Study Surface Area and Pore Size Distribution on Synthetic Zeolite X using BET, BJH and DFT Methods

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Abstract. The characterization of zeolite X synthesized from Bintan bauxite using nitrogen physisorption technique that employs the BET, BJH and DFT equations was proposed to improve the understanding of the pore characteristics of zeolite X. The BET, BJH and DFT methods were chosen because the characteristics of the synthesized zeolite were characterized using a scanning electron microscope (SEM) showed a typical morphology for zeolite X and zeolite A crystals and the presence of amorphous phase in small abundance. Evaluation is needed to understand the characteristics of micropore, mesoporous and macropore of zeolite X as a synthesis and the best methods. The data obtained show that the DFT method is the most appropriate and superior model to describe the pore size distribution of synthesized zeolite X.

1. Introduction
Porous materials with superior characteristics for various purposes continue to be sought for use in surface area, pore size, surface reactivity or a combination of these properties. For example, catalyst engineering to obtain active catalysts with superior product selectivity can increase the uniformity of pores and surface reactivity of porous materials such as zeolite. Porous materials also offer attractive solutions for storage applications such as carbon capture and sequestration or storage of methane (CH₄) and hydrogen (H₂) for energy use. Nanoporous materials such as sequenced carbon and metal-organic frameworks (MOFs), among others, have been extensively evaluated for the storage of gases such as carbon dioxide (CO₂), CH₄, and H₂ due to their large pore volume and high surface area [1]. The structure of these nanoporous materials must be fully characterized to attribute the favourable structural features to the gas storage performance. Structural characterization includes methods such as X-ray diffraction (XRD), nuclear magnetic resonance (NMR), and scanning electron microscopy (SEM); However, gas absorption may be most appropriate to analyze and evaluate because it can measure the entire range of micropores and mesopores, to macropores in abundant materials [2].

Measurement of pore characteristics in zeolite using the liquid N₂ adsorption technique provides rich information and can be used to study the characteristics of synthetic zeolite in depth. Zeolite is a crystalline material with a porous structure with a size range of nanometers, a three-dimensional framework composed of aluminosilicate tetrahedral with charge balancing ions that can be exchanged on its surface. Having such characteristics makes zeolites can be used as catalysts, ion exchangers, and adsorbents. The application of zeolite as a catalyst is used in petroleum, the adsorbent in natural gas purification, and ion exchange in water purification. Zeolite is also often used in agriculture, namely as a carrier of nutrients in fertilizers [3].
Zeolites can be distinguished according to different standards, with pore openings being the most attention-grabbing due to their applied potential. Zeolites can be classified as (i) small pore zeolites, consisting of channels bounded by eight-membered rings with a pore diameter of 4, (ii) medium pore zeolites, consisting of channels bounded by ten membered rings with a pore diameter of 5–6, (iii) large pore zeolite, consisting of channels bounded by 12 member rings with a pore diameter of 7, and (iv) extra-large pore zeolite, consisting of channels bounded by more than 12 member rings and pore diameters greater than 7. Channel dimensions represent other zeolite criteria because zeolitic materials can include one-dimensional, two-dimensional, and three-dimensional pore structures, depending on the arrangement of the channels. In addition, zeolitic materials have also been classified as low silica (Si/Al atomic ratio 1), intermediate silica (1.5 <Si/Al atomic ratio<10), or high silica (Si/Al atomic ratio> 10). Low silica zeolites are hydrophilic due to their high proton content and highly negatively charged framework. On the other hand, high silica zeolitic materials are hydrophobic due to a predominantly covalent Si-O-Si bridge. The NaA zeolite offers excellent CO2/N2 selectivity compared to FAU due to the narrow pore window. Many large porous zeolites with channels formed by openings of more than 12 rings are known, but all of them [4].

Gas adsorption is significant for the characterization of various porous materials. Of all the gases and vapours available and can be used as an adsorbent, nitrogen remains universally superior. With the help of easy-to-use commercial equipment and online data processing, it is now possible to use nitrogen adsorption at 77 K for routine quality control and investigation of new materials. Synthetic zeolites from natural materials often produce products with a mixture of crystalline phases such as sodalite, zeolite A and X, and amorphous, so it is essential to evaluate the synthesized product using the N2 physical adsorption method. Information on the surface area provides information about the surface area formed, the pore distribution provides information about the size distribution of the formed pores. For this purpose, several approaches were used as the most useful evaluation tool for the synthesized zeolite [5].

2. Method
Gas adsorption manometry is a method commonly used to determine nitrogen adsorption isotherms at liquid nitrogen temperature (77 K), volumetric determinations (or as the BET volumetric method). Successive amounts of adsorption are introduced, and at each stage, the system is given sufficient time to reach equilibrium, which is adjusted by a series of single points on the adsorption isotherm.

Adsorption is carried out for measurements at relative external pressures. However, since the filling of the molecular dimension micropores (i.e. ultramicropores) occurs at p/p0 10-4, it is necessary to carry out high-resolution adsorption measurements to assess primary micropore filling. Therefore, sample controlled thermal analysis was used to determine the adsorption isotherm, using Micromeritics ASAP 2020, with liquid nitrogen (N2) as the working fluid supplemented by helium (He) as filler and cleaning gas. Adsorption-desorption data processing using microactive software.

3. Results and Discussion
The synthesized zeolite X shows a crystalline phase of zeolite X, a crystalline phase of the faujasite type, as shown in Figure 1 shows a typical prismatic morphology of a faujasite zeolite crystal, but with impurities in the form of an amorphous phase and crystal zeolite A. Along with the length of hydrothermal time, zeolite A is formed. Hydrothermal time affects crystal growth. The longer the hydrothermal time, the higher the crystallinity produced, the smaller the size of the crystals formed. The crystallinity formed increases, and the type of phase formed changes with increasing hydrothermal time. Zeolite formed at the beginning of the hydrothermal period, namely zeolite A and faujasite (FAU). These two types of zeolite have a metastable structure, so they are replaced with zeolite P.

Various zeolite phases need to be confirmed using liquid nitrogen physisorption data to picture the structure and pore characteristics accurately. BET can provide surface area information, and further processing using a de-Boer t-plot can provide information on the abundance of internal and external pores. The study using BJH is expected to provide information if the zeolite X synthesized material
has meso-sized pores (2-50 nm), while DFT is used to determine the distribution of pore sizes below 2 nm.

![SEM of Zeolite X as synthesized from Bintan bauxite](image)

**Figure 1.** SEM of Zeolite X as synthesized from Bintan bauxite shows crystalline and amorphous phase.

Analysis of the SEM images presented in Figure 1 shows the morphology of zeolite X with a prismatic shape dotted with grains and a thin layer of an amorphous phase and a small amount of zeolite A in the form of cubes. The morphology shows the abundance of zeolite X due to the synthesis is the dominant phase and amorphous and zeolite A as mineral impurities. Characterization using gas adsorption-desorption is needed to provide an overview of the pore characteristics of the synthesized zeolite. The characterization results are presented in Figure 2.

![Isotherm adsorption-desorption of N2 at 77 K into as-synthesized Zeolite X from Bintan bauxite](image)

**Figure 2.** Isotherm adsorption-desorption of N2 at 77 K into as-synthesized Zeolite X from Bintan bauxite

Figure 2. shows the adsorption-desorption pattern of the as-synthesized zeolite is type I isotherm pattern. The adsorption-desorption pattern of the synthesized zeolite is the type I indicates that the
material is microporous. At low P/P₀, the adsorption showed this saturation, indicating that the pores followed the Langmuir adsorption model for micropores. An increase in pressure until P/P₀ is close to one does not indicate an increase in the volume of nitrogen gas absorbed. This indicates the absence of mesopore in the zeolite sample. The desorption process shows a small hysteresis, and this may come from the amorphous phase that forms macropores as the external surface. Further data processing using BET confirmed the existence of micropores, and data processing using the BJH and DFT equations showed pore characteristics.

**Figure 3.** BET plot N₂ physisorption of as-synthesized zeolite

**Figure 4.** Pore size distribution of as-synthesized zeolite X by BJH plot of desorption N₂ physisorption.
Figure 5. The pore size distribution of as-synthesized zeolite X by DFT plot of N\textsubscript{2} physisorption.

Figure 4 and Figure 5 show a graph of the desorption pattern of BJH and DFT, which shows the pore distribution of the synthesized zeolite sample. The BJH desorption graph shows that the zeolite synthesized in the mesoporous diameter is in the range of 40 Angstroms. This shows that the use of BJH to characterize the pores of the synthesized zeolite is not accurate, considering that the pore of zeolite X is at 13 Angstroms, while that of zeolite A is at 7 Angstroms. This discrepancy is due to the use of BJH, which has high accuracy for porous materials in the mesopore range but is less sensitive for use on microporous materials. Meanwhile, the DFT showed three peaks of the pore distribution at 14, 17 and 22 Angstroms. This shows a very close value to the theoretical, where zeolite X has a pore of 13 Angstroms. These results align with those obtained by other research groups in characterizing shale nanopores using the DFT equation [6].

4. Conclusions
The difference between the calculation results and the simulation of the pore distribution graph using BET, BJH, and DFT is quite significant, so it can be concluded that to analyze the distribution in the micropore range such as the synthesized zeolite, the DFT method is the most appropriate and superior model.

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