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Analysis of the Textural Characteristics and Pore Size Distribution of a Commercial Zeolite using Various Adsorption Models

¹Muhammad Afiq Aizzuddin Musa, ²Chun-Yang Yin and ¹Robert Mikhail Savory

¹Faculty of Chemical Engineering, Universiti Teknologi, Shah Alam, 40450 Selangor, Malaysia

²School of Chemical and Mathematical Sciences, Murdoch University, Murdoch, WA 6150, Australia

Abstract: Analysis of the textural characteristics and pore size distribution of a commercial zeolite (Sigma Aldrich, product No. 96096) have been conducted experimentally using a surface analyzer by measuring the N₂ adsorption isotherm at 77 K. The resulting data were fitted to several well-known adsorption models, i.e., the Brunauer-Emmett-Teller (BET) model, the de Boer model, the Dubinin-Redushkevich (DR) model, the Barret, -Joyner-Halenda (BJH) model, the Horvath-Kawazoe (HK) model and the Density Functional Theory (DFT) model. The zeolite was found to be highly microporous with a BET surface area of 609 m² g⁻¹. The HK model is rather limited in terms of pore volume distribution analysis and not appropriate for analysis of nanoporous materials that exhibit a wide porosity range compared to BJH and DFT model that cover much wider range (micropore, mesopore and macropore) than HK model that cover until micropore range.

Key words: Zeolite, brunauer-emmett-teller (BET), de boer, dubinin-redushkevich (DR), barret-joyner-halenda (BJH), horvath-kawazoe (HK), density functional theory (DFT)

INTRODUCTION

A zeolite is a hydrated aluminosilicate mineral composed of symmetrically stacked alumina and silica tetrahedra forming an open and stable three-dimensional structure with a negative charge (Sabeha *et al.*, 1994; Burgess *et al.*, 2003; Rozic *et al.*, 2000). Such materials possess natural porosity, because they exhibit crystal structures composed of windows, cages and supercages (USEPA, 1998), Zeolites can be classified into two types; natural and synthetic. Thus far, 40 variants of natural zeolites have been discovered while 118 synthetic zeolite types have been catalogued by the Structure Committee of the International Zeolite Association. The natural zeolites are limited in their window size (pore size) and are all hydrophilic (USEPA, 1998). Examples of natural zeolites include chabazite, clinoptilolite and mordenite (Virta, 1999). Synthetic zeolites are specifically developed for specific functions that aim to eliminate the limitations of natural zeolites. Zeolite-Y, zeolite-β and ZSM-5 are some of the synthetic zeolites commonly used in many applications and research (Cooper *et al.*, 2002). Some synthetic zeolites are similar to absorbent carbon materials (Barakat, 2008) since both can be considered as hydrophobic (having a high affinity for organics and a low affinity for water) and can adsorb organic vapors composed of molecules smaller than their pore sizes (USEPA, 1998; Marcilly, 2003).

Zeolites are highly versatile nanoporous materials used in various industrial applications. A good example is their usage in the field of catalysis where they are used as reaction media or carriers for reactive substances. They can also be used as molecular sieves (Donk *et al.*, 2003; Amokrane *et al.*, 2007; Karge and Weitkamp, 2008) due to their uniform pore sizes where chemical constituents can be selectively separated based on their molecular sizes. Other industries that use zeolites include water treatment, agriculture (soil treatment) (Abdi *et al.*, 2006; Al-Busaidi *et al.*, 2007; Khan *et al.*, 2008), dairy animal (improve the quality of the animal) (Bozkurt, 2006; Incharoen *et al.*, 2009) and construction (as an additive in cement) (Jana, 2007). They can also be used as gas storage materials (Donk *et al.*, 2003; Nijkamp *et al.*, 2001) and as a catalyst (Ahmed *et al.*, 2002; Hassan *et al.*, 2009). A very significant aspect of zeolites is their unique texture (surface area and pore volume). These textural characteristics dictate how well a particular zeolite type can function in a specific application.

The main objective of this study is to compare the textural characteristics of a commercial zeolite described by different adsorption models. The findings may be used to facilitate future selection of the best adsorption model to characterize the physical properties of zeolite-based adsorption systems.

MATERIALS AND METHODS

The textural characteristics (surface areas, pore size and pore volume) of an activated zeolite purchased from Sigma Aldrich (product No. 96096) were determined by measuring the N₂ adsorption and desorption isotherms at 77 K using a Quantachrome Autosorb-1 micropore surface area analyzer. The sample was degassed under vacuum at 120°C for 16 h prior to measurement in order to remove any residual moisture.

RESULTS AND DISCUSSION

N₂ adsorption isotherm and BET surface area: Figure 1 presents the N₂ gas adsorption/desorption isotherm for the zeolite at 77 K. The isotherm curve has a well-defined plateau and can be classified as Type 1 in accordance with the IUPAC classification (highly microporous). Primary adsorption occurs at low relative pressures (<0.1) which indicates the formation of a highly microporous material with the possibility of a narrow pore size distribution. The limiting uptake, in this case, is governed by the accessible micropore volume rather than the internal surface area (Sing *et al.*, 1985). The slightly enhanced uptake of N₂ at P/P₀ values greater than 0.9 suggests the presence of a small quantity of macropores (pores larger than 500 Å). The isotherm also exhibits a small degree of hysteresis, indicating the presence of some mesopores and the possibility of capillary condensation. The total accessible micropore volume present can be regarded as the adsorption space and the process by which this occurs is micropore filling in accordance with the IUPAC definition which is distinct from surface coverage which takes place on the walls of open macropores or mesopores (Sing *et al.*, 1985).

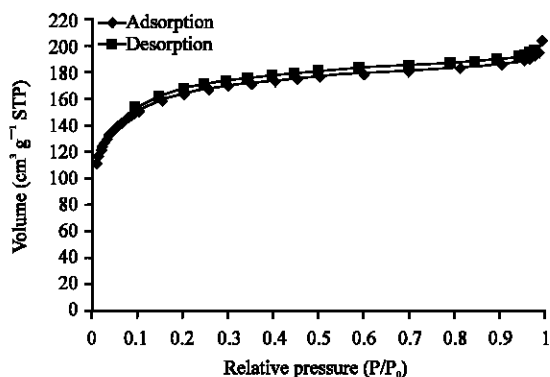


Fig. 1: Nitrogen gas adsorption/desorption isotherm for the zeolite at 77 K

The Brunauer-Emmett-Teller (BET) surface area has been experimentally determined to be 609 m² g⁻¹ which is significantly larger than those for natural porous materials, such as clay (10-100 m² g⁻¹) activated graphite (119 m² g⁻¹) and other types of zeolite and porous carbons (Rouquerol *et al.*, 2002).

T-method micropore analysis: Figure 2 presents the t-plot which corresponds to the presented N₂ adsorption/desorption isotherm in Fig. 1 from which the microporous textural properties have been determined with respect to the gradient and intercept. The micropore volume (De Boer *et al.*, 1966) micropore area and external surface area have been determined to be 8.74×10² cm³g⁻¹, 2.25×10² m² g⁻¹ and 3.84×10² m² g⁻¹, respectively. The De Boer model seems to describe the experimental isotherm data well with respect to the relatively high correlation coefficient value of 0.9699.

DR-method micropore analysis: Figure 3 presents the Dubinin-Redushkevich (DR)-plot for the zeolite also from which the microporous textural properties have been

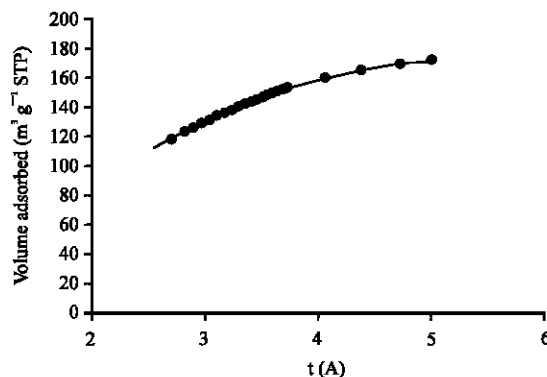


Fig. 2: T-plot for the zeolite

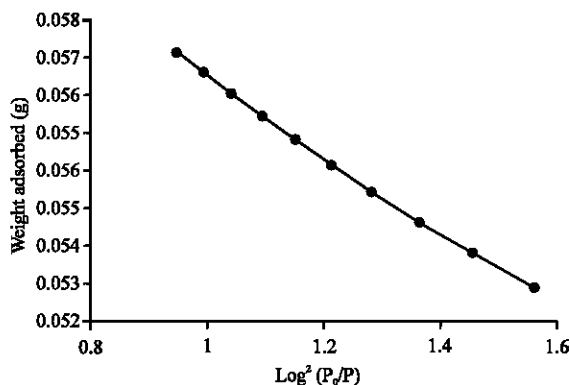


Fig. 3: DR-plot of the zeolite

determined with respect to the gradient and intercept. The micropore volume, micropore surface area and average pore width have been determined to be $2.70 \times 10^{-1} \text{ cm}^3 \text{ g}^{-1}$, $7.59 \times 10^2 \text{ m}^2 \text{ g}^{-1}$ and 40.63 \AA , respectively. The adsorption energy has been estimated to be 6.40 kJ mol^{-1} . With respect to the correlation coefficient value, 0.9990, it is indicative that the DR model describes the isotherm data better than the de Boer model.

Differential pore volume and surface area distributions:

Figure 4 presents the differential pore volume distributions expressed with respect to the Barret-Joyner-Halenda (BJH) model, the Horvath-Kawazoe (HK) model and the Density Functional Theory (DFT) model. The application of these models is a consequence of their extensive usage as in-built models by many surface

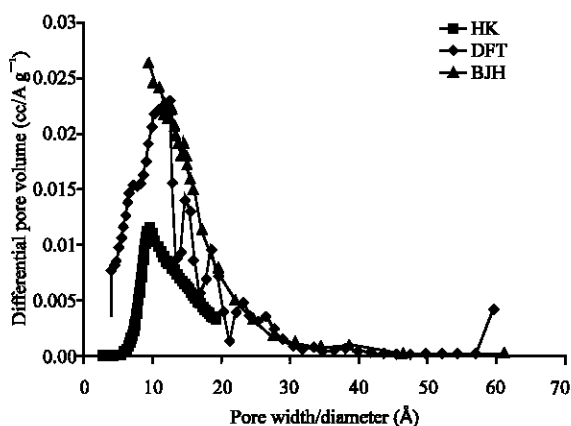


Fig. 4: Differential pore volume distributions determined using the HK, DFT and BJH models

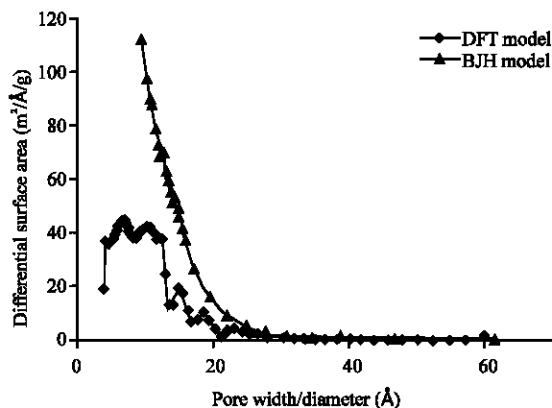


Fig. 5: Differential surface area distributions determined using the DFT and BJH models

analyzer systems. The classical pore size BJH model developed in 1951 which is based on the Kelvin equation and corrected for multilayer adsorption, is most widely used for calculations of the pore size distribution in the mesoporous and part of the macroporous range (Barrett *et al.*, 1951; Groen *et al.*, 2003). The HK model designed to describe the slit-shape pores frequently observed in carbon materials is primarily used to determine the pore sizes of predominantly microporous materials (Horvath and Kawazoe, 1983). The DFT model (Evans and Tarazona, 1984) is a complex quantum mechanical model that enables determination of the textural properties of porous materials with pores of all sizes with respect to the equilibrium density profile of a fluid in contact with a surface.

The results presented in Fig. 4 indicate that the HK model is limited with respect to the pore volume distribution analysis, since it only yields differential pore volume values within the microporous range. This limitation may be a consequence of assuming that the zeolite possesses a slit-shaped morphology and it can therefore be concluded that this model is inappropriate for the analysis of nanoporous materials that exhibit a wide porosity range. Both the BJH and DFT models evidently cover a far more extensive range of pore sizes, extending well into the mesoporous range, than the HK model.

Figure 5 presents the differential surface area distributions determined using the BJH and DFT models. The DFT surface area distribution curve exhibits an apparent plateau in the pore width range of 5-10 Å. The BJH model is more appropriate for the analysis of pores in the mesoporous range, hence it can be concluded that the DFT model may be more suitable for the analysis of materials exhibiting a wide range of porosities.

CONCLUSIONS

The textural characteristics and pore size distribution of a commercial zeolite, determined from an experimentally determined N_2 adsorption/desorption isotherm, have been evaluated with respect to various adsorption models. The zeolite has been found to be highly microporous with a BET surface area of $609 \text{ m}^2 \text{ g}^{-1}$ with respect to the de Boer and DR models. The HK model is limited with respect to pore volume distribution analysis and is therefore deemed inappropriate for the analysis of nanoporous materials exhibiting a wide porosity range. The BJH model appears unable to provide significant information pertaining to pore widths below approximately 10 \AA , hence it is concluded that

the DFT model may be more suitable for pore size distribution analysis of materials exhibiting a wide degree of porosity.

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