Performance of Dubinin-astakhov and Dubinin-raduchkevic Equations to Evaluate Nanopore Volume and Pore Size of MCM-41 Particles

N. Saeidi, M. Parvini*, M. R. Sarsabili

School of Chemical, Gas and Petroleum Engineering, Semnan University, Semnan, Iran

ABSTRACT

MCM-41 particles were synthesized using inorganic raw materials and Cetyltrimethylammonium bromide (CTAB). The textural properties and structure of MCM-41 particles were characterized by X-ray diffraction (XRD), scanning electron microscope (SEM), transmission electron microscope (TEM) and N₂ adsorption-desorption methods. To study performance of Dubinin-Astakhov and Dubinin-Raduchkevic isotherm models in evaluating mesopore volume and pore size of MCM-41, the mesopore volume and pore size of several MCM-41 samples were calculated by means of the two-mentioned isotherm models and by utilizing N₂ adsorption isotherms and XRD data. The results were compared with the mesopore volume and pore size calculated by other methods. The results showed that the calculated mesopore volume and pore size on the samples with the fraction of mesopore volume > 0.9 had not good consistency with XRD data and the results obtained by other methods. However, the calculated mesopore volume and pore size on the samples with the fraction of mesopore volume ≤ 0.9 were in good agreement with XRD data and other advanced simulation techniques.


NOMENCLATURE

\(w\) Represents the volume of adsorbate filling the micropores (cm³/g)
\(V\) Volume of pores
\(S\) Surface area
\(a_m\) Molecular area of nitrogen
\(V_{total}\) Total pore volume
\(D_{XRD}\) Mesopore diameter for MCM-41
\(V_p\) Mesopore volume
\(d_{XRD}\) XRD interplanar spacing
\(T\) Temperature
\(P/P_0\) Relative pressure
\(w_{0}\) Maximum volume of adsorbent per adsorbed mass (cm³/g)
\(\theta\) situation of the first low-angle peak
\(\lambda\) wavelength of Cu Ka radiation
\(m\) mass of an electron
\(E_0\) Characteristic energy of adsorption
\(P_0\) Saturation vapor pressure
\(R\) Universal gas constant
\(d_0\) Mean diameter of the adsorbate molecule
\(\Delta G\) Differential Gibbs energy of adsorption
\(A\) Differential molar work of adsorption
\(\rho\) Density of the silica
\(a_0\) Lattice parameter

*Corresponding Author’s Email: m.parvini@sun.semnan.ac.ir (M. Parvini)
1. INTRODUCTION

MCM-41 was introduced in 1992. Thereafter, there have been five major courses for studying this material. These entail characterization, mechanism of formation, synthesis of new materials based upon MCM-41, control of textural characterizations and various industrial applications [1, 2]. MCM-41 material is very interesting for many of researchers because its structural properties (mesopore structure) provides the pore size needed for different applications i.e., catalysts for various fine chemical syntheses and adsorbing a relatively wide range of size of molecules of gas and liquid [2, 3]. Therefore, it is very vital to control and examine morphology of MCM-41. The textural properties of MCM-41 are very often determined by gas (N$_2$) adsorption isotherm and XRD data [2, 4-8].

The empirical form of an adsorption isotherm was identified in 1926 by Freundlich [9] and later deduced theoretically from the Langmuir equation [10] extended into heterogeneous surfaces considered to be a composite theoretically from the Langmuir equation [10] extended by Freundlich [9] and later deduced by J. J. Teller (BET) equation was derived for multilayer adsorption [12]. It is clear that together with the concept of multilayer adsorption (leading to the BET equation) the theory of volume filling of micropores is one of the most motivating concepts taking up the principal position in adsorption science [13]. Based on the Weibull distribution of adsorption potential, the introduced equation by M. M. Dubinin [13] was considered to be a semi-empirical one. The basic relations are the Dubinin–Astakhov (DA) and Dubinin–Raduchkevic (DR) equations [14, 15]. The DA and DR equations have very often been applied for evaluating micropore volume of porous material such as activated carbon. In such works, the mesopore volume of sample was obtained by subtracting the total pore volume and the micropore volume of a sample [16-18]. The mesopore volume of MCM-41 was frequently calculated by Barrett–Joyner–Halenda (BJH) method [4-6, 19]. It is worthy to say using DA and DR equations to calculate mesopore volume and pore size of MCM-41 samples is swift and neat, and also the respective procedure to reach the desired results by these two models is easier and faster than that of BJH method. However, there is a questionable matter about accuracy in such functions. To the best of our knowledge, performance of using DA and DR equations to calculate mesopore volume and pore size of MCM-41 particles has not been examined yet.

In the present study, the MCM-41 particles were synthesized. XRD pattern, N$_2$ adsorption-desorption isotherm, TEM and SEM were applied to examine the crystal structure, morphology and porosity of the synthesized MCM-41. Then, the mesopore volume and pore size of several MCM-41 samples were calculated using Dubinin–Astakhov and Dubinin–Raduchkevic equations. For this purpose, nitrogen adsorption isotherms and XRD data were used. Finally, the results were compared with the mesopore volume and pore size calculated using other methods.

2. EXPERIMENTAL

2. 1. Material Cetyltrimethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS), aqueous ammonia (25% w/w) and ethanol (96%) were purchased from Merck. Deionized water was used as the main solvent. All chemicals were used in as-purchased condition without further purification.

2. 2. Synthesis of MCM-41 Particles The mesoporous silica was synthesized following the procedure reported by Grun et al. [20] with several alterations. In this synthesis, the source of silicon was tetraethylorthosilicate (TEOS) and the structure-directing agent was Cetyltrimethylammonium bromide (CTAB). The surfactant (15.1 g) was dissolved in deionized water (100.02 g) in ambient condition. Then, the ammonia solution (37.38 ml) was added to the solution. After about 10 min stirring at 200 rpm, a clear solution was obtained. Afterward, Ethanol (151.89 ml) was added to the solution. After about 20 min, TEOS (4 ml) was slowly added to the clear solution. The resulting milky solution was stirred at 200 rpm for 2 hours. Finally, the white precipitate was filtered and washed with deionized water and then dried at 100 $^\circ$C for 48 hours. The silicate powder was calcined in air at 550 $^\circ$C for 6 hours with 1 $^\circ$C min$^{-1}$ of heating rate to remove the CTAB.

2. 3. Characterization The XRD patterns were obtained by using a PW1840 diffractometer employing Cu K$_\alpha$ radiation ($\lambda = 1.54056$ Å), $\theta$–$2\theta$ geometry and a scintillation detector. The diffraction pattern was recorded at 0.04$^\circ$ steps and 0.5 second per step. The measurements were made in ambient conditions. A morphological characterization of the MCM-41 was carried out with a scanning electron microscope (MIRA//TESCAN). The transmission electron micrographs (TEM) were attained on a Philips (CM120) transmission electron microscope device with a field emission gun at an acceleration voltage of 120 kV. The nitrogen adsorption and desorption isotherms for the MCM-41 sample was measured at $-196$ $^\circ$C on a Belsorp 18 (BEL Japan, Ltd.). The sample was heated at 200 $^\circ$C for 2 hours and degassed overnight. The specific surface area was determined by the Brunauer–Emmet–Teller (BET) method [11] using $a_m$ (N$_2$ = 16.2 Å$^2$), where, $a_m$ is the molecular area of nitrogen at $-
3. THEORETICAL APPROACH

The isotherm models, Dubinin-Astakhov and Dubinin-Raduchkevic equations are given respectively, in the following forms [14, 15]:

\[
w = w_0 \exp \left[ -\left( \frac{A}{\beta E_r} \right)^n \right]
\]

(1)

\[
w = w_0 \exp \left[ -\left( \frac{A}{\beta E_r} \right)^n \log \left( \frac{P}{P_0} \right) \right]
\]

(2)

In Equations (1) and (2), \( w \) represents the volume of adsorbate filling the micropores in the unit mass of adsorbent (cm\(^3\)/g), at temperature \( T \) and relative pressure \( P/P_0 \), where \( w_0 \) is the maximum volume of adsorbent per adsorbed mass, the micropore volume (cm\(^3\)/g). Also, \( B \) is a parameter characterizing the microporous structure; \( \beta \) is the affinity coefficient of the characteristic curves; \( E_r \) is the characteristic energy of adsorption. The constant \( n \) is an equation parameter and \( A \) is the differential molar work of adsorption i.e., the differential Gibbs energy of adsorption, \( \Delta G \), which is defined by Equation (3) as follows [14]:

\[
A = -\Delta G = RT \ln \left( \frac{P}{P_0} \right)
\]

(3)

It must be noted that the DA equation is valid at the micropore filling mechanism, over a range of \( N_2 \) relative partial pressure \( P/P_0 \) varying from 0.01 to 0.30 [12, 16]. Accordingly, the BET surface area of the MCM-41 was calculated on this range of relative partial pressure. The mesopore volume and the pore size of MCM-41 were determined based on BJH method [20]. The mean pore diameter was also calculated using \( D = 4V/S \) [21], where \( V \) is the volume of pores, and \( S \) the surface area. The total pore volume, \( V_{\text{total}} \), was obtained using the adsorbed nitrogen at a relative pressure \( P/P_0 \) of approximately 0.09.

\[D = \frac{2d_{100}}{\lambda} \]

(5)

where, \( d_{100} \) is the XRD interplanar spacing calculated by Equation (6)[22, 23]:

\[
d_{100} = \frac{\lambda}{2\sin \theta}
\]

(6)

where, \( \lambda \) is the wavelength of Cu Ka radiation and \( \theta \) the location of the first low-angle peak \( ^0 \).

In Equation (4), the mesopore volume, \( V_p \), can be calculated using various methods including BJH method. The mesopore volume can also be computed by subtracting the total pore volume of sample, \( V_{\text{total}} \), from the micropore volume of sample obtained by both DA and DR models, \( w_0 \). Therefore, Equation (4) is rewritten as follows [6]:

\[
D = C \alpha \left( \frac{\rho (V_{\text{mic}} - w_0)}{1 + \rho (V_{\text{mic}} - w_0)} \right)
\]

(7)

where, \( C \), \( w_0 \), \( \alpha \), and \( \rho \) parameters are the same as the parameters introduced in Equations (4), (1), (5) and (4), respectively. Also, \( V_{\text{total}} \) denotes total pore volume of the sample.

4. RESULT AND DISCUSSION

4.1. Characterization of MCM-41 Particles

XRD experiment was performed to determine the specific structure of the sample. The result of XRD analyses are illustrated in Figure 1. It can be deduced that the structure of MCM-41 particles is very well arranged and has the same patterns as the MCM-41 synthesized by other authors [2, 24-27]. The major characterization of MCM-41 can be studied from presence of three distinctive reflections at 2\( \theta \) equal to 2.2, 4.6 and 5.8 which corresponded to hkl reflection planes 100, 110 and 200, respectively. This means that the synthesized sample has a hexagonal and regular array [27].

The morphology, shape, and approximate particle size of MCM-41 sample were characterized by scanning electron microscope. As can be seen in Figures 2a and b, the synthesized MCM-41 sample has a narrow particle size distribution and uniformly spherical particles. Also, it can be said that the particle size of sample is approximately less than 1000 nanometers. Figure 3 presents transmission electron micrographs of the synthesized MCM-41. The internal morphology observed in Figure 3 shows a uniform pore size on the sample.
Figure 1. XRD pattern of synthesized MCM-41 particles.

Figure 2. SEM micrographs of synthesized MCM-41 particles: (a) 10.00 kx, (b) 50.00 kx.

Figure 3. TEM view of synthesized MCM-41 particles.

Figure 4a illustrates nitrogen adsorption-desorption isotherm of the synthesized MCM-41, sample S. It can be seen that the sample behaves as mesoporous material during nitrogen adsorption-desorption experiment. The aforementioned behavior is according to IUPAC categorization [28]. A linear increment in nitrogen adsorption takes place at relatively low relative pressures due to monolayer adsorption before the steep nitrogen uptake inside the mesopores. Accordingly, there is micropore filling at low relative pressure. Afterward, at higher pressures an extended multilayer zone and a sharp pore condensation stage can be observed. The steep gas uptake is due to the capillary condensation of nitrogen inside the mesopores. This implies that the synthesized MCM-41 has a narrow pore size distribution. This matter is consistent with the results obtained from XRD experiment. The adsorption and desorption curve demonstrates an obvious loop (type H1 by IUPAC categorization) corresponding to capillary condensation and evaporation on open cylindrical pores at each ends. Furthermore, the higher relative pressure for the capillary condensation is associated with the larger pore size [29]. Tzong-Horng Liou [4] synthesized MCM-41 materials by means of the resin waste at varied hydrothermal operation times and temperatures, molar ratios of water to surface agents (CTAB), gelation pH, and drying temperatures.

Figure 4b shows the nitrogen adsorption-desorption isotherms for (b) the data reported by Tzong-Horng Liou [4], and (c) the data reported by Favas et al. [6].

Figure 5. Change trend of the error difference $\Delta$ versus the fraction of mesopore volume.
Thus, the adsorption isotherms were fitted using partial pressure (Equation (2)) is valid over two ranges of $N_2$, that is, $P/P_0$ varying from 1E-7 to 0.02 and 0.02 to 0.1, respectively. Table 2 presents the results of the micropore volume $V_{\text{p}}$, from fitting the adsorption isotherms of samples S, S1, S2, S3 and S4 to both the DA and DR equations. With attention to the correlation coefficients, $R_2$, it can be deduced that the adsorption isotherms have properly correlated to both isotherm models.

Table 1 lists the textural properties and the XRD data of samples S, S1, S2, S3 and S4. As can be seen in Table 1, the properties of the synthesized MCM-41 sample S are very close to other samples. However, the BET surface area of the sample S is higher than samples S1, S2 and S3. Also, the mean pore size, $D_p$, of sample S is the lowest among the other samples. The interplanar distance, $d_{001}$, and the lattice parameter, $\alpha_0$, also were calculated and reported in Table 1.

4.2. Analysis of Theoretical Approach

As mentioned earlier, the DA equation (Equation(1)) is valid over a range of $N_2$ relative partial pressure $P/P_0$ varying from 1E-7 to 0.02, and the DR equation (Equation (2)) is valid over two ranges of $N_2$ relative partial pressure $P/P_0$ varying from 1E-7 to 0.02 and 0.01 to 0.1. Thus, the adsorption isotherms were fitted to the DA and DR equations over ranges of $N_2$ relative partial pressure varying from 1E-7 to 0.02 and 0.01 to 0.1, respectively. Table 2 presents the results of the micropore volume $V_{\text{p}}$, from fitting the adsorption isotherms of samples S, S1, S2, S3 and S4 to both the DA and DR equations. With attention to the correlation coefficients, $R_2$, it can be deduced that the adsorption isotherms have properly correlated to both isotherm models.

Table 1. Structural parameters of the MCM-41 samples under study

<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>$V_{\text{total}}$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\text{p}}$ (cm$^3$ g$^{-1}$)</th>
<th>$D_p$ / Å</th>
<th>$d_{001}$ / Å</th>
<th>$\alpha_0$ / Å</th>
<th>Reference Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1163</td>
<td>0.903</td>
<td>0.814$^a$</td>
<td>30.9</td>
<td>40.1</td>
<td>46.3</td>
<td>Present work</td>
</tr>
<tr>
<td>S1</td>
<td>696</td>
<td>0.649</td>
<td>0.617$^b$</td>
<td>37.3</td>
<td>37.9</td>
<td>43.8</td>
<td>[4]</td>
</tr>
<tr>
<td>S2</td>
<td>860</td>
<td>0.744</td>
<td>0.717$^b$</td>
<td>34.4</td>
<td>38.4</td>
<td>44.3</td>
<td>[4]</td>
</tr>
<tr>
<td>S3</td>
<td>1033</td>
<td>0.887</td>
<td>0.859$^b$</td>
<td>34.0</td>
<td>37.5</td>
<td>43.3</td>
<td>[4]</td>
</tr>
<tr>
<td>S4</td>
<td>1205</td>
<td>0.981</td>
<td>0.754$^b$</td>
<td>32.5</td>
<td>35.8</td>
<td>41.4</td>
<td>[6]</td>
</tr>
</tbody>
</table>

Abbreviations: $S_{\text{BET}}$, BET specific surface area; $V_{\text{total}}$, total pore volume; $V_{\text{p}}$, micropore volume; $D_p$, mean pore diameter; $d_{001}$, interplanar distance; $\alpha_0$, lattice parameter.

$^a$ Adsorbed nitrogen at a relative pressure ($P/P_0$) of approximately 0.99.

$^b$ Value assessed by BJH method.

$^c$ Value assessed by a plot [32].

$^d$ Value assessed using $4V_{\text{total}}/S_{\text{BET}}$.

Table 2. DA and DR’s $w_0$ of the MCM-41 samples under study

<table>
<thead>
<tr>
<th>Sample</th>
<th>$w_0^{\text{DA}}$ (cm$^3$ g$^{-1}$)</th>
<th>$w_0^{\text{DR}}$ (cm$^3$ g$^{-1}$)</th>
<th>$R_2^{\text{DA}}$</th>
<th>$R_2^{\text{DR}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.162</td>
<td>0.226</td>
<td>0.981</td>
<td>0.983</td>
</tr>
<tr>
<td>S1</td>
<td>-</td>
<td>0.192</td>
<td>-</td>
<td>0.986</td>
</tr>
<tr>
<td>S2</td>
<td>-</td>
<td>0.231</td>
<td>-</td>
<td>0.967</td>
</tr>
<tr>
<td>S3</td>
<td>-</td>
<td>0.275</td>
<td>-</td>
<td>0.987</td>
</tr>
<tr>
<td>S4</td>
<td>0.198</td>
<td>0.277</td>
<td>0.987</td>
<td>0.972</td>
</tr>
</tbody>
</table>

Abbreviations: $w_0^{\text{DA}}$, the micropore volume calculated using DA equation; $w_0^{\text{DR}}$, the micropore volume calculated using DR equation; $R_2^{\text{DA}}$, Correlation coefficient in fitting the isotherm data to DA equation; $R_2^{\text{DR}}$, Correlation coefficient in fitting the isotherm data to DR equation.

Table 3. Mesopore volume of MCM-41 samples under study

<table>
<thead>
<tr>
<th>Sample</th>
<th>$V_\ell$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\ell1}$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\ell2}$ (cm$^3$ g$^{-1}$)</th>
<th>$V_{\text{total}}$ (cm$^3$ g$^{-1}$)</th>
<th>$\Delta V_{\ell1}$</th>
<th>$\Delta V_{\ell2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>0.814</td>
<td>0.741</td>
<td>0.677</td>
<td>0.9</td>
<td>8</td>
<td>16</td>
</tr>
<tr>
<td>S1</td>
<td>0.617</td>
<td>-</td>
<td>0.457</td>
<td>0.95</td>
<td>-</td>
<td>25</td>
</tr>
<tr>
<td>S2</td>
<td>0.717</td>
<td>0.513</td>
<td>0.96</td>
<td>-</td>
<td>28.4</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>0.859</td>
<td>-</td>
<td>0.612</td>
<td>0.97</td>
<td>-</td>
<td>28.7</td>
</tr>
<tr>
<td>S4</td>
<td>0.754</td>
<td>0.783</td>
<td>0.704</td>
<td>0.77</td>
<td>3</td>
<td>6</td>
</tr>
</tbody>
</table>

Abbreviations: $V_\ell$, the mesopore volume obtained by subtracting $V_{\text{total}}$ from $w_0^{\text{DA}}$, $V_{\ell1}$, the mesopore volume obtained by subtracting $V_{\text{total}}$ from $w_0^{\text{DR}}$.

$\Delta V_{\ell1} = V_{\ell1} - V_{\ell2}$

$\Delta V_{\ell2} = V_{\ell2} - V_{\text{total}}$

$\% \Delta V_{\ell1} = \left( \frac{V_{\ell2} - V_{\ell1}}{V_{\ell2}} \right) \times 100$
In this study, the mesopore volume of samples were calculated by subtracting \( V_{\text{total}} \) from \( V_b \) and compared with the obtained mesopore volume using other methods. Table 3 summarizes the results. As can be seen in Table 3, with increasing the fraction of mesopore volume, \( \Delta \) is increased (Figure 5). Additionally, on samples S1, S2 and S3, with the fraction of mesopore volume \( > 0.9 \), the error difference \( \Delta \) is higher than 20%. Likewise, the lowest error difference \( \Delta \), around 5%, is observed on sample S4, its fraction of mesopore volume is equal to 0.77. Finally, it can be said that on the samples with the fraction of mesopore volume \( \leq 0.9 \), the calculated mesopore volumes have good consistency with the mesopore volumes obtained from other methods.

Also, with attention to the results of samples S, S4, S1 and S2, \( \Delta P_b \) and \( \Delta P_d \), it can be said that the mesopore volume obtained using DA model; \( V_{P_{1}} \), is more consistent than the one calculated by DR model; also, \( V_{P_{2}} \), with that obtained using BJH and \( \alpha_p \) plot methods.

Equations (4) and (7) were applied to calculate the pore diameter of samples. In fact, the mentioned calculations were performed to examine that whether the obtained pore diameter of samples using Equation (7) would be consistent with the calculated pore diameter of samples by Equation (4) and also with the results using other methods.

It must be mentioned that in Equation (4) \( V_q \) values were used as mesopore volume (see Table 1). Table 4 shows the results. As can be seen in Table 4, in all samples, the pore diameters calculated by Equation (7) have good consistency, \( \Delta_{V_{DA}} \), with the obtained pore diameter using Equation (4). Moreover, the consistency on samples S and S4, with the fraction of mesopore volume \( \leq 0.9 \), is better than that of other samples, with the fraction of mesopore volume \( > 0.9 \).

Likewise, the calculated pore diameters of samples S and S4 using Equation (7) are very close, \( \Delta_{Eq_{7}} \) and \( \Delta_{Eq_{7}} \), to the obtained pore diameter of the samples by BJH and NLDFT methods, respectively. However, these consistencies on sample S4 are further, the error differences \( \Delta \) are lower, than sample S.

### 5. CONCLUDING REMARKS

Evaluation of mesoporosity and pore size of MCM-41 particles by an accurate method is very important. BJH method are very often used for the purpose. The method is somewhat complicated and time consuming. Therefore, using a simpler and faster method instead of BJH is very useful. DA and DR equations can be used to calculate the mesoporosity of the MCM-41 samples. The procedure are swift and neat. However, accuracy of the methods to assess mesopore volume and pore size of the MCM-41 particles have not been studied yet. In this study, the mesopore volume and pore size of several MCM-41 samples were calculated using Dubinin-Astakhov and Dubinin-Radushkevich isotherm models and by utilizing nitrogen adsorption isotherms and XRD data. The results were also compared with the mesopore volume and pore size calculated by other methods. It was concluded when fraction of mesopore volume is higher than 0.9 the calculated mesopore volume and pore size of the samples were in good consistency with XRD data and other advanced simulation techniques.

### 6. REFERENCE


2. Anbia, M., and Davijani, H.A. and "Preparation and structural characterization of a novel nanoporous carbon (cmk-3) functionalized with ethylenediamine its use in removal of cu(ii) and pb(ii) ions from aqueous media", *International Journal of*


Studying Performance of Dubinin-astakhov and Dubinin-raduchkevic Equations to Evaluate Nanopore Volume and Pore Size of MCM-41 Particles

N. Saeidi, M. Parvini, M. R. Sarsabili

School of Chemical, Gas and Petroleum Engineering, Semnan University, Semnan, Iran

PAPER INFO

Paper history:
Received 15 February 2014
Received in revised form 18 June 2014
Accepted 26 June 2014

Keywords:
Nitrogen Isotherm Data, MCM-41
Dubinin-astakhov and Dubinin-Raduchkevic Equations
Nanopore (Mesopore) Volume
Pore Size

doI: 10.5829/idosi.ije.2014.27.10a.04