

THE NEW SYNTHESIS OF POTASSIUM-EXCHANGE ZEOLITE A

Amal N. Al-Mumaiz, Jalil R. Ugal^{*}, and Nada S. Ahmed

Chemical Engineering Department – College of Engineering – University of Baghdad – Iraq

^{*} Al-Basil State Company

ABSTRACT

A process of ion exchange was used to prepare the potassium-exchanged zeolite A using the sodium form of zeolite A (locally manufactured) and 1N KCl solution. Shaping of the prepared zeolite in the form of cylindrical particles 2.5 mm in diameter, 4-8 mm long, was carried out using kaolin clay as a binder. Different physical and mechanical properties (such as porosity bulk density, pore volume, crushing strength, loss on attrition and the adsorption capacity) were examined to specify the suitable weight percent of the binder which offer good mechanical properties for the agglomerates with appreciable physical properties. It was concluded that, a percentage of 25% kaolin was the optimum percentage.

INTRODUCTION

Zeolite molecular sieves being of growing importance, have made significant inroads in the processes of purification as general and the adsorption separation processes on particular. It is the benefaction of these materials to have an ordered aperture size for which they can separate molecules based upon size and configuration with a selectivity that is not found in other solid adsorbents (Othmer, 1981; Vanghan, 1988).

All zeolites have a high affinity for water and other polar molecules and could be used for drying gases and liquids. However, in many instances, secondary reactions such as polymerization of a coadsorbed olefin may take place. This is avoided by using the potassium – exchanged form of zeolite A, also termed 3A, for the removal of water from unsaturated hydrocarbon streams including ethylene (Otto, 1962). These minute pores (3Å) permit only water to be adsorbed since reaction materials cannot reach the adsorbent surface. Zeolite 3A had pushed activated alumina away from ethylene plants (particularly in the drying of the gas from the pyrolysis furnace containing a mixture of H₂ plus C₂ to C₁₀ olefins, paraffins and acetylenes), it'd offered advantages for this service, such as, using two-bed unit instead of three with reduction in size, and the recovery of a fraction of olefins which was coadsorbed in the alumina units and lost in the plant fuel header on regeneration (Davis & Manchanda, 1974).

The drying of ethanol (window size of 0.45 nm) is best carried out using this zeolite. Water molecules can pass through the crystal cavity

while ethanol molecules are excluded. This reflects the molecular sieving effect of zeolites (Crittenden and Thomas 1998).

EXPERIMENTAL WORK

Preparation was accomplished using zeolite 4A synthesized in the factory of catalysts of Al-Basil Company, while the kaolin clay was brought from Al-Ga'a ra area of western Iraq. Chemical analysis for both above mentioned materials were made in Ibn-Sina Company, and listed in Table(1). The process of cation exchange in the zeolite family is well known to be temperature dependent (Breck 1974), so high temperatures were tried. The concentration of the salt solution was the most affecting parameter for appreciable degree of exchange. (Zeki 2000) so, various experiments were tried, each time the degree of exchange was examined by analyzing for the Na₂O (residual or left) in the prepared zeolite, compared with the original percentage of Na₂O present in zeolite 4A. This analysis, based on weight percent, was made in the Geological Survey and mining Company Table (2). Each experiment, 25 g of zeolite 4A were mixed with 200 ml of KCl solution in a round bottom flask and placed in a shaker water bath (Type GFL, F. G. BODE & Co. Hamburg 60) which provides an excellent control on temperature during the experiment time. The prepared was agglomerated in the form of cylindrical pellets 2.5 mm in diameter and 4-8 mm long, by pressing the zeolite- kaolin paste manually into a cylindrical cavity. There was some difficulty in this step. It was that, when the

paste was compressed through the die, it turned into liquid and the pellets did not keep their shape. So it was impossible to make pellets with 10% kaolin, as was previously planned to try (10,20,25,30) wt%. More binder was added (to the sample of 10%) until the 14% kaolin was sufficient to make a moldable paste. This behavior was due to the lack of plasticity, which is greatly dependent on the cation present in the zeolite (Searle and Grimshaw 1959 ; Hammon 1986). The next steps were, drying (at 120 °C for two hours) (Minachave 1973 and Bashir 1997);and calcination at 650 °C for two hours (Drost 1966 and Mahdi 1997). Then characterization of the new adsorbent was made by the measurement of the important physical and mechanical properties.

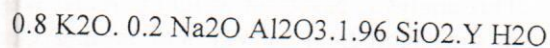
RESULTS AND DISCUSSION

Preparation step

It was concluded by examining the results shown on Table (2) for the preparation step, that increasing the temperature and time of contact had increased the extent of exchange but this increase was small and was not enough to obtain a 75% exchange as was recommended. The increasing of the concentration of the salt solution had a better effect on the exchange within the crystal lattice. An 80% exchange was obtained by the following conditions :

A temperature of 94 °C , concentration of 1N for KCl solution, and time of 8 hours. The ratio of SiO₂ to Al₂O₃ is calculated in mole ratio by the aid of the data given in Table (1),and it was found equal to 1.96. Broussard and Shoemaker(1960) had found this ratio equal to 2 for zeolite type A. it is a characteristic value for certain type of zeolite

According to this result, the structure formula is identified as



An X-ray structural analysis was made to the prepared zeolite and its pattern is given by Fig (9), and by comparing it with the standard pattern which is shown in Fig(10), it was concluded that the prepared zeolite is of good crystallinity except for slight changes which attributed to the standard pattern that was taken for a sample with 100% exchange (Reed and Breck,1956).

Agglomeration step

Water content for the prepared agglomerates differs according to the amount of binder added .There is always an optimum amount of water that makes a moldable paste depending on the physical and chemical nature of the binder. It was found by examining Fig(1) that this amount decreases as the amount of kaolin increases.

Physical properties

Binders are well known to offer mechanical strength to the agglomerates but causes to decrease the physical properties for they acts as dilluents (Haden 1963; Breck 1974) .So the addition of kaolin clay was found to decrease the porosity Fig(2),pore volume Fig(3) and, the adsorption capacity for water vapor Fig(4).This is attributed to the decrease in the porous media and in the amount of micropores originally present in the zeolite , therefore the internal area would be decreased. This may be due to the blockage of the micropores resulting from the sintering of fines and the combination of semi-molten impurities during the thermal treatment of the clay. Sintering occurs when many crystals grow markedly in size without any change in crystallographic type. So each initial particle merges with its neighbors and the spaces between particles progressively decrease and finally disappear. (Searle and Grimshaw 1959). Then the void spaces between the sintering crystallites vanish and an increase in the density of the impact is predicted. The addition of kaolin clay leads to increase particle (bulk)densities, see Fig(5). This increase is by making solid bridges and interlocking bonds of different mechanisms. The change in the physical properties is greatly affected by the shrinkage that occurs in clays during drying and calcination. It is defined as the reduction in volume of the structure because of the loss of large amount of surface water through evaporation, and is greatly increased at the initial rate of drying when the moisture content is high. Fig(6) demonstrates that the adsorption isotherm for water vapor is of type I classification that is favorable to adsorption (as do most zeolites) and posses a saturation limit corresponding to complete filling.(Breck 1974).

Mechanical properties

Prepared adsorbents of different catalysts gain a sufficient mechanical strength when mixed with an inert binder. The increase of this property is obvious by examining Fig(7) and Fig(8), for the diametrical (radial) crushing strength is increased and the weight lost by attrition is decreased as more binder is added. Zeolite particles are held together by strong bonds resulting from sintering of minor clay particles and the dissolution of solid material which becomes concentrated during the course of drying by forming solid bridges and held the parent particles together forming a dense packing, all these functions will lead to valuable mechanical properties for a pellet at a given condition. However, this will cause reduction in the physical properties. So one can see that pellets with high crushing strength and attrition resistance, have low porosity, pore volume and eventually low adsorption capacity, which is the most effective property for the prepared adsorbents in the present work. Thus one must compromise the results.

Sample optimization was made by selecting a sample of appreciable porosity, pore volume, maximum adsorption capacity, good strength and attrition resistance. Thus samples containing 25% kaolin were found to have the most preferable properties.

CONCLUSIONS

The following conclusions were deduced from the present study:

1. Zeolite 3A was prepared by an ion exchange process using zeolite 4A and KCl solution, and it was found that a temperature of 94°C and time of mixing of 8 hours with 1N KCl solution, were suitable to obtain an exchange of 80%.
2. Agglomerates with low binder content (14 % kaolin) were found to have high physical properties such as, porosity, pore volume and adsorption capacity.
3. Agglomerates with high binder content (30 % kaolin) were found to have good mechanical properties such as, crushing strength and attrition resistance.
4. The best sample was selected with appreciable physical and mechanical properties and was the sample containing 25 % kaolin as a binder.

REFERENCES

- Bashir B.N. "Preparation Of Zeolite-Binder Agglomerates From Locally Available Raw Materials As Cylindrical Pellets" Thesis Of M.Sc. Univ. Of Baghdad (1997).
- Breck D.W. "Zeolite Molecular Sieves Structure Chemistry and Use", John Wiley and Sons. New York (1974).
- Broussard L. and Shoemaker D.P., "The Structures Of Synthetic Molecular Sieves", J. Of Am. Chem.Soc. , 82,1041 (1960).
- Crittenden B.D. and Thomas W.J "Adsorption Technology and Design"; Butterworth - Heinemann, Oxford (1998).
- Davis K. and Manchanda "Drying of gases and liquids/ Unit operations for drying fluids" U.Carbid Company ,Chem. Eng., Sep;16,1974.
- Drost W. ,Union Carbide Corp. Chem. Abs., (3396b),65(1966).
- HadenW.L., Metuchen and Dzierzanowski F.J., "Method for producing Synthetic Crystalline Aggregates", U.S. Patent 3,100,684 (1963).
- Hammon U. and Kottor M., "Preparation of Pellets With Well-Defined Pore Structure", Int. Chem. Eng., Vol.26,4,(1986).
- Mahdi A.S., "Preparation Of Zeolite-Binder Agglomerates From Locally Available Raw Materials As Spherical Particles", Thesis Of M. Sc. Univ. Of Baghdad (1997).
- Minachave K.M.,Chem. Abs. (149973),79,(1973).
- Othmer K., "Encyclopedia of Chemical Technology", Vol. 15 (1981).
- Otto et al, Chem. Abs. (2909c),56,(1962).
- Reed T.B. and Breck D.W., "Crystal Structure Of Synthetic Zeolite Type A", J. Am.Chem. Soc.78, 5872(1956).
- Searle A.B. and Grimshaw R.W, "The Chemistry and Physics Of Clay And Other Ceramic Materials". 3rd Ed., Interscience Publisher Inc., New York (1959).
- Vanghan D.E.,Chem. Eng. Prog.,84,2,(1988).
- Zeki N.S.A., "Preparation of Zeolites 3A and 5A (From Locally Available Raw Materials)And Their Extrusion With Different Binders", A Thesis of M. Sc., Univ. Of Baghdad (2000).

Table (1) Chemical analysis of zeolite 4A and kaolin

Constituent	Weight % Zeolite 4A	Weight % Kaolin
SiO ₂	35.90	50.1
Al ₂ O ₃	31.19	32.8
Na ₂ O	12.60	0.27
K ₂ O	0.40	0.66
MgO	0.23	0.24
CaO	0.21	0.28
TiO ₂	2.01	1.27
Fe ₂ O ₃	1.13	1.24
L.O.I	15.2	12.3

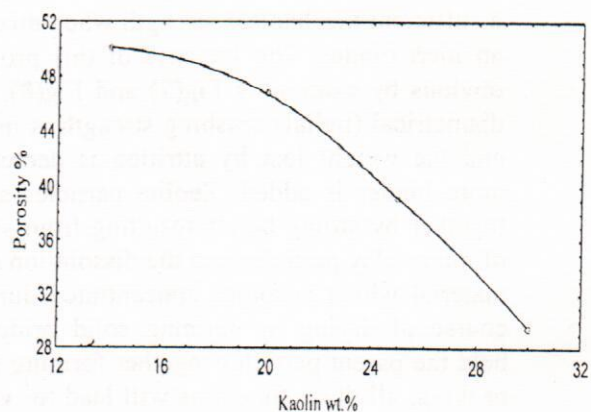


Fig. (2) The effect of kaolin on porosity

Table (2) Design of experiments for the preparation step

Temperature °C	Time (h)	Na ₂ O % in 3A	% Exchange 3A
At 0.2 N KCl 77	16	10.2	19.0
At 1N KCl 77	24	1.8	85
94	8	2.28	80

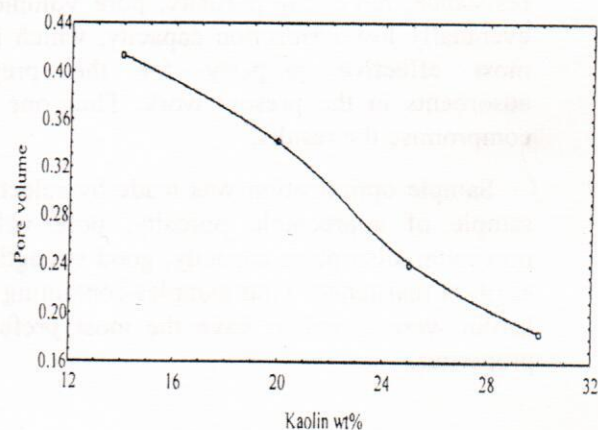


Fig. (3) The effect of kaolin on pore volume

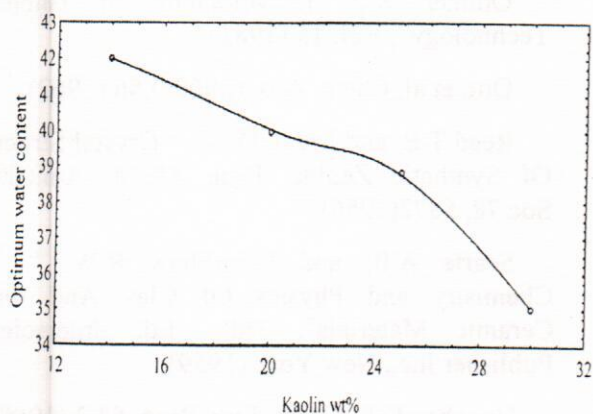


Fig. (1) Optimum water content for agglomeration

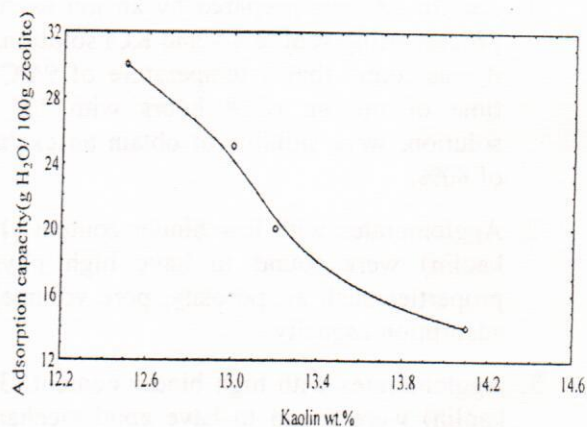


Fig. (4) The effect of kaolin on adsorption capacity

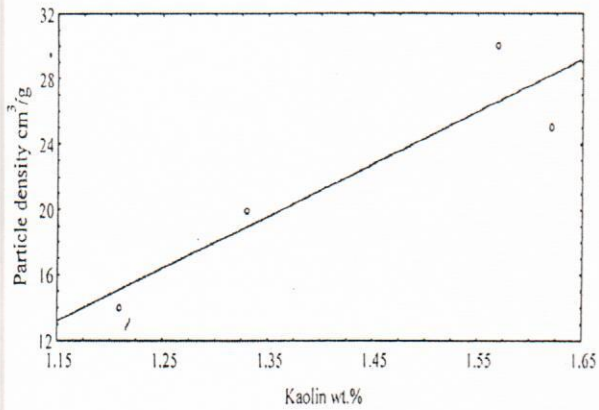


Fig. (5) The effect of kaolin on the particle density

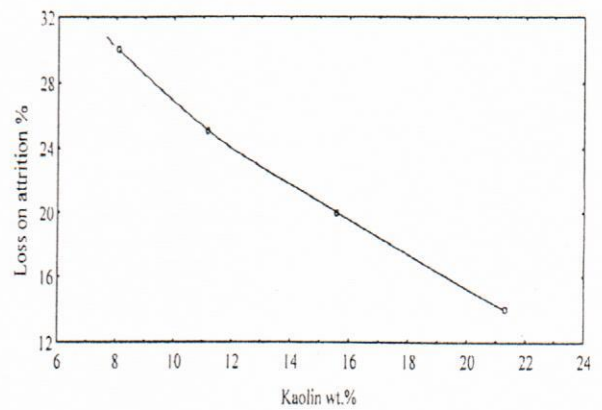


Fig. (8) The attrition resistance of pellets of zeolite

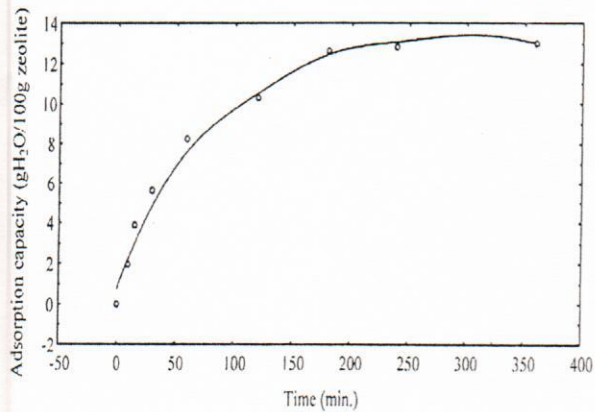


Fig. (6) Adsorption isotherm of water vapor on zeolite

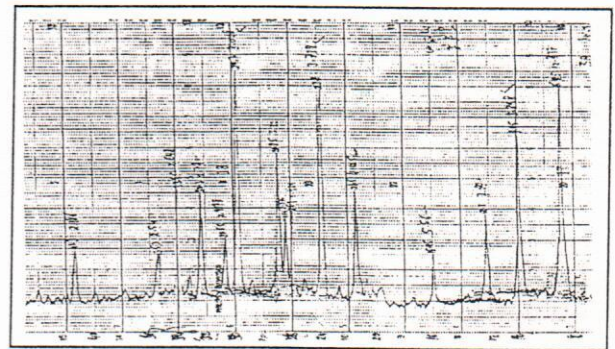


Fig. (9) X-ray pattern for the zeolite 3A prepared in the present work

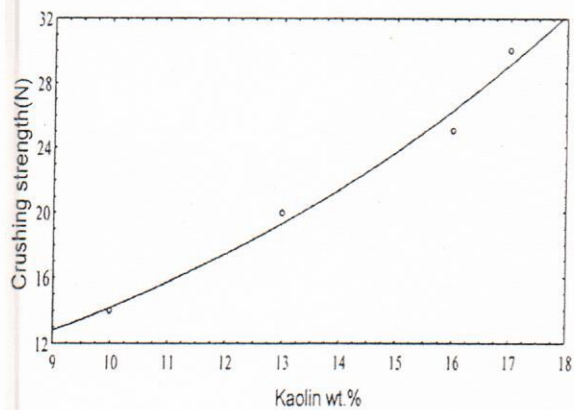


Fig. (7) The effect of kaolin on the crushing strength of zeolite

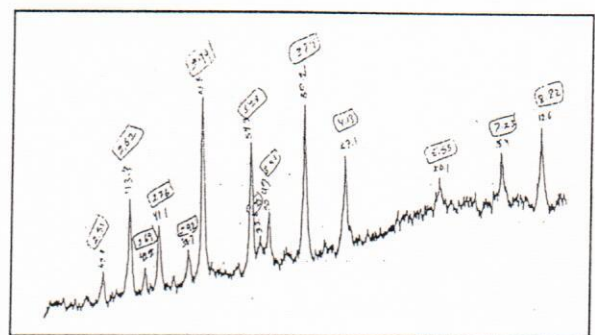


Fig. (10) X-ray pattern for the standard zeolite 3A (imported)