Influence of activated carbon surface oxygen functionalities on SO$_2$
physisorption – Simulation and experiment

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Abstract

The influence of the gradual oxidation of carbons on SO$_2$ physisorption was studied, by comparison of experimental and simulated SO$_2$ adsorption isotherms. The results confirmed a significant impact of surface groups on the SO$_2$ adsorption. The simulations also revealed a similar, to that observed experimentally, effect of the increase in the percentage of the smallest micropores on adsorption isotherms. The isotherms were analysed using the CMMS model. The conclusion is that this model seems to be a good and sensitive tool for studying SO$_2$ physisorption mechanism since a very good qualitative agreement between the experimental and simulated data was observed.

1. Introduction

Sulphur dioxide (SO$_2$) is one of atmospheric pollutants which contribute to acid rain. The emission of SO$_2$ is mainly due to the combustion of sulphur-containing fuels [1–3]. Different methods are used to reduce the emission of this gas [1]. The adsorption process, as one of these methods, has been studied very frequently due to its simplicity and low cost [4]. Thus, SO$_2$ adsorption on carbonaceous materials (mainly activated carbons) is still a subject of interest of different researchers [5–10].

In our previous paper [11] we studied SO$_2$ physisorption on a series of activated carbons obtained via the modification of a starting sample by a heat treatment in different atmospheres and at various temperature values. Our results revealed that the interactions between SO$_2$ molecules and carbon surface oxygen groups are crucial during the physisorption of this adsorbate. These observations were confirmed by the description of adsorption isotherms using the cooperative multimolecular sorption model (CMMS) proposed by Malakhov and Volkov [12]. It was shown that the equilibrium constants of CMMS equation were linearly correlated with the oxygen contents. The porosity of the considered carbons was similar, however, there were some differences between pore size distributions, BET surface areas and pore volumes. These differences may also have some influence on the obtained results. On the other hand, the porosity of the samples was characterised by low-temperature N$_2$ adsorption and, as was shown previously [13], the presence of surface functionalities may affect the pore size distributions calculated from adsorption isotherms, especially in the case of adsorbates having the quadrupole moment (like N$_2$).

Thus, computer simulations seem to be the simplest way to test the influence of oxygen surface groups on SO$_2$ physisorption on activated carbons. Using the so-called virtual porous carbon (VPC) [14,15] makes it possible to strictly control the porosity of carbon during the introduction of surface groups. This is, due to the reasons mentioned above, practically impossible in the case of real experiments.

In this communication, Monte Carlo simulations are used to systematically study the influence of surface oxygen groups on SO$_2$ physisorption on activated carbons. We consider three starting VPCs generated previously [16]. Oxygen functionalities are introduced on the surface using the previously proposed virtual oxidation procedure [13]. For simplicity, only carbonyl groups are investigated (as it was shown by Jorge et al. [17] who considered water adsorption, the type of oxygen-containing group is not of critical importance, since more complex groups can effectively be represented by simpler sites). Simulated adsorption isotherms were fitted by CMMS model. The obtained results are compared with discussed above and the previously published experimental data [11].

2. Simulation details

2.1. Simulation boxes

Three, differing in porosity, VPCs were used. They were generated following the procedure described previously [16] using simple Metropolis Monte Carlo method and one of the most sophisticated carbon force field, i.e., carbon EDIP potential proposed by Marks [18,19]. We chose the structure having density equal to 0.6, 0.8 and 1.0 g/cm$^3$ and denoted as d0.6, d0.8 and...
d1.0, respectively. Basing on these VPCs, three series of carbons containing a systematically increasing number of carbonyl groups were generated using the virtual oxidation procedure [13]. The following numbers of carbonyl oxygen atoms were introduced: 34, 68, 102, 136 and 170 for the d0.6 structure, 32, 64, 96, 128 and 160 for the d0.8 structure, and 30, 60, 90, 120 and 150 for the d1.0 structure, respectively. The subsequent VPCs were denoted as dxx_yyy, where xx is the density of starting carbon and yyy is the number of carbonyl groups. Figure 1 presents schematically all the considered VPCs and applied notation.

The porosity of studied VPCs was characterised by a geometrical method proposed by Bhattacharya and Gubbins (BG) [20]. The implementation of the method was described in details elsewhere [16,21]. Table S1 in Supplementary data collects the basic characteristics of the considered VPCs.

2.2. Simulations of SO2 adsorption isotherms

SO2 adsorption isotherms on all the generated VPCs were simulated using hyper parallel tempering Monte Carlo (HPTMC) method proposed by Yan and de Pablo [22]. The simulations were performed for ambient temperature, i.e., $T = 298$ K. For each system, 63 replicas (corresponding to the relative pressures from $1.0 \times 10^{-6}$ to 1.0) were considered. The HPTMC simulations utilised $5 \times 10^6$ cycles (one cycle = 100 attempts of the change of each replica state) [23]. The first $1 \times 10^6$ cycles were discarded to guarantee equilibration.

For SO2 molecules we used three-centre rigid model of Ribeiro [24]. The same force field was used successfully by others to simulate SO2 adsorption on carbon nanotubes [25]. The energy of interactions of SO2 molecules pair was calculated as the sum of interaction between pairs of centres:

$$
U_g(r, \omega_1, \omega_2) = \sum_{i=1}^{n} \left[ U_{lj}^g(r_i) + U_{elec}^g(r_i) \right]
$$  (1)

where $r$ is the distance between the molecules, $\omega_1$ and $\omega_2$ determine their angular orientation, $r_{ij}$ is the distance between the pair of centres, $U_{lj}^g$ and $U_{elec}^g$ represent the energy of dispersive and electrostatic interactions between them, respectively. The dispersive interactions were modelled using Lennard–Jones potential [26]. Cut-offs were realised by the switching function in a quintic form [27]:

$$
U_{lj}^g(r_{ij}) = 4\sigma_{ij} \left[ \frac{\sigma_{ij}}{r_{ij}} \right]^6 - \frac{\sigma_{ij}}{r_{ij}} \right] \times S(r_{ij})
$$  (2)

where $\sigma_{ij}$ and $\epsilon_{ij}$ are the collision diameter and the potential well depth, respectively, and $S$ is the switching function [27]:

$$
S(r_{ij}) = \begin{cases} 
1 & r_{ij} \leq r_{cut} \\
-6 \left( \frac{r_{ij} - r_{cut}}{r_{cut} - r_{cut}} \right) & r_{cut} < r_{ij} < r_{cut} \\
0 & r_{ij} \geq r_{cut} 
\end{cases}
$$  (3)

$r_{cut}$ is the cut-off distance and $r_{cut}$ is the distance at which the switching function starts to apply.

The energy of electrostatic interactions was calculated using the potential proposed by Fennel and Gezelter [28]:

$$
U_{elec}^g(r_{ij}) = \begin{cases} 
\epsilon_i \epsilon_j \left[ \frac{\epsilon_{ij} \sigma_{ij}}{r_{ij}} \right] + \frac{\epsilon_{ij}}{r_{ij}} & r_{ij} < r_{cut} \\
0 & r_{ij} \geq r_{cut} 
\end{cases}
$$  (4)

where $q_i$ and $q_j$ are the values of the charges of the centres, $\epsilon_0 = 8.8543 \times 10^{-12} \text{ C}^2/\text{Nm}$ is the dielectric permittivity of free space, and $\sigma = 2.0 \text{ nm}^{-1}$ [28] is the damping factor. Eq. (4) is a simple alternative to the Ewald summation [28].
Table 1
The values of LJ potential parameters and point charges applied in simulations.

<table>
<thead>
<tr>
<th>Object</th>
<th>Geometric parameters</th>
<th>Centre</th>
<th>$\sigma$ (nm)</th>
<th>$\epsilon/k_B$</th>
<th>$\eta/e$</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>$\xi_{SO} = 0.14321$</td>
<td>S</td>
<td>0.3585</td>
<td>154.4</td>
<td>+0.470</td>
<td>[24]</td>
</tr>
<tr>
<td></td>
<td>$\phi_{SO} = 119.5^\circ$</td>
<td>O</td>
<td>0.2903</td>
<td>62.3</td>
<td>-0.255</td>
<td></td>
</tr>
<tr>
<td>VPC</td>
<td>$\xi_{VPC} = 0.1233$</td>
<td>C$^c$</td>
<td>0.3400</td>
<td>28.0</td>
<td>-</td>
<td>[17]</td>
</tr>
<tr>
<td></td>
<td>$\phi_{VPC} = 119.5^\circ$</td>
<td>C$^c$</td>
<td>0.3400</td>
<td>28.0</td>
<td>+0.500</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>O</td>
<td>0.2960</td>
<td>105.8</td>
<td>-0.500</td>
<td></td>
</tr>
</tbody>
</table>

Note:

$^a$ Non-carbonyl group atom of C.

$^b$ Carbonyl group atom of C.

The energy of solid–fluid interactions for a molecule at a given location was also calculated as the sum interaction between the pairs of centres:

$$U_{ij} = \sum_{i,j=1}^{NC} \left[ U_{ij}^L(r_{ij}) + \sum_{l=1}^{NCO} \sum_{k=1}^{3} \left( U_{kj}^L(r_{kj}) + U_{ik}_{NCO}^L(r_{ik}) \right) \right]$$

(5)

where $NC$ is the number of non-carbonyl atoms of C and NCO is the number of carbonyl groups.

Table 1 collects all the values of parameters applied in simulations. Cross-interaction parameters were calculated using Lorentz–Berthelot mixing rules [26]. We used the same $r_{cut}$ value (equal to 1.5 nm) for both dispersive and electrostatic interactions. We also assumed $r_{min} = 1.4$ nm. The isosteric enthalpy of adsorption ($q^e$) was calculated from the theory of fluctuations [16,26].

2.3. Description of simulated isotherms by CMMS model

For the description of simulated adsorption isotherms, we used (as previously [11]) the CMMS model [12] in the form:

$$q = \frac{a_n K_0 h}{(1 - K_a h)(K_0 h + w^2(1 - K_a h))}$$

(6)

where

$$w = \frac{1}{2} \left( 1 - \frac{K_1 h}{1 - K_a h} \right) \sqrt{\left( 1 - \frac{K_1 h}{1 - K_a h} \right)^2 + \frac{4K_0 h}{1 - K_a h}}$$

(7)

$s$ and $a_n$ are the adsorption and adsorption capacity, respectively, $h$ is the relative pressure (i.e., the ratio of gas-phase pressure ($p$) to saturated vapour pressure ($p_0$)), $K_0$ is the equilibrium constant for sorption of the central unit on the primary site, $K_1$ is the equilibrium constant for sorption of the side unit on the primary site, and $K_{an}$ is the equilibrium constant for sorption of the site associate.

Simulated isotherms were fitted by the CMMS model (Eqs. (6) and (7)) using the genetic algorithm proposed by Storn and Price [29] which was previously successfully applied by us for the description of different experimental data sets (see for example [30-32]). The goodness of the fit was estimated using the determination coefficient ($DC$) defined as:

$$DC = 1 - \frac{\sum (a_{obs,i} - a_{sim,i})^2}{\sum (a_{sim,i} - \bar{a}_{sim})^2}$$

(8)

where $a_{obs,i}$ and $a_{sim,i}$ are the predicted by the model and the simulated adsorption amount for $i$th point, and $\bar{a}_{sim}$ is the average value of simulated adsorption.

3. Experimental data

For the purpose of this study we use SO$_2$ adsorption isotherms (at 273 K) on the series of 10 carbons obtained by the heat treatment (at various temperatures and in different atmospheres) of commercial activated carbon D43/1 (CarboTech, Germany) [11].

The samples preparation, their characterisation and details of measurements were described previously [11].

4. Results and discussion

Figure 2 shows some representative experimental SO$_2$ adsorption isotherms on carbons having low, medium and high oxygen contents. In order to minimise the influence of differences in structural characteristics of carbons (like the surface area or the pore volume) the isotherms were normalised dividing the data by adsorption capacities ($a_n$) obtained from the fit by CMMS model.

The rise in oxygen contents causes the change in the shape of isotherms. The isotherms become sharper, i.e., a lower pressure value is necessary to obtain a certain coverage. The differences in the shape of isotherms are reflected by the values of the constants of CMMS model ($K_0$ and $K_1$) – see Table 3 and Figure 6 in [11]. The rise in oxygen content is connected with the increase in the values of these parameters.

Figure 3 shows the histograms of pore diameters of all the considered VPCs. All the structures are strictly microporous (i.e., pore sizes do not exceed 2 nm). In the case of the raw carbons (i.e., d0.6, d0.8 and d1.0) one can see that a decrease in the percentage of wider micropores ($d_{off} > 1$ nm) passing from the d0.6 structure to the d1.0 one. On the other hand, the virtual oxidation practically does not change the porosity of VPCs (there are observed only very small changes for the widest pores). Thus, as it was mentioned above, the applied simulation methodology makes it possible to study separately the influence of the porosity and the presence of oxygen functionalities on SO$_2$ adsorption.

The next figure compares simulated SO$_2$ adsorption isotherms and related isosteric enthalpy of adsorption for all the considered VPCs. The gradual virtual oxidation causes analogous changes in the shapes of isotherms for all the carbons. The influence of the oxygen functionalities is the most pronounced for low pressure values. The isotherms become sharper with the rise in the number of carbonyl groups. This is a consequence of the increase in the adsorption energy caused by the electrostatic interactions of SO$_2$ molecules with CO groups having a dipole moment [33]. So, at the same pressure value the higher number of molecules is adsorbed in the pores of VPCs having higher oxygen contents and

![Figure 2](image_url)
the lower pressure value is necessary to obtain the same coverage. Consequently, the pressure of pore filling decreases with the increase in the number of groups. The observed changes are analogous to the experimental observations – see Figure 2. Therefore, the performed simulations are an independent confirmation of a significant impact of the presence of surface oxygen groups on SO$_2$ physisorption. The changes in the mechanism of the process are also confirmed by the movies in the Supplementary data. They

![Figure 3. The histograms of pore diameters for the series of oxidised VPCs based on the d0.6 (a), d0.8 (b) and d1.0 (c) structures. The subsequent histograms are shifted by 0.17 from the previous ones.](image)

![Figure 4. The comparison of SO$_2$ adsorption isotherms (T = 298 K) and related isosteric enthalpy of adsorption for all the considered VPCs. The arrows show the direction of changes connected with the rise in the number of carbonyl groups.](image)
reveal the above-described regularities. The differences in the energy of SO$_2$ adsorption are also reflected by the regular changes of the isosteric enthalpy of adsorption. On the other hand, for the high pressure values the virtual oxidation is connected with a slight decrease in the value of adsorption capacity. This is caused mainly by the rise in the adsorbent mass caused by the introduction of oxygen atoms.

The comparison of isotherms for the raw VPCs (i.e. d0.6, d0.8 and d1.0; the lowest black curves on Figure 4) reveals also a significant influence of porosity on SO$_2$ adsorption. The rise in the contents of the smallest micropores ($d_{\text{eff}} < 1$ nm) causes the change in the shape of isotherms similar as the introduction of oxygen functionalities. Isotherms become sharper passing from the d0.6 structure up to the d1.0 one. This is due to a higher adsorption potential energy in smaller pores. The energetic differences are reflected by the increase in isosteric enthalpy of adsorption. Hence, not only the presence of high number of surface oxygen groups is the feature of the optimal carbon for SO$_2$ physisorption, but this carbon should also have a large amount of small micropores with a diameter below 1 nm, as it was also suggested in earlier reports [34,35]. The performed simulations may also suggest some caution in the interpretation of experimental data, because the influence of surface functionalities may be difficult to distinguish from the influence of changes in porosity which may be caused by an experimental procedure of introducing oxygen groups.

The details and some new insights into the adsorption mechanism can be obtained from the analysis of animations (Supplementary data) and the solid–fluid potential energy profiles (for selected systems) shown in Figures 5 and S1–S3 in Supplementary data. One can observe that the introduction of surface oxygen groups causes two important effects. Some molecules are adsorbed at the vicinity of groups, however, the appearance of functionalities also rises the potential energy at the curved fragments of the structure. Since electrostatic interactions are long ranged one can observe the densification of SO$_2$ molecules even at places where the groups are absent.

Table S2 in Supplementary data collects the values of the best-fit parameters obtained from the fitting of the simulated isotherms by the CMMS model (Eqs. (6) and (7)). The quality of data description is satisfactory as evidenced by the high values of the determination coefficient. The differences in the shape of isotherms are mainly reflected by the changes in the values of parameters connected with adsorption on primary sites (i.e. $K_0$ and $K_1$). On the other hand, the values of association constant ($K_{\text{ass}}$) are close to zero for all the simulated isotherms. This is connected with their shape and the presence of the final plateau for the high pressure values. The observed decrease in adsorption capacity caused by a gradual oxidation is reflected by the decrease in the values of $a_{\text{par}}$ parameter. Figure 6 presents the correlations between the oxygen contents and the parameters $K_0$ and $K_1$ for experimental data (a) and for simulated isotherms (b–d). One can observe that both values are linearly correlated with the oxygen contents. These regularities confirm the above-described influence of oxygen groups on the mechanism of SO$_2$ physisorption via the increase in the energy of adsorption. The behaviour of both experimental and simulated data is similar, but there are also some differences. In the case of the best-fit parameters obtained from experimental isotherms the $K_0$ values are higher than the $K_1$ ones. A reverse situation occurs for the simulated data. However, comparing the data for d0.6, d0.8 and d1.0 series one can see the reduction in differences between both values with increasing in the percentage of the smallest micropores. In the case of the most oxidised structures
of d1.0 series the constants $K_0$ and $K_1$ have similar values. This regularity may suggest that a further reduction in pore sizes may reverse the relation between the values of both constants (i.e. $K_0$ become higher than $K_1$). Despite the fact that experimentally investigated carbons contain not only narrow micropores but also wider pores (see Figure 4 in [11]), the ratio of $K_0$ and $K_1$ constants is different than in the case of the considered strictly microporous VPCs. The possible explanation of this can be the limitations in the experimental procedure of isotherms measurements. The isotherms were measured only for the range of $p/p_0 < 0.33$ [11]. In this range, mainly the adsorption in the smallest pores contributes to the total adsorption value. So, lack of the data for a high-pressure range may affect the obtained results.

5. Conclusions

We have studied the influence of the gradual oxidation of carbons on SO$_2$ physisorption. The comparison of the experimental and simulated data of SO$_2$ adsorption has confirmed the significant impact of surface functionalities on the mechanism of the adsorption process. The main reason is the increase in the adsorption energy due to electrostatic interactions of SO$_2$ molecules with carbonyl groups having dipole moment. The results of simulations have also revealed an important role of carbon porosity. The increase in the percentage of the smallest pores ($d_{\text{eff}} < 1$ nm) has caused the similar changes in the shape of isotherms as the introduction of carbonyl groups. So, the optimal carbon for SO$_2$ physisorption should not only contain a high number of oxygen functionalities but also have the high contents of the smallest micropores. The results of the performed simulations may also suggest some caution in the interpretation of experimental data, because the influence of surface functionalities may be difficult to distinguish from the influence of changes in porosity caused by an experimental oxidation procedure.

The fit of isotherms by the CMMS model has led to the conclusion that this model is a useful and sensitive tool in the study of the SO$_2$ adsorption mechanism. The differences in the constants of the model ($K_0$ and $K_1$) have reflected the systematic changes in the shape of isotherms. The values of these constants (obtained from the simulated data) have been linearly correlated with the oxygen contents. The analogous correlation has been observed for the experimental data. This fact is an independent confirmation of the performed simulations validity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2013.05.060.

References