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Research Paper

Synthetic Zeolites- Structure Properties and Application Area

Chemistry

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ABSTRACT

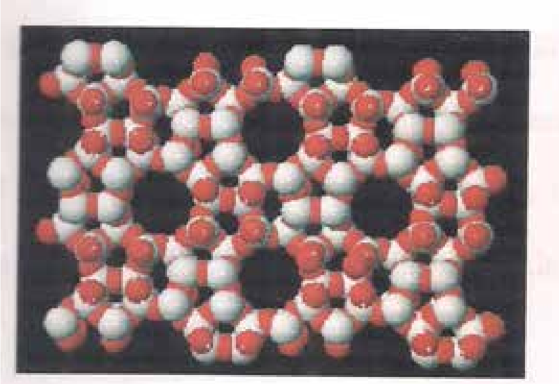
The synthesis of zeolites their properties & applications, due to their unique porous properties they have attracted the attention of many researchers, major user of zeolites in the field of ion exchange, ammonia removal, water softing, adsorption is the also main uses. The purpose of this paper synthesis of zeolites & their structure. The study is focused on the application of the zeolites in various fields.

3-Introduction-

Identification of Zeolite as a mineral goes back to 1756, when a swedish mineralogist, fredish cronstedt, He observed that upon rapidly heating a large amount of steam was obtained [1]. Thus, this material was named "Zeolite" from the greek words meaning "boiling stones" , that is , because of ability to froth when heated to about 200^0C. After their discovery Zeolites are considered as separate group of minerals found in volcanic rocks for a period of hundred years. Natural Zeolites are found as a result of chemical reactions of the volcanic ash and alkaline water a few thousand millennia ago. They have been used in various parts of the world for centuries.

4. Structure and Properties

Zeolites are crystalline, micro-porous, hydrated alum-silicate minerals that contain alkali and alkaline earth metals. Their frameworks are composed of $[SiO^4]^{4-}$ and $[AlO^4]^{5-}$ tetrahedra, which corner share to form different open structures. The tetrahedra are linked together to form cages connected by pore openings of definite sizes. The pore size range from 0.3-1 nm [2]. The negative charge on the lattice is neutralized by the positive charge of the cations located within the material's pores. Each AlO_4 tetrahedron in the framework bears a net negative charge which is balanced by additional nonframe work cations like sodium $[Na^+]$, potassium $[K^+]$, or $[Ca^{2+]}$ These univalent and/or bivalent metal cations may be replaced via ion-exchange to other ions. Because of electrostatic forces it is not possible to make an Al-O-Al bond. They are made up of "T- atoms" which are tetrahedrally bonded to each other with oxygen bridges. Other "T- atoms" such as P, Ga, Ge, B and Be can also exist in the framework. A general formula for a zeolite can be written as: $\mathbf{M_{2/n}:Al_2O_3:xSiO_2:yH_2O}$, where M is the charge balance cation, n – the charge of the cation, x is generally ≥2, and y is the water in the voids of the zeolites [3]. More than 50 natural zeolites are discovered, six of them in large deposits: analcime, chabazite, clinoptilolite, heulandite, natrolite, phillipsite, and stilbite .



5- Zeolite synthesis -

The synthesis zeolites are used commercially more often than natural zeolites due to purity of crystalline products and the uniformity of particle sizes. the sources for early synthesized zeolites were standard chemical reagents.much of the study of basic zeolite science was done on natural zeolites. the main advantages of synthetic zeolites in comparison to naturally occurring zeolites are that they can be engineered with a wide variety of chemical properties and pore sizes and that they have greater thermal stability .The zeolite synthesis involves the hydrothermal crystallization of aluminosilicate gels (formed upon mixing an aluminate and silica solution in the presence of alkali, hydroxides and / or organic bases) or solutions in a basic environment .the crystallization is in a closed hydrothermal system at increasing temperature ,autogenous pressure and varying time (few hours to several days) . The type of the zeolite is affected by the following factors [4-6].

Composition of the reaction mixture (silica to alumina ratio; OH; inorganic cations).

1- Increasing the Si/Al ratio strongly affects physical properties of zeolites
2- OH modifies the nucleation time by influencing transport of silicates from the solid phase to solution .
3- inorganic cations acts as structure directing agents and balance the frame work charge. they affect the crystal purity and product yield.
4- Nature of reactants and theis pretreatments. the zeolite synthesis is carried out with inorganic as well as organic precursors. the inorganic precursors yielded more hydroxylated surfaces whereas the organic precursors easily incorporated the metals into the network.
5- Temperature of the process. the rate of crystallization is directly proportional to temperature while the rate of nucleation is inversely proportional to temperature.
6- Reaction time crystallization parameter must be adjusted to minimize the production of the other phases while also minimizing the time needed to obtain the desired crystalline phase.
7- P^H of reaction mixture. The process of zeolitezation is carried out in alkaline medium (pH>10)
8- other factor the synthesis can carried out on a continuous or semi continuous mode , which enhances the capacity , making it compatible for industrial applications.

Applications.

1-Water softening -

The largest commercial market of synthetic zeolites, estimated of about 1.3 million tons per annum is as water softening "buildes" in detergent for Formulations.In 1973 the German company "Henkel" patented Formulation incorporating zeolite NaA as a water softener [7]. In 1978 "procter and Gamble" introduced zeolite NaA in its laundry detergents [8], and nowadays, most of the commercial washing powders contain zeolite, instead of harmful phosphates, banned in many parts of the world because of the risk of water eutrophication [9]. since detagents ingredients have to be pure, synthetic zeolite obtained from chemical regents on high grade natural row materials are commonly used for this purpose, Nevertheless, some recent studies have demonstrated that some waste- derived zeolites, obtained by appropriate technology ,could compete the commercial products in this applications for example, hui and chao [10] succeeded to obtain single-phase zeolite 4A (NaA) sample in pure form with a high crystallinity (up to 95%) by applying step- change of synthesis temperature during Ht treatment of CFA. the calcium binding capacity of these zeolite 4A samples and the commercial detergent grade zeolite 4A (valfor 100) were tested for usage as a detergent builder (see table 1) the select show that

Table-1 Ca^{2+} sorption properties of commercial & CFA derived NaA according [10]

Zeolite	Zeolite origin	Ca2+ conc, mg 1-1	Ca2+ sorption, mg g-1	Ca2+ , removal %
NaA	Commercial	40	40	100
NaA	CFA derived	40	37-41	100
NaA	Commercial	80	76	100
NaA	CFA-derived	80	57-75	82-94

4- Ammonia removal

The removal of ammonia by natural zeolitic materials was widely investigated in the last few decades and the most important results were reviewed in several papers [11-13,14,15]. They indicate that clinoptilolite and mordenite are the most effective natural zeolite for ammonia removal [16,17,18,19,20], due to their high selectivity for ammonium ion in the presence of competing cations (such as K^+, Ca^{2+} and Mg^2+), across a wide range of NH_4^+ concentration [20].

The actual ammonia adsorption capacity and efficiency of NH_4^+ removal process depend upon the type of zeolite used, contact time, initial concentration of ammonia, temperature, the amount of zeolite loading, its particle size and presence of competitive ions [14,15]. The influence of thesefactors has been discussed in several researches on the kinetics and equilibrium of ammonia sorption from model solutions or real effluents [21,22,20,23,24,25-27,28]. Summarized experimental data for the ammonia adsorption performance of some natural and synthetic zeolites are presented in table 2.

Table-2 ammonia adsorption on some natural & synthetic zeolites

Zeolite	Zeolite origin	$NH_4^+{}_{conc}$ mg1^{-1}	Zolite dosage	NH_4^+ Sorption mg g^{-g}	NH_4^+ Removal %	References
Clinoptilolite	New Zealand	10-200	10	1.3-11.9	98-46	20
Clinoptiolite	Modified with Nacl	121	2.5	18.3	29	21
Clinoptiolite	USA	5.4		18.4	61	17
Heulandit +mordenite	Turkey	60	10		80	25
NaY	RHA-derived	50	2.5	42.7	71	28

5-Ion exchange-

Zeolite with a negative charge provides an ideal trap for positive cations such as sodium, potassium, barium and calcium and positively charged groups such as water and ammonia both carbonate and nitrate ions are attracted by the negative charge within zeolites. therefore alkali and soil alkali metallic cations are attracted in the some way and water can be absorbed by zeolite [29] Absorbed cations are relatively mobile due to their weak attraction and can be replaced using the standard ion exchange techniques, making zeolites good ion exchangers .

6- Heavy metals removal –

Heavy metals are generally considered to be those whose density exceeds 5g cm^{-3} [30]. A large number of elements fall into this category,but the ones of relevance in the environmental context are Cd,Cr,Cu,Ni,Zn,Pb and hg[30].heavy metals are well known with their toxicity. zeolites have beed widely explored for heavy metals immobilization form natural or industrial water. some of those concerning the application of natural zeolites for heavy metals removal have been reviewed in [13] .if is known that the immobilization of heavy metals ions from aqueous solutions by zeolites is quite a complicated process,consisting of ion exchange & adsorption and is likely to be accompanied by precipitation of metal hydroxide complexes on active sites of the particle surface.

Similarly to the sorption of ammonia, the heavy metal cations removal efficiency depends upon the type ,dose and grain size of zeolite used ,contact time ,pH, temperature, initial metal concentration and to a significant extent to the presence of competitive ions , Experimental data for the sorption of heavy metal contains by natural & synthetic zeolites are presented in table 3 summarizes data for cation exchange selectivity of heavy metal ions on natural and synthetic zeolites.

Table-3 heavy metal adsorption on some natured and synthetic zeolites .

Metal ions	Zeolite	Zeolite origin	Metalconc. mg1^{-1}	Zeolite dosage G1^{-1}	Met-al sorption Mg g^{-1}	Metal removal	Reference
Ag^+	Clinoptiolite	Bulgaria	500	5	32.2	43	[31]
Ag^+	Beneficiated	USA	1072	4		94-96	[32]
Ag^+	Beneficiated mordenites	USA	1072	4		38-75	[32]
Cr^{3+}	Naturalscolecite	Brazil	50-250	17	3.0-14.5	100-96	[33]
Cr^{3+}	Clinoptiolite	Greece	100	10	4.1		[34]
Cu^{2+}	Heulandite	Ecuador	635		3.9		[35]

7- Conclusion—on the base of the reviewed publication it concluded that, due to their unique properties, zeolites have a great potential as effective sorbent materials for a lagre number of water treatment applications , such as water softening ,ammonia removal, removal of heavy metals ,ion exchange and many others.

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