Adsorption properties and porous structure of sulfuric acid treated bentonites determined by the adsorption isotherms of benzene vapor

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Abstract: In a previous paper, adsorption isotherms of benzene vapor on natural bentonite from Ginovci, Macedonia, and forms acid activated with 10% and 15% solutions of hydrochloric were interpreted by means of the Dubinin–Radushkevich–Stoeckli and Dubinin–Astakhov equations; the investigation has been continued with bentonites acid activated with 10% and 15% solutions of sulfuric acid where X-ray analysis indicates smaller structural changes. Using the above equations, the heterogeneity of the micro-pores and the energetic heterogeneity of the bentonites were determined from the differential distribution of the micropore volume with respect to the structural parameter of the equations characterizing the microporous structure and to the molar free energy of adsorption. Activated bentonites obtain bigger pores but also a certain quantity of new small pores appear during acid activation with the higher concentration of acid. The micropore volumes, determined from the adsorption of benzene vapor, of bentonites treated with 10% and 15% solution of hydrochloric acid (144.60 cm³ kg⁻¹ and 110.06 cm³ kg⁻¹, respectively), decrease in comparison with that of natural bentonite (162.55 cm³ kg⁻¹). In contrast, the values of the micropore volume for bentonites treated with 10% and 15% solutions of sulfuric acids increase (169.19 cm³ kg⁻¹ and 227.74 cm³ kg⁻¹). That is due to the difference in the structural changes occurring during activation with hydrochloric and sulfuric acids. The values of the free energy of adsorption of benzene vapor for natural bentonite are higher than those of the acid activated bentonites, what is in accordance with the structural and porosity changes.

Keywords: adsorption, benzene, bentonite, chemical activation, Dubinin–Radushkevich–Stoeckli and Dubinin–Astakhov equations.

INTRODUCTION

Acid treated bentonites have been used as effective adsorbents and solid acid catalysts for many years. In order to remove impurities and various exchangeable cations and to produce a homogeneous and well defined material, natural bentonite have been treated in different ways, most frequently with inorganic acids.
Montmorillonite, the basic mineral in bentonite, belongs to a group of microporous adsorbents.\textsuperscript{4,5} Dubinin and his co-workers\textsuperscript{6,7} describe adsorption by microporous adsorbents with the theory of volume filling of micropores. The heterogeneity of the microporous structure and the energy heterogeneity are important characteristics of an adsorbent. The heterogeneity of the micropore structure, related to the dimensions of micropores, and the energetic heterogeneity of the micropores of adsorbents depend on their pore size distribution and the nature of the active adsorption centers. The energetic heterogeneity, in most cases, is a direct consequence of the geometric heterogeneity. Therefore, the consideration of the structural and energetic heterogeneities separately in the sense of adsorption phenomenon in porous adsorbents is connected with some uncertainties.\textsuperscript{8}

In a previous paper,\textsuperscript{1} natural and bentonites acid activated with 10 % and 15 % solutions of HCl were analyzed. As a result of the changes in the montmorillonite structure, the micropore volume of the acid activated bentonites decreased compared with that of natural bentonite. The investigation has been continued in this work with bentonites acid activated with 10 % and 15 % solution of sulfuric acid where X-ray analysis\textsuperscript{9} indicates smaller structural changes occur. The adsorption isotherms of benzene vapor on the bentonites have been analyzed by means of the Dubinin–Radushkevich–Stoeckli and Dubinin–Astakhov equations.\textsuperscript{1,8}

The distribution of the micropore volume, \( W_0 \), with respect to the parameter \( B \) (parameter characterizing the microporous structure) can be expressed by a Gaussian distribution function.

The Dubinin–Radushkevich–Stoeckli equation is applied for the determination of the degree of structural heterogeneity of natural and acid activated bentonites.
The linear form of the Dubinin–Astakhov equation is:
\[
\ln W = \ln W_0 - \frac{A n}{E_0^n}
\]
where \( A \) is the differential molar work of adsorption, \( \text{i.e.} \), the change of the Gibbs free energy of adsorption, \( E_0 \) is a characteristic energy of adsorption and \( n \) is an equation parameter.

The mode and mean values of the differential molar work of adsorption can be calculated from the following expressions:\(^{10}\)
\[
A_{\text{mode}} = \beta E_0 \left( \frac{n-1}{n} \right)^{1/n}
\]
\[
A_{\text{mean}} = \beta E_0 \Gamma \left( \frac{1}{n} + 1 \right)
\]
where \( \Gamma \) is the gamma function.

The present paper describes an attempt to determine the adsorption properties of bentonite acid activated with a 10 % solution and with a 15 % solution of sulfuric acid. For comparison, the values of the parameters for bentonites activated with a 10 % solution of HCl (B10Cl) and a 15 % solution of HCl (B15Cl), as well as for natural bentonite are also presented.

EXPERIMENTAL

Natural bentonite from Ginovci, Macedonia (in the text labeled as B) has the following chemical composition: SiO\(_2\) 68.22 %, Al\(_2\)O\(_3\) 21.32 %, Fe\(_2\)O\(_3\) 3.21 %, MgO 4.15 %, CaO 2.03 %, Na\(_2\)O 0.40 %, K\(_2\)O 0.40 %, H\(_2\)O + CO\(_2\) 8.06 %. The montmorillonite contents of the bentonite is around 85 % and has a monoclinic structure. Mg\(^{2+}\) and Ca\(^{2+}\) are the most abundant natural interlayer cations.\(^{11}\)

Bentonite, with a particle size less than 0.2 mm and dried at 105 °C, was treated with 10 % and 15 % sulfuric acid (labeled as B10S and B15S, respectively), by a standard procedure.\(^{4}\)

According to X-ray analysis, the changes in the montmorillonite structure are more expressed for samples that were treated with hydrochloric acid.\(^{9}\)

Adsorption isotherms of benzene vapor on the natural and acid activated bentonites were determined by a modified flow method.\(^{1}\)

RESULTS AND DISCUSSION

The parameters of the Dubinin–Radushkevich–Stoeckli and Dubinin–Astakhov equations were determined from linear forms, Eqs. (1) and (5). The values of \( y \) and \( z \) were calculated using Eqs. (3) and (4), the parameter \( B \) was accepted from the Dubinin–Radushkevich equation as a first approximation for the value of \( B_0 \).\(^{8}\) Using different values of \( \Delta \), the data of \( W^* \) were calculated. The value of \( \Delta \) which gave the best agreement between the experimental data and the Dubinin–Radushkevich–Stoeckli equation was selected.

The values of the parameters of the equations for B10S and B15S, as well as those for B, B10Cl and B15Cl are listed in Tables I and II.

The micropore volume, determined from the adsorption of benzene vapor on the bentonites activated with 10 % and 15 % solutions of hydrochloric acid, Table I,
are smaller than that for natural bentonite. On the other hand, the values of the micropore volume for the bentonites treated with 10 % and 15 % solutions of sulfuric acids are higher. This is due to differences in their structural changes occurring during activation with hydrochloric and sulfuric acids. The X-ray analysis show that the bentonites treated with the 10 % and 15 % solutions of HCl have a more destroyed structure compared with those of bentonites treated with the corresponding concentrations of H$_2$SO$_4$ solutions. This was confirmed by chemical analysis of the acid activated bentonites.

<table>
<thead>
<tr>
<th>Bentonite</th>
<th>$W_o^0 / \text{cm}^3 \text{ kg}^{-1}$</th>
<th>$\Delta / K^2$</th>
<th>$B_0 / K^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>162.55</td>
<td>1.4x10^{-6}</td>
<td>1.4x10^{-6}</td>
</tr>
<tr>
<td>B10Cl</td>
<td>144.60</td>
<td>1.6x10^{-6}</td>
<td>6.1x10^{-6}</td>
</tr>
<tr>
<td>B15Cl</td>
<td>110.06</td>
<td>2.4x10^{-6}</td>
<td>5.2x10^{-6}</td>
</tr>
<tr>
<td>B10S</td>
<td>169.19</td>
<td>2.6x10^{-6}</td>
<td>7.7x10^{-6}</td>
</tr>
<tr>
<td>B15S</td>
<td>227.24</td>
<td>2.8x10^{-6}</td>
<td>6.5x10^{-6}</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bentonite</th>
<th>$n$</th>
<th>$E_o / \text{kJ mol}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>3.0</td>
<td>8.09</td>
</tr>
<tr>
<td>B10Cl</td>
<td>3.0</td>
<td>7.74</td>
</tr>
<tr>
<td>B15Cl</td>
<td>1.0</td>
<td>7.93</td>
</tr>
<tr>
<td>B10S</td>
<td>2.2</td>
<td>7.10</td>
</tr>
<tr>
<td>B15S</td>
<td>1.7</td>
<td>7.66</td>
</tr>
</tbody>
</table>

Treatment with the solutions of HCl (especially the 15 % HCl one), in addition to dissolving the admixtures (dolomite, calcite, biotite, etc.), result in the montmorillonite structure becoming a disordered montmorillonite silicagel one. Such a change of the montmorillonite structure during acid activation can be the reason for the decrease of the amount of remanent water after drying and the limited penetration of the benzene molecules, which is more expressed for the B15Cl sample.

On the other hand, the treatment of natural bentonites with 10 % and 15 % solutions of H$_2$SO$_4$ results in samples without the admixture (with a higher percent of montmorillonite) and with only small structural changes. Therefore, probably, the results of the adsorption of the benzene vapor show that after activation with 10 % and 15 % solutions of H$_2$SO$_4$, the micropore volume increases.

The dispersion $\Delta$ increases from B to B15Cl and from B to B15S, which means that the degree of microporous heterogeneity increases in the same direction.

The pore sizes after acid treatment of bentonite are bigger (the value of $B_0$ in Table I). There is a possibility that the smaller increase of the pore sizes for B15Cl and B15S as compared with B10Cl and B10S is the result of the appearance of a
certain number of small new pores during acid activation with the higher concentration acids. The same assumption can be made for the small increase of the characteristic energy of adsorption $E_0$ for samples B15Cl and B15S, listed in Table II. $E_0$ is an indirect measure of the pore size, it increases when the pore size decreases.

The adsorption isotherms of benzene vapor on B10S and B15S according to the Dubinin–Radushkevich–Stoeckli and the Dubinin–Astakhov equations are presented in Fig. 1 and 2, respectively. The remarkably good fit of the experimental isotherm to the equations is evidenced by the linearity of the plots.

Fig. 1. Adsorption isotherms of benzene vapor on bentonites, plotted according to the Dubinin–Radushkevich–Stoeckli equation.

Fig. 2. Adsorption isotherms of benzene vapor on bentonites, plotted according to the Dubinin–Astakhov equation.
The differential distribution curves of volume filling of the micropores with respect to the parameter $B$, determined from Eq. (1), are presented in Fig. 3.

From Fig. 3 it is evident that the natural bentonite has more a homogeneous micropore structure as compared with acid activated ones. The differential distribution curves of volume filling of the micropores for the acid activated bentonites are shifted to the region of the bigger pores, which is more expressed for B10S. This shows that B10S and B15S have bigger pores than natural bentonite.

As the adsorption equilibrium is governed by the free energy of adsorption, the energetic and structural heterogeneities of microporous adsorbents can be determined from the differential distribution of volume filling of the micropores with respect to the differential molar work of adsorption (i.e., the free energy change of adsorption).

![Fig. 3. Differential distribution of micropore volume with parameter $B$.](image)

![Fig. 4. Differential distribution of micropore volume with free energy of adsorption.](image)
adsorption). The energetic characteristics of the B, B10S, and B15S samples obtained from their differential distribution of micropore volume, \(W\), with a differential molar work of adsorption, \(A\), are presented in Fig. 4.

The broader distributions of the acid activated bentonites, B10S and B15S indicates that they have a higher degree of energetic heterogeneity than natural bentonite because of their more developed porous structure.

The mode, \(A_{\text{mode}}\), and mean, \(A_{\text{mean}}\), values of the differential molar work of adsorption in this distribution were evaluated using Eq. (6) and Eq. (7) and they are given in Table III.

**TABLE III. Values of \(A_{\text{mode}}\) and \(A_{\text{mean}}\)**

<table>
<thead>
<tr>
<th>Bentonite</th>
<th>(A_{\text{mode}} / \text{kJ mol}^{-1})</th>
<th>(A_{\text{mean}} / \text{kJ mol}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>7.25</td>
<td>7.26</td>
</tr>
<tr>
<td>B10S</td>
<td>5.39</td>
<td>6.29</td>
</tr>
<tr>
<td>B15S</td>
<td>4.54</td>
<td>6.85</td>
</tr>
</tbody>
</table>

The decrease of the values of \(A_{\text{mode}}\) and \(A_{\text{mean}}\) for B10S is due to the increase of the pore sizes in the absence of exchangeable cations and also to the partial removal of cations from the octahedral sheets, which results in weaker interaction of the benzene molecules with the adsorption centers.

The increase of \(A_{\text{mean}}\) for B15S as compared with B10S (Table III) may be connected with the appearance of a certain number of small new pores during acid activation with a 15 % solution of sulfuric acid, as was mentioned before.

**CONCLUSION**

The analyses of the adsorption isotherms of benzene vapor on natural bentonites and bentonites acid activated with 10 % and 15 % solutions of sulfuric acid show that chemical treatment results in more developed porous structures. The micropore volume and pore sizes for B10S and B15S increase, but B15S shows the emergence of small new pores.

The results confirm that the structural changes in the montmorillonite structure of natural bentonite after acid activation with 10 % and 15 % solutions of sulfuric acid are not as large as those after treatment with 10 % and 15 % solutions of hydrochloric acid.\(^1,9\) Probably, this is the reason for the difference in the porosity of bentonites treated with solutions of \(\text{H}_2\text{SO}_4\) and \(\text{HCl}\).
АДСОРПЦИОНА СВОЈСТВА И ПОРОЗНА СТРУКТУРА БЕНТОНИТА ТРЕТИРАНОГ РАСТВОРУМ СУМПОРНЕ КИСЕЛИНЕ ОДРЕЂЕНИ ИЗ АДСОРПЦИОНИХ ИЗОТЕРМИ БЕНЗЕНОВИХ ПАРА

СНЕЖАНА БРЕЗОВСКА, БИЉАНА МАРИНА, ДОНО БУРЕВСКИ, БИЉАНА АНГУШЕВА, ВАСА БОШЕВСКА И ЛЕПА СТОЈАНОВСКА

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У претходно објављеном раду испитиване су адсорпционе изотерме бензена на природном бентониту из Македоније и бентониту после његове хемијске обраде раствором хлороводоничне киселине концентрације 10 мас% и 15 мас%. Испитивање је настављено на кисеолактираном бентонитима са 10 % и 15 %-ним растворима сумпорне киселине где су, према рендгенсконанализи мање промене у структури монаморионити. Коришћене су Dubinin–Radushkevic–Stoeckli и Dubinin–Astakhov једначине. Помоћу тих једначина одређивана је хетерогеност микропорозне структуре и енергетска хетерогеност преко диференцијалне дистрибуције запремине микропора у односу на структурни параметар који карактеризује микропорозну структуру и у односу на моларну свободну енергију адсорпције. Активирани бентонит има веће поре али истовремено током активације са киселом већи концентрације, настали су па мана диаметром. Волумени микропора, одређени адсорпцијом бензенових пара на бентонит активиран са 10 % и 15 %-ним растворима HCl (144,60 cm₃ kg⁻¹ и 110,06 cm₃ kg⁻¹) одговарајући), мањи су у односу на природни бентонит (162,55 cm₃ kg⁻¹). С друге стране, вредности волумена микропора за бентонит третиран са 10 % и 15 %-ним растворима H₂SO₄ расти у већом концентрације киселине (169,19 cm₃ kg⁻¹ и 227,74 cm₃ kg⁻¹) и у њима су од вредности за природни бентонит. То се може, највероватније, объјаснити разликом у насталим структурним променама током активације хлороводонијом и сумпорном киселином. Вредности свободне енергије адсорпције за природни бентонит су веће у односу на активиран бентонит, што се такође може объјаснити насталом променом у структури и величини пора.

(Примљено 2. априла, ревизирано 7. јула 2004)

REFERENCES