Preparation of Type 4A Zeolite from Iraqi Kaolin: characterization and properties measurements

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ABSTRACT

Molecular sieves or zeolites are an important widespread industrial material of unique chemical structure, which are used in most industrial plants as an adsorbent for gases or even as catalysts.
Zeolite 4A was prepared from Iraqi kaolin using ion exchange technique to insert sodium ion in kaolin structure. It was characterized by X-ray diffraction and tested for water adsorption capacity to test the reliability of this kaolin as a raw material for zeolite production, and this seems to be the case.

KEYWORDS: Type 4A Zeolite, Iraqi Kaolin, metakaolin, adsorption capacity.

INTRODUCTION

Zeolite are crystalline, hydrated alumino-silicates of group I and II elements, in particular, sodium, potassium, magnesium, calcium, barium and strontium. Over 150 synthetic and 40 naturally occurring zeolites are known (Marcus and Cormier, 1999). Initially only natural zeolites are used, but more recently synthetic forms have been made on industrial scale giving rise to tailor made zeolites that are highly replicable. Structurally, zeolites are framework alumino-silicate which are based on infinitely extending three dimensional AlO_4 and SiO_4 tetrahedral linked to each other by sharing all the oxygen (Berck,1974; Richardson,1989).They can be represented by the empirical formula:

$$M_{2/n}O \cdot Al_2O_3 \cdot x\ SiO_2 \cdot yH_2O$$
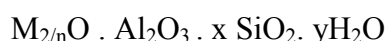
In this oxide formula, x is generally equal to or greater than 2 since tetrahedral AlO_4 are joined only to tetrahedral SiO_4 and, n is the valency of the cation.
They have three properties that make them unique and deserving of a separate category.
1. They are highly crystalline with well defined structure encloses the aluminum silicate framework cavities occupied by large ions and water molecules, the cavities opening ranging from 0.8-1 nm in diameter which are the order of molecular dimension. Size and shape of these pores determine which molecules enter the cavities and which are excluded, so they are called molecular sieves.
2. Cations with in the cavities are easily replaced with a large number of different valency cations which exert large number of electrostatic or polarizing forces across the small dimension of the cavity.
3. The introduced cation into the cavities by ion exchange will have separate activities of their own; this facilitates the opportunity of dual function catalysts involving acidity with other activities. Zeolite A is synthesized in the sodium form and has the general chemical formula:

$$Na_{12}[AlO_2 \cdot SiO_2]_{12} \cdot 27H_2O$$

According to Database of Zeolite Structure (2002), Zeolites type A classified into three different grades, 3A, 4A and 5A, all of which posses the same general formula but has different cation type. When 75 % of its sodium is replaced by potassium, it is referred to as zeolite (3A). Alternatively replacing of sodium by calcium gives rise to type (5A) one.

Synthetic zeolites are widely used in industry as adsorbent for various gases and vapors (Chandrasekhar and Pramada, 1999) and as catalysts for many petroleum industries of great importance in industrial application as described by (Speight,1999) They are used for drying of gases and liquids from low humidity where it shows a higher adsorption capacity than other adsorbents. They have a high tendency to adsorb water and other polar compounds, for examples, NH_3, H_2S, SO_2 and CO_2 and a good capacity at very low temperatures if compared with other adsorbents.

Traditionally, zeolites are commercially produced from hydro gels of sodium aluminate and silicate and was the work of (Cooperthwaite, 1986). However, production of zeolites from clay, as a source of alumina and silica are being continuously investigated with positive results. Of the work done by (Atta, 2007) for synthesis of Faujasite zeolites from Kankara Kaolin clay and (Chandrasekhar and Pramada, 1999) for zeolite synthesis using Kerala Kaolin.

The aim of this manuscript is to prepare zeolite type 4A from Iraqi Kaolin and characterize and test its activity.

MATERIAL AND METHODS
Materials
Kaolinite clay: The Kaolinite clay used in the present investigation was supplied from Doukhla site in the west part of Iraq with the chemical composition of $Al_2Si_2O_5(OH)_4$.

2.1.2. Sodium hydroxide:
8M sodium hydroxide solution was used in the preparation of 4A zeolite for the ion exchange procedure.

Preparation of zeolite type 4A
The preparation was done using the following steps:

Calcination of the raw kaolinite

A process in which the kaolinite was exposed to high temperature of about $550^{\circ}C$ for about 1.5 hrs time where its structure is destroyed and any undesired volatile matter was removed and converted to a metakaolinite, a material which readily accepts and exchanges sodium as a guest in its structure and having the chemical composition given in Table 1.
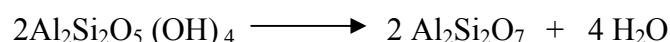The chemical reaction in this step is:

$$2Al_2Si_2O_5(OH)_4 \longrightarrow 2\,Al_2Si_2O_7 \;+\; 4\,H_2O$$

Table 1.The chemical composition of Doukhla kaolinite used in the preparation of type 4A zeolite.

Constituent	Weight (%)
SiO_2	50.10
Al_2O_3	32.80
Na_2O	0.27
TiO_2	1.27
Fe_2O_3	1.24
MgO	0.24
CaO	0.28
K_2O	0.66
L.O.I , wt %	12.30

Ion Exchange

The procedure of (Rollman and Valyocsik, 1982) was employed, the above produced metakaolinite was treated with sodium hydroxide solution with a ratio of 1:5 and refluxed heated to 90 ^{o}C with a continuous vigorous stirring for 4 hr in order to insert the sodium ion in the metakaolinite structure where the following reaction occurs:

$$6Al_2Si_2O_7 + 12\ NaOH \longrightarrow Na_{12}\ (AlO_2)_{12}(SiO_2)_{12}.27H_2O + 6\ H_2O$$

Concentration of sodium hydroxide higher than the usual one was experimented in order to accelerate the ion exchange process because we used a raw materials and not pure aluminate and silicate.

Washing, Filtration and Drying

The treated kaolin slurry was left to settle for several hours and was washed three times with distilled water to remove the excess unreacted sodium hydroxide. Then it was filtered by any suitable mean and dried in an oven at 110 ^{o}C for three hr.

Formulation and Calcination

This is important because most fixed bed reactors necessitate that zeolites have to be formulated to spheres, extrudates or tablets. Zeolite powder obtained above was crushed, milled and a suitable grain size (Bashir ,1997; Flank,1989) was mixed with 15 % raw metakaolinite and 30 % water to make a paste that can be easily dealt with and then passed through a laboratory extruder to obtain extrudates of about 1.6 x 3 mm dimensions, this was then dried at 80 ^{o}C for 3 hrs and finally calcined for another 4 hrs at 500 ^{o}C.

Characterization

The elemental composition analysis of raw kaolin and prepared zeolite were obtained using X-ray fluorescence (Siemens D500) and metal content analysis being determined by standard atomic absorption method. Pore volume was determined experimentally using liquid impregnation method as described by (Satter and Charles 1980, Richardson, 1989, Karim, 2010). Hardness was determined with the ERWEKA.TBH28 hardness meter (Le Pag and Miquel, 1976) while crushing value was determined by placing 25 g of the sample under pressure of 18kN for 20 minutes and measure the amount of powder that pass through 53 micrometer mesh as a percent relative to the total weight. Loss on ignition (L.O.I) was calculated from the weight being lost after roasting the sample at 900 ^{o}C for three hours.

For powder X-ray diffraction patterns were recorded using a Phillips X-ray diffract meter and peaks were compared and assigned by comparison with the published data from the international zeolite association (Database of Zeolite Structure, 2002) and those of typical compounds given in (ASTM, 1986 powder diffraction files).

The Bulk density was determined by placing a weight catalyst in a graduated cylinder then shakes it by vibrator and read the volume of it and then calculate the density i.e. it is the packing or load density of the reactor.

Testing of the Efficiency
The adsorption capacity of any adsorbent as dimensionless quantity was defined as the weight of adsorbate being adsorbed by 100 g of adsorbent; it can be represented as a percent ratio or as miliequivalent adsorbate. It was tested for the prepared samples as explained by (Aderemi, 2004; ASTM, 1986; Armor 1995) in a simple laboratory designed apparatus where air saturated with water vapor is passed over a previously weighted sample of 4A zeolite and the increase in weight resulted from the adsorption of water on zeolite is then monitored and measured after a suitable time.

RESULTS AND DISCUSSION
The chemical analysis of the prepared type 4A zeolite ,shown in Table 2, indicats that the major components of the zeolite present in the structure in addition to trace amounts of impurities associated the raw kaolin used in the preparation and can not be removed through out the preparation procedure used and this have no effect on the activity as will be seen later.

Table 2. Chemical analysis of prepared zeolite, type 4A

Constituents	Weight %
SiO_2	35.90
Al_2O_3	31.19
Na_2O	12.60
K_2O	0.40
MgO	0.23
CaO	0.21
TiO_2	2.01
Fe_2O_3	1.13
L.O.I, wt %	15.20

A powder X-ray diffraction pattern from prepared type 4A zeolite is shown in Figure1.This pattern is just a plot of the X-ray intensity scattered from the sample versus the scattering angle (Bragg angle,2θ).The positions and intensities of the peaks in the diffraction pattern are a fingerprint of the crystalline components that are presents in the sample. In Table 2 ,we list the peak positions and intensities (area under the peaks) that can be expected for a of 4A

zeolite pure sample. Additional peaks in the powder diffraction pattern would indicate the presence of a crystalline impurity. The nature of the impurity could be established and it is not essential that the identity of the sample be confirmed exactly by powder diffraction as the synthesis is reliable.

Table 3.Powder diffraction peaks positions and intensities for prepared zeolite 4A

2θ	d/Å*	I%	2θ	d/Å	I%
7.26	12.17	63	38.02	2.36	7
10.24	8.63	38	39.49	2.28	1
12.54	7.05	26	40.16	2.24	5
16.18	5.47	21	41.54	2.17	18
17.76	4.99	1	42.22	2.14	11
20.50	4.33	5	42.88	2.11	7
21.72	4.09	49	43.52	2.08	6
22.94	3.87	2	44.18	2.05	25
24.04	3.70	71	44.85	2.02	1
26.16	3.40	21	47.34	1.919	21
27.16	3.28	79	47.94	1.896	10
29.10	3.07	2	49.14	1.853	2
30.00	2.98	100	49.74	1.832	7
30.86	2.90	15	52.02	1.757	7
32.58	2.75	23	52.60	1.739	45
33.40	2.68	7	53.18	1.721	7
34.24	2.62	80	54.32	1.688	25
35.76	2.51	9	54.82	1.637	5
36.54	2.46	8	56.48	1.628	12

*The d-spacing, d , is calculated from the scattering or Bragg angle 2θ

The physical properties of the prepared samples are demonstrated in Table 4 which shows that a relatively good adsorption capacity of 23 was obtained, a value that correspond to 92 % efficiency basing on maximum adsorption capacity of 25 in most zeolites type 4A. In addition to that other properties such as crushing strength, attrition, porosity etc., which are not very far or even consistent with those mentioned in literatures by (Atta, 2007) and documented in Database of Zeolite Structure (2002).

The main object in the preparation is to select clay that satisfies the stochiometric ratio of silicate and aluminate to build the AlO_4 and SiO_4 in zeolite structure.

Table 4. The major properties and characteristics of the prepared zeolites 4A.

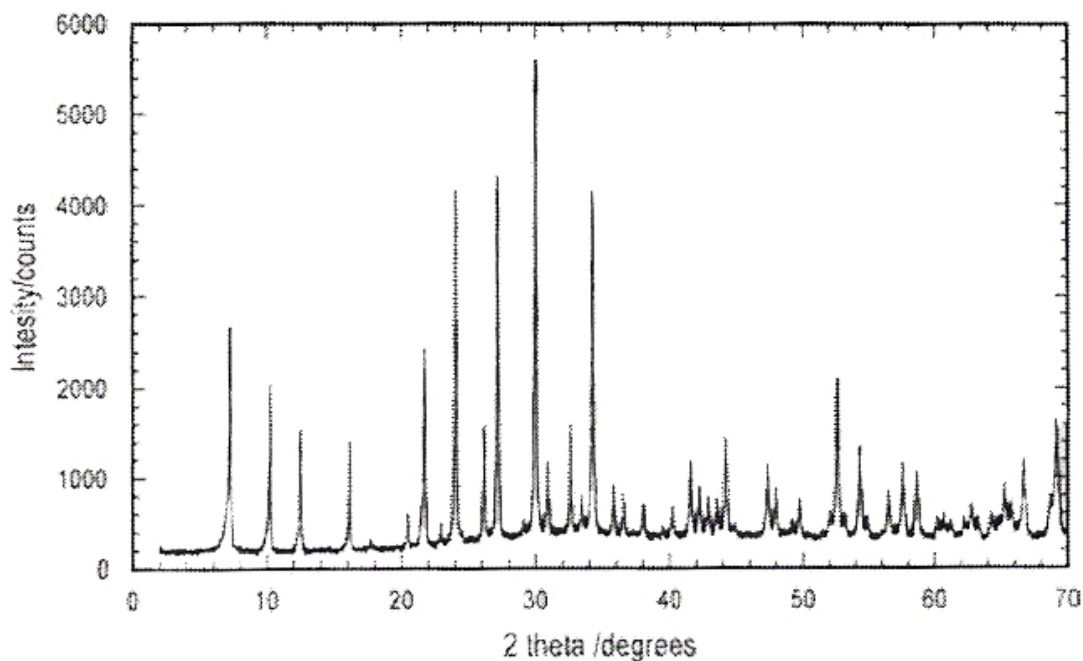| Form	Extrudates
Particle size, mm	1.6 x 3
Bulk density, g/cm^3	0.721
Pore diameter, Å	4
Pore volume, cm^3 / g	0.45
Porosity, %	0.55
Crushing strength , N	16.00
Attrition , wt %	7.35
Moisture , wt %	1.21
Adsorption capacity as g H$_2$O/100g zeolite	23.0
Efficiency %	92
pH (5% slurry)	9.5
Loss of ignition, wt %	7.23

Figure 1. X-ray diffraction pattern of prepared type 4A zeolite

CONCLUSIONS

We may state that it is possible to use Iraqi kaolinite clay to prepare type 4A zeolite by converting it to metakaolinite via calcinations at 550 ^{o}C and then using sodium hydroxide for ion exchange to insert the sodium ion in its structure. The structure was characterized by XRD spectroscopy and water adsorption capacity of 92% efficiency was obtained.

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تحضير الزيولايت نوع (4A) من الكاؤولين العراقي

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الملخص

الزيولايت او المناخل الجزيئية هي مواد مفيدة ذات استخدامات صناعية واسعة ، وتركيبها الكيميائي فريد ، وتستخدم في معظم الوحدات الصناعية كمواد ماصة سطحياً (امدصاصية) للغازات أو حتى كعوامل مساعدة.

في هذا البحث تم تحضير الزيولايت نوع (4A) من الكاؤولين العراقي، وقد تم تشخيص تركيبه ودراسة خصائصه واختباركفاءته ألأمدصاصية للماء وذلك لمعرفة إمكانية استخدام الأطيان العراقية كمواد أولية لتصنيع وإنتاج الزيولايت ، وهكذا أثبتت الفحوصات والنتائج التي تم إجراؤها في هذا البحث.