Void space and cavity measurement of the prepared zeolite y using X-ray diffracting modelling

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Abstract

Zeolite was synthesized using a solitary gel technique with Iraqi kaoline. Zeolite 's specific structural nature makes it difficult to use X-ray diffraction (XRD) to evaluate a single crystalline characteristic. Structural analysis to estimation and visualization of one crystal geometric properties by CrystalMaker software was carried out using XRD and the simulation of a crystal pattern using a Rietveld refinement technique using Maud software. This paper describes the Crystal Maker software suite, which includes the visualization, modelling and diffraction simulation of modular programs for crystal and molecular structures. The fundamental reasoning for the program is explored and a variety of applications are given for teaching and research in crystal chemistry and molecular dynamics.

Keywords: *computer software; Crystal Maker; crystal structure visualization; diffraction simulation; molecular modelling*.

1. INTRODUCTION

Zeolites are very common types of crystalline aluminosilicate materials that have an open-frame structure and are thus commonly used. [1, 3]. NaY zeolite demonstrates a faujasite-type structure with saturated sodium (Na+) cations, which plays an important role in the petrochemical industry because it has some favourable characteristics including high catalytic activity, atomic surface ratio, measurable surface area and surface energy [6]. NaY zeolites have been frequently used for separation and ion exchange as well as acid catalysts for size and shape based catalytic reactions due to their molecular micro-porosity [7]. Zeolite catalysis -focusing on refining and processing of hydrocarbons -now encompasses a wide variety of processes related to crude oil and natural gas upgrading [8]. Since several years, the crystalline solids of the synthetic zeolite microporous have been developed in a large number of industrial processing plants, the zeolite Y is a highly adjective molecular sieve of the Faujasite family. The pore diameter of 0.74 nm and the pore structure are three-dimensional [4, 5]. The Rietveld method is the least square refinement, which focuses on a number of atomic structural, reference and peak profile parameters once the measured pattern best fits the observed model (experimental model). According to Lutterotti et al. [9] and to Wenk et al. [10], for different studies, literature has shown that Rietveld texture analysis was also carried out using synchrotron diffraction images and Charge Coupled Devices Camera (CCD) or an image plate detector [11]. Rietveld specification for texture analysis is conducted meaningfully from powder XRD data, as much more knowledge can be produced than traditional methods of peak identification. It also allows unit cell dimensions to be described, crystallite sizes / forms, micro-strain in a crystal lattice, atomic coordinates / bond lengths, substitutions / vacancies, phase quantities and texture effects [12, 13, 14].

For the study of zeolite structure, the Rietveld method was successfully applied to solve the topology of zeolite frameworks, occupancies of cation sites, lattice positions, templates or guest molecules and the location of clusters inserted into the structure [15].

CrystalMaker is designed to auto-detect ~30 different file Models, making it possible to immediately load each files by drag-and-drop to the same window. Multi-structure files (e.g. ICF, PDB or XYZ) have their separate structures loaded into the same screen as the "View" thumbnails for quick comparison or animation [16, 17].

New molecules can be formed by selecting atoms from a palette and adding them to the main window, with bonds. Using the Relax Molecule command using an energy minimiser the resulting geometry can be optimised. The minimizer uses the Monte-Carlo algorithm to gradually relax the structure. The algorithm is designed to be available and low-risk: using the existing bonding to infer bond form and carbon hydridization, and without needing additional user feedback (e.g. entry of parameters which could lead to incorrect results). CrystalMaker uses a structured set of interatomic potentials as part of the modeling process. Which include best-available Molecular Mechanics 3 [18] and Universal Force Field [19] short-range interaction potentials plus long-range Williams [20] and UFF potentials. Although these are intended specifically for small organic molecules. From crystal structure to diffraction mechanism: Crystal Maker and Single Crystal can be connected in such a way that rotating the structure causes its diffraction pattern (and stereographic projection) to rotate in Single Crystal Visualisation and study of crystal structures using tools from CrystalMaker [21]. CrystalMaker can be expanded to provide X-ray and neutron powder diffraction visualization and analysis through Crystal Diffract ®. This allows for a two-way sharing of data between the two programs, enabling users to model crystal structures in CrystalMaker and Simulate the respective powder diffraction pattern in Crystal Diffract with a single menu order. Crystal Diffract is also a stand-alone program that can be used to create new structural crystal models, or to install structures from text files (including CIF) or CrystalMaker. In this paper the zeolite was prepared and the XRD analysis will performed. First the refinement using Maud will provide the necessary parameters for the crystal maker to find the other single crystal parameter such as the void space and cavity.

2. Methodology of NaY zeolite

Kaolin was sifted to a particle size of about 75µm. Kaolin was mixed with particles as small as 75µm using 40 Per cent of sodium hydroxide solution (kaolin / NaOH) = 1/1.5 g / g and fused at 850 ˚C for 3 hours (State Geological Survey and Mining Company supplied kaolin clay). The electromagnetic stirrer shown in Figure 1-A applied 50 g of fused kaolin and 63 g of sodium silicate to 500 ml of deionized water under constant stirring at 50 °C for 1 hour. The pH 13.3 slurry was placed in a 1000 ml glass jar (Figure 1.B) and aged for 24 hours in a programmable electrical furnace (Figure 1.C) at 50 °C. The component has been crystallized at 100 °C for 48 hours in a programmable electrical furnace. Using the Buckner funnel, the crystalline mass was purified using a vacuum pump (Figure 1.D), and cleaned with deionized water until the pH level reached 11.7. The washed crystalline was dried at 100 °C for 16 hours, using programmable electric furnace.

The NaY support chemical analysis (XRF) was done by wet chemical analysis and performed in the Geological and Mining State Company Table 1.

Table 1. Chemical analysis (XRF) of kaolin and NaY

Component Wt%	***NaY***	***Kaolin***
SiO_2	41.50	49.64
Fe_2O_3	1.09	1.72
AL_2O_3	20.85	34.05
CaO	1.10	1.10
L.O.I.	20.30	12.28
Na_2O	13.46	0.46
Others	1.7	0.75

Table 2. Properties of chemical used in zeolite preparation

Component	***chemicals***	***Purity***	***Company***
Sodium Hydroxide	NaOH	97 %	Hopkin & Willims
Sodium Silicate	Na_4SiO_4	99 %	BDH limied Pool England

Table 3. Properties of zeolite preparation

Test	***Result***
Bulk density	0.5998 gm/cm3
Surface area	210.3347 m2/g
Grain crushing strength	***1*** N/mm

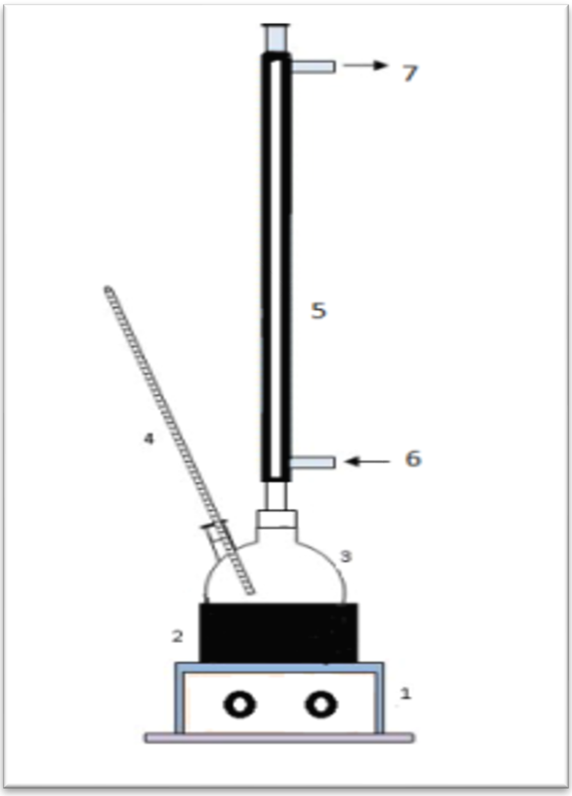

Figure 1. A schematic diagram of the laboratory mixing unit. 1. Heating and magnetic Stirrer (2) water bath (3) 2 necks flask (4) Thermometer (5) condenser (6) Chilled water in (7) Chilled water out.

Figure 1.B 1000 ML GLASS JAR.

Figure 1.C Programmable Electrical Furnace.

Figure 1.D the Vacuum Pump.

3. RESULT AND DISCUSSION

3.1 XRD analysis

X-ray diffraction is an effective and useful technique for the study of crystalline materials commonly used in physics, MSE and chemistry [22].

X-ray diffractometry (XRD analysis) is the method to determining the phases and the crystal structure of the samples. It is a foundational technique for any material development, including advanced materials and thin films. The X-ray beam hits the sample and the light diffracts the crystalline pattern. An interference pattern is then created which is observed by the detector. The pattern found is unique to each crystalline phase and to a substance comprising multiple phases. This means that studying such diffraction patterns provides a fingerprint that can potentially be analyzed in order to re-engine the phases and composition of the sample. Among the forms in which zeolites are classified and separated from other zeolites and other crystalline substances, the pattern of x-ray powder diffraction was found to be a useful method. The diffraction effect is attributable to the interference that an object creates in the wave bath, and the pattern of varying intensity that occurs is called diffraction pattern. Diffraction happens when the measurements of the diffraction medium are equal to the wavelength of the radiation. X-rays have wavelengths similar to molecular bond lengths and atom spacing in crystals. Through studying the pattern of X-ray diffraction, a clear image of the position of atoms can be drawn even in complex crystal structures. The X-Ray diffraction maps the force against the angle of diffraction [23].

Drastic variations in the strength of individual peaks in the Y and X X XRD patterns can result from variations in the distribution of electron density within the zeolite unit cell. The distribution of electron densities depends on the degree to which pores in the zeolite are filled with guest molecules, and the nature of the guest molecules. The guest molecule H2O absolutely fills the pores in this XRD process. Pressure variations may also occur if some or all of the cations in Y and X are exchanged with other cations. X-ray diffractometry was used for crystal structure analysis, and various techniques exist. "Powder system" which uses a wide-angle goniometer, an automatic counter diffractometer, is one of the common XRD instruments X-rays typically used for carbon materials are the Cu Kα radiation, which is monochromatic either by crystal reflection (monochrome) or by the use of a filter whose K absorption wavelength falls between the Cu K5-007 and Kβ wavelengths, but which is still a double diffraction line caused by Kα1 and Kα2 radiation with a slight difference in wavelength.

(0.1540562 and 0.1544390 nm, respectively). Figure 2 shows the diffraction pattern of the prepared zeolite Nay

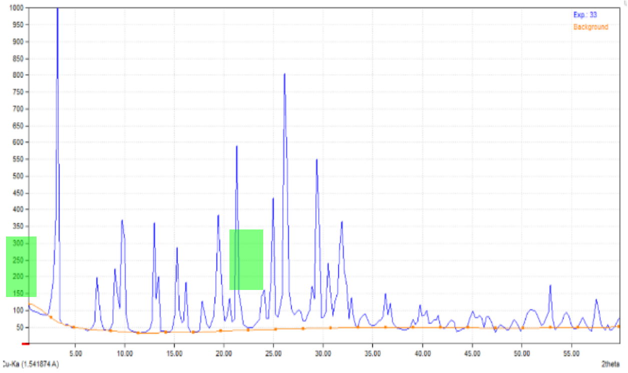

Figure 2. X-ray diffraction pattern for prepared NaY zeolite.

Growing zeolite crystal has its own specific pattern that can be used as a guideline for the determination of the solid crystal phase and is used as a fingerprint for each zeolite. The prepared zeolite was compared with standard crystal pattern taken from the open source COD (crystallographic open database). The purity of the solid crystal will be calculated by contrasting the X-ray diffraction pattern of the sample with the X-ray diffraction template of the standard that can be collected from the national Zeolite association [24]. Prepared zeolite produces SiO_2/Al_2O_3=3.3 and this value is within the range of silica to aluminum for regular zeolite (2 to 15) [25].

X-ray diffraction pattern was determined for prepared NaY zeolite as shown in Figure 2. The relative crystallinity of NaY zeolite was obtained by comparing the sum of the combined peak intensities of the sample and the reference, and peak intensities were used to assess the region below the peaks of the highest intensities [26].

The area values below the peaks were used for the calculation of relative crystallinities in percent by equation (1) and were equivalent to 145.65 per unit for prepared NY zeolite and are considered to be well above 100 per cent [27].

$$relative\ crystallinity\ of\ NaY\ \% = \frac{Sx}{Sr}\ X\ 100 - -\text{Eq. 1}$$

Sx= sum of integral peak intensities for the sample NaY.

Sr= sum of integral peak intensities for the reference NaY.

The relative crystallinity value is the same for the prepared NaY zeolite as reported by [28]. They used the same preparation process as mentioned bove to prepare NaY zeolite and the relative crystallinites were 133.3 present

3.2 RIETVELD REFINEMENT ANALYSIS

The Rietveld refinement analysis was carried out with the program MAUD. Figure 3 shows the X-ray pattern of the prepared zeolite with the standard one from the COD. The prepared zeolite was accurately fitted with the standard one which further indicate the phase of the zeolite. The Rietveld refinement analysis was performed and the concordance factors were convergent into lower Rp=16.4%, Rwp=18.1%, RB=19.1%, suggesting that these atoms belong to the structure portion of the structure created by the in order to obtain a fair structural model for the framework atoms, restrictions were applied to the angles and bonds of both Si and Al tetrahedral. The angles were constrained to 110.0° with a standard deviation of 0.1°, and the bond distances of the Si, O atoms were constrained to 1.59 Å with a standard error of 0.02 Å and those of the Al, O atoms were constrained to 1.71Å with standard error 0.02 Å.the retfield refinement finding was compatible Psycharis [29] finding in term of accuracy and refinement. With the Table 4 shows the result of the crystal parameter after rietveld refinement analysis.

Table 4. crystal parameter of the zeolite y after rietveld refinement analysis.

Structure type	Crystal
Chemical Formula	$Na_{70.56}Al_{17.0}Si_{120.96}O_{384}$
Z	1
Space Group	Fd$\bar{3}$ m [origin 2]
Crystal System	Cubic
a	29.4460 (30) Å
Cell Volume	25531.652 $Å^3$
Asymmetric unit	12 sites
Unit Cell	1008 sites /unit cell 0.0253 atoms/ $Å^3$
Density	0.8508 g/cm^3
Visible Site	1048

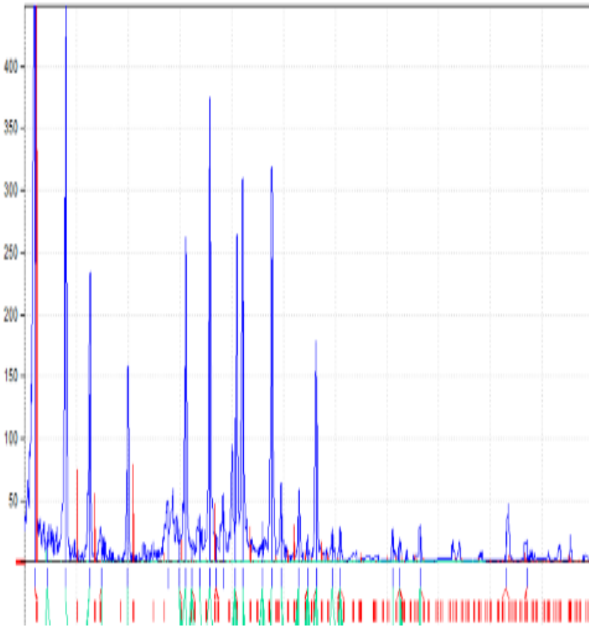

Figure 3. Rietveld refinement analysis and standard comparison using Maud.

3.3 CRYSTALMAKER MODING

Exploring coordination environments Different resources are available for the understanding of coordination environments in crystals or molecules. Radial clusters or shells can be positioned around the specified atom or position. An interactive coordination histogram can also be shown through the "Distance Explorer" as shown in Figure 4. The results are displayed in a tabbed interface, displaying a color-coded histogram, or a sortable distance chart. The "Crystal Coordination file" is a useful output tool. It lists all coordination units per unit cell, describing the fractional and orthogonal coordinates and the distances in each central atom. This file can be used for the study of rigid-unit-modes in lattice dynamical calculations, as recently demonstrated in the case of negative thermal expansion in MOF-5 [5].

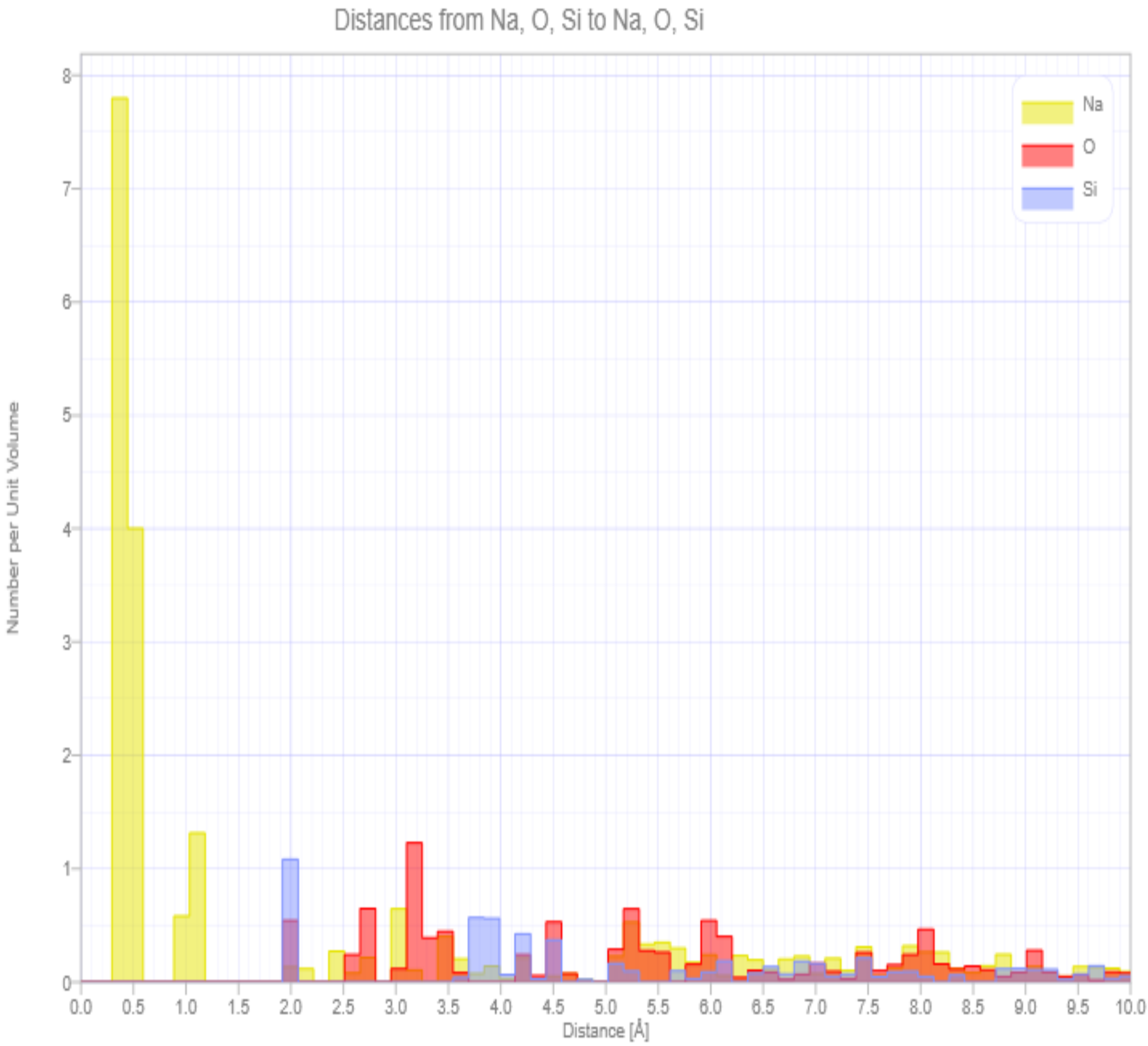

Figure 4. Distance Explorer of zeolite atom.

Distance from atom and angle of the crystal structure according to the lattice spacing of the prepared zeolite is shown in Tables 5 and 6

Table 5. Lattice spacing and distance of the prepared zeolite.

D-spacing	Distance
d (1 1 1)	17.00066 Å
d (1 0 1)	20.82147 Å
d (0 0 1)	29.44600 Å
d (0 1 1)	20.82147 Å

Table 6. Lattice spacing and angle of the prepared zeolite.

D-spacing	Angle
[1 0 0] and [0 0 1]	90.0000°
[1 1 0] and [0 0 1]	90.0000°
[1 1 1] and [0 0 1]	54.7356°
[0 1 1] and [0 0 1]	45.0000°

The floating "Model Inspector" window offers detailed control over the styles of individual model elements, such as atom spheres, thermal ellipsoids, polyhedrons and bonds. Interatomic bonding and, therefore, coordination polyhedrals can be generated automatically shaown in Figure 5. The Browser of the Spacegroup. The crystal editor, demonstrating the editing of the fields. Of the atomic radii plus 15%.

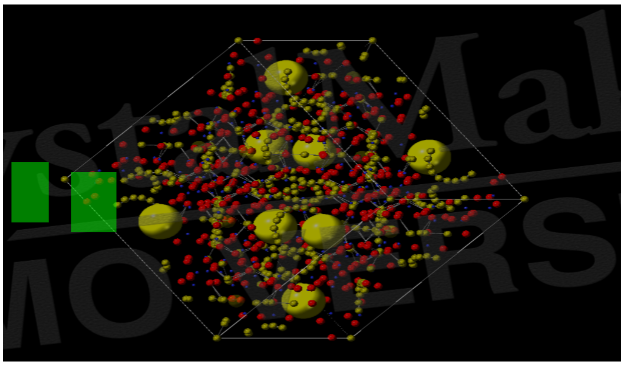

Figure 5. single crystal structure and atom representation using sphere model.

The final calculations were for the porosity and the cavity as shown in Table 7.

Table 7. Void and cavity analysis for the prepared zeolite.

Porosity data for	zeolite y
Unit cell volume:	25531.65 Å^3
Filled space:	4739.17 Å^3 (18.56%) per unit cell
Void space:	20792.49 Å^3 (81.44%) per unit cell
Located 2 unique cavities with a precision of	1.0E-007 Å
Cavity 1: Cav5.9 at (0.121690, 0.121690, 0.624329);	radius = 5.866392 Å (volume = 845.6719 Å^3)

3.4 ZEOLITE TESTS

3.4.1 Sodium Content

Sodium content of prepared faujasite type NaY zeolite was determined by wet chemical analysis at the State Geological Survey and Mining Company. Sodium is commonly reported as a weight per cent sodium oxide (Na2O) on the catalyst. It is important for fresh zeolite to contain very low sodium levels to reduce zeolite hydrothermal stability and to react with zeolite acid sites and to reduce catalytic activity. Sodium is commonly reported as sodium or soda (Na2O) weight percentage on a catalyst [30].

3.4.2 Surface area

Catalyst surface area was measured using the BET method Thermo Finnegan form, an apparatus located at the Petroleum Production and Research Centre, Ministry of Oil.

The surface area of the prepared catalyst was determined by nitrogen physical adsorption at the temperature of the liquid nitrogen using BET (Brunauer, Emmett, and Teller) method, and equal to 210 m^2/g. The most preferred surface area for catalytic converters with gamma alumina support is greater than 100 m2/g [31].

A high surface area is evident due to the micro porosity of the prepared zeolite powder [32]. Increased surface area usually increases the catalytic activity. In comparison, the high surface area typically has a high proportion of small pores that are hydrothermally less stable than large pores. [33]. The result of surface area agreed with [34] and [35].

3.4.3 Bulk density

The bulk density is determined by the Petroleum Research and Development Center by placing a determined weight of zeolite granules in a cylinder of 2 cm inside diameter and the cylinder was shaken for a specified time by the Autotap-Quantchrome / US bulk density device. The bulk density is the ratio of the weight of the zeolite granule to the volume of the sample inside the cylinder after shaking.

$$d_b = W/V \qquad \text{Eq.2}$$

Where:

d_b= bulk density g/cm^3.

W=weight of zeolite granules g.

V= volume of zeolite in the cylinder cm^3.

The apparent bulk densities of powdered, granular, flaked materials are highly dependent on the way in which the particles are packed together due to their cohesion and shape effects. In addition, the handling or vibration of particulate matter causes smaller particles to move into spaces between larger particles. The geometric space occupied by the powder decreases and the density of the powder increases. The bulk density is equal to 0.599 g / cm3. The result of the bulk density was agreed with Rawland (1964).Whose invent the range of bulk density for the zeolite between 0.5 to 1 g/cm^3.

4. CONCLUSION

The findings presented show the properties of the crystal structure and the feasibility to successfully calculate the parameters of the zeolite y crystal using MAUD 2.94 and CrystalMaker 10.5.0. Software. Rietveld refinement method using MAUD successfully measures the deviated parameters of the zeolite y crystal structure. The results from the retvield refinement were used to create the new crystal structure to be modelled and characterized using the crystal maker software with is a new method to apply for identifying the potential of the prepared zeolite based on its prepared crystal structure.

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