure. As a matter of fact, the water is usually regarded only as solvent, so its role on formation of zeolite has rarely been studied.

In hydrothermal synthesis water is used as the only solvent which is supposed to be in large excess. Investigation about the effect of water on formation of zeolite would be difficult to explore if water content in crystallization mixture can not be adjusted over a wide range. With use of another solvent, however, change of water content in a large range becomes possible. The synthesis data in this paper demonstrate that water can play a significant role on the structure of the formed zeolite and the rate of crystallization.

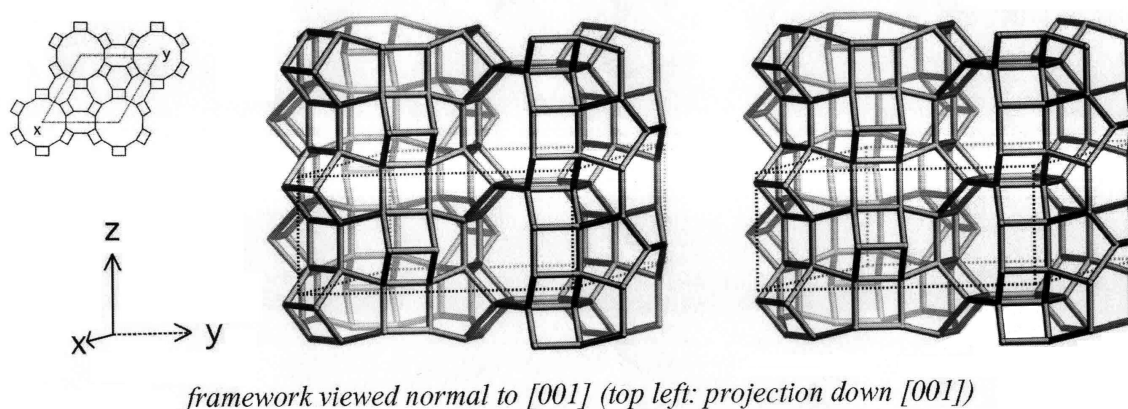


Fig.6. Framework of a Zeolite

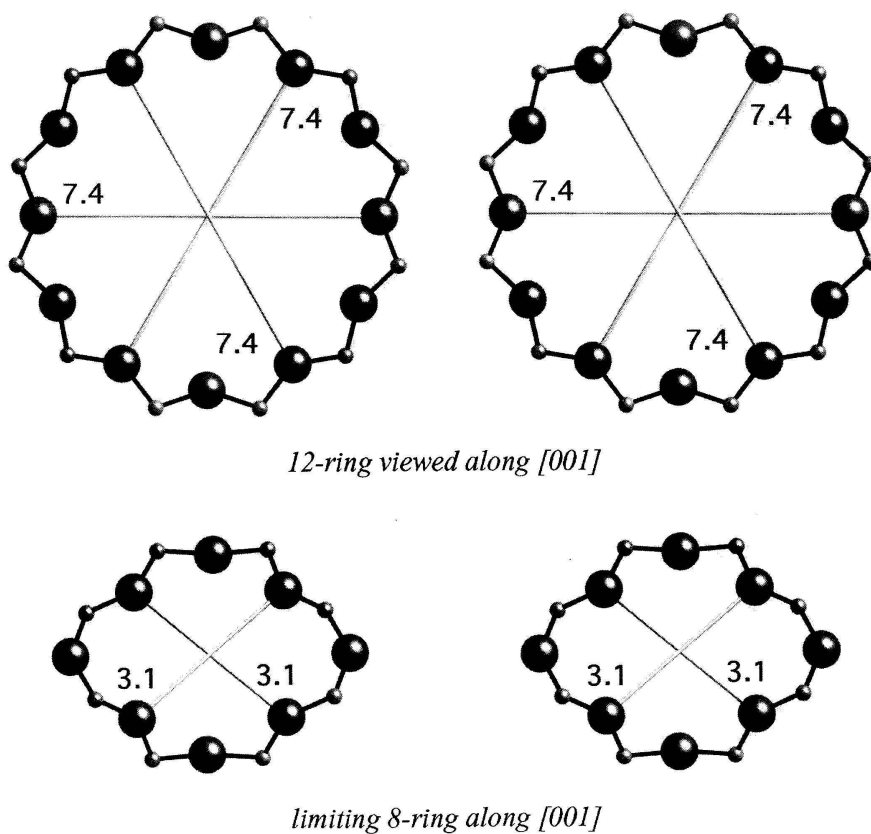


Fig 7.The ring structure of a Zeolite

REFERENCES

1. R.M. Barrer, *The Hydrothermal Chemistry of Zeolites*, Academic press, London, 1983.
2. W.M. Meier and D.H. Olson, *Atlas of Zeolite Structure Types*, Butterworth, London, 1987.
3. B.Cekova and all., MK patent 900649A