SYNTHESIS AND ACCEPTOR-DONOR CHARACTERISTICS OF ORDERED MESOPOROUS SILICAS

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This research effort has been focused on the synthesis of ordered mesoporous silicas (MCMs) and the characterisation of the donor–acceptor properties of them via the comparison of different methods for obtaining and refining results. The DN values denoting the donor number on the Gutmann scale and the AN* values denoting the acceptor number on the Riddle-Fowkes scale have been chosen in the estimation of the electron acceptor parameter $K_a$ and electron donor parameter $K_d$ values. The values of the parameters for different compositions of probes, having different acceptor–donor properties, illustrate the need for establishing the accurate number of probes to introduce a new chromatographic test to supplement the Grob test. Complementary information has been obtained via X-ray photoelectron spectroscopy, energy dispersive X-ray spectroscopy and pH-metric tests.

Keywords: inverse gas chromatography, MCMs, acceptor–donor properties.

INTRODUCTION

The silica adsorbents MCM41 are rated to the ordered mesoporous silica materials. These adsorbents contain hexagonal mesopores non-connected to one another and create a honey comb structure. An essential property of the materials is the possibility, during synthesis to predict and control the dimension and volume of pores in the obtained adsorbent. The MCM41 group has homogeneous pores with the dimensions ranging from 1.5 nm to 10 nm [1].

Very few papers concerning the problem of testing the acceptor–donor properties of MCMs by inverse gas chromatography have been published to date. As it is commonly known, the adsorbate–adsorbent interactions, i.e., the molecular probe and/or probe–the ordered mesoporous silica adsorbent, can be regarded as van der Waals interactions and/or other specific ones.

The total standard free energy of transferring one mole of adsorbate from the gas phase to the standard state on the adsorbent surface, known as the energy of adsorption, can be calculated on the basis of the specific retention volume referred to one gram of adsorbent in the column and to the column temperature, $V_{r}^{st}$, as follows [1]:

$$\Delta G_{ads}(\text{I}) = -RT \ln \left( \frac{p_{s,ads}}{\pi S_{nat}} \frac{V_{r}^{st}}{\Delta S_{ads}} \right)$$

$$\Delta G_{ads}(\text{II}) = \Delta H_{ads} - T \Delta S_{ads}$$

where: $p_{s,ads}$ – the reference pressure is equal to 1 atm (101325 N/m$^2$);
$\pi_s$ – the two-dimensional pressure for the adsorbed state, 0.338 $10^{-3}$ N/m;
For such a characterised system the $p_s$, $\pi_s$ and $S_{ad}$ parameters are constant, and the equation (1) takes the following form: 
$$\Delta G_{ads} = -RT \ln V_{ads}^{(s)} + \text{const},$$
for which the value of the constant strongly depends on the chosen reference state of the adsorbed molecule.

**THEORETICAL**

As it is commonly known acid-base properties of the tested solid have a decisive influence on the value of the specific contribution of the enthalpy of adsorption of the test substance:

$$-\Delta H_{ads}^{\pi} = K_s \cdot DN + K_D \cdot AN$$

(3)

where: $\Delta H_{ads}^{\pi}$ - the contribution of the specific enthalpy of adsorption of the probe on the tested surface,

$K_s$ and $K_D$ - the parameters characterizing the ability of the tested surface to behave as an acceptor or a donor of electrons, respectively,

$AN$ and $DN$ – the acceptor number and donor number of the probe, respectively.

Gutmann has also introduced the concept of an acceptor number $(AN)$, to supplement $DN$ and to measure the strength of the Lewis acidity or electrophilicity of a liquid. It enables a direct comparison of the $K_s$ and $K_D$ values and an estimation of the surface nature by employing the following equation [1]:

$$\frac{-\Delta H_{ads}^{\pi}}{AN_i} = K_s \frac{DN_i}{AN_i} + K_D$$

(4)

where $i$ denotes a probe.

The main aim of the paper is to characterize the acceptor–donor properties of the ordered mesoporous functionalized silica adsorbents by means of inverse gas chromatography.

Voelkel described in his paper another method of determining the $K_s$ and $K_D$ parameters by the direct use of the $\Delta G_{ads}^{\pi}$ value, which introduces the contribution of the entropic term [1]:

$$\Delta G_{ads}^{\pi} = \Delta H_{ads}^{\pi} - T \Delta S_{ads}^{\pi}$$

(5a)

Thus the equation (3) has become the following form:

$$\frac{\Delta G_{ads}^{\pi}}{AN_i} = K_s \frac{DN_i}{AN_i} + K_D$$

(5b)

where $\Delta G_{ads}^{Sp}$ is the specific component of the free energy. Actually it is the vertical distance between the point for the total free energy of the polar probe and the point for the total free energy of a hypothetical $n$-alkane on the reference line having the same value on the abscissa.

**EXPERIMENTAL**

**Adsorbents Synthesis and Adsorbates**

The synthesis of the tested MCMs has been carried out as follows: ca. 15.34 g of surfactant $C_{16}H_{33}(CH_{3})_3N+Br^-$ (n-heksadecyltrimethylaminobromide) of 99% purity
and ca. 73 cm$^3$ of redistilled water and ca. 3.6 cm$^3$ 5M NaOH have been placed in a conical flask. The obtained solution has been mixed for ca. one hour, and it changed its colour to a milky one. After adding surfactant, redistilled water and NaOH p.a. and tetraethoxysilane [Si(OC$_2$H$_5$)$_4$] p.a. the solution became a lyogel at the beginning of mixing and in the end it took on the consistency of porridge. During the synthesis of the modified adsorbents, after ca. one hour of mixing of the surfactant, redistilled water and NaOH, ca. 13.4 cm$^3$ tetraethoxysilane, and ca. 0.7 cm$^3$ modifier were added:

HS-C$_3$H$_6$Si(OC$_2$H$_5$)$_3$ – in the case of synthesis of MCM41-C16-SH, C$_6$H$_{17}$NO$_3$Si – in the case of synthesis of MCM41C16-NH$_2$.

After adding reagents, separately for every solution, the mixture of tetraethoxysilane and modifier has been mixed for ca. one hour. The consistencies of the solutions have changed during mixing: in the case of the synthesis MCM41C16-SH and MCM41C16-NH2 the solutions became a gelatinous liquid and with time they became milky. The aforesaid changes were faster in the case of the MCM41C16-NH$_2$ adsorbent.

The characteristics of the MCMs tested were elucidated on the basis of the results obtained via low-temperature N$_2$ adsorption data, XPS, XRD and AFM tests, and reported earlier [2].

**The EDX Tests**

The results of the elemental analysis obtained by means of the EDX tests are collated in Table 1 and the spectra for the C16 material is depicted in Figure 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage: %</th>
<th>Si</th>
<th>C</th>
<th>O</th>
<th>S</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>-C16</td>
<td></td>
<td>34.11</td>
<td>3.70</td>
<td>53.26</td>
<td>-</td>
<td>4.82</td>
</tr>
<tr>
<td>-C16-SH</td>
<td></td>
<td>37.96</td>
<td>4.97</td>
<td>48.24</td>
<td>2.25</td>
<td>3.99</td>
</tr>
<tr>
<td>-C16-NH$_2$</td>
<td></td>
<td>33.18</td>
<td>8.73</td>
<td>47.83</td>
<td>1.17</td>
<td>5.12</td>
</tr>
</tbody>
</table>

# alumina and chloride are treated as impurities

The content of oxygen in all MCMs tested here is relatively high. The C16-SH material contains sulphur atoms and the C16-NH$_2$ adsorbent also contains these atoms. Apart from that, all adsorbents contain relatively small amounts of nitrogen. In the case of the C16-NH$_2$ material the nitrogen content is rather lower than expected.

**Chromatographic Tests**

The chromatographic measurements of the aforementioned probes were undertaken using a Unicam type 610 gas chromatograph fitted with an on-line Unicam 4880
chromatography data handling system which was switched on when a sample was injected. The instrument was equipped with a flame ionization detector.

For all the tested systems the asymmetric elution peaks were obtained, for which the retention times depended on the amount of adsorbate injected onto column. The retention times were determined at the infinitely low coverage of the MCM surface with probe molecules and estimated on the basis of the first statistic moment, \( m_1 \), i.e. the centres of gravity of the peaks.

The specific retention volumes were calculated by employing the retention times determined for the infinite dilution of probe and referred to 1 gram of the MCM in the column:

\[
V'_{st} = \frac{3}{2} \left( \frac{p_o}{p_r} \right)^2 \left( \frac{p_o}{p_r} \right)^2 \frac{F_i (\psi_i - t) T}{T_f \left( \frac{p_o - p_{H2O}}{p_r} \right)} \frac{T}{m_{ads}}
\]  

In the equation (6) \( t \) - is the hold-up time, \( F_i \) - is carrier gas flow-rate measured by a soap flow-meter at the column temperature, \( T_f \) - is the column temperature, \( T_f \) - is the temperature of the flow-meter, \( p_r \) - is pressure at the inlet of the column, \( p_o \) - is ambient pressure, \( p_{H2O} \) - is the pressure of water vapour at the ambient temperature, \( m_{ads} \) - is the total mass of adsorbent in the chromatographic column.

**DISCUSSION**

Based on the theoretical considerations discussed earlier the values of the \( K_A \) and \( K_D \) parameters have been calculated by employing the equations (4) and (5b). They are collated in Table 2, and the corresponding plots are depicted in Figures 2–4.

The values of the quotient \( \frac{K_A}{K_D} \) suggested that the MCMs surfaces tested here have electron acceptor properties.

The chromatographic test made by means of our composition of probes will characterize the acceptor–donor properties and it will be a complement to the Grob test.

Table 2. The KA, KD and KA/KD values (characterized by the values of the linear regression coefficient, \( r \), and the standard deviation values for linear regression, SD) calculated for the tested adsorbents and the \( \alpha_{v/N} \) values employed for labelling abscissa without taking into consideration the entropic effect.

<table>
<thead>
<tr>
<th>Equation</th>
<th>Adsorbent</th>
<th>KA</th>
<th>KD</th>
<th>KA/KD</th>
<th>r</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>C16</td>
<td>0.56</td>
<td>0.42</td>
<td>1.3</td>
<td>0.9943</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>C16-SH</td>
<td>0.59</td>
<td>0.32</td>
<td>1.9</td>
<td>0.9916</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>C16-NH₂</td>
<td>0.51</td>
<td>0.29</td>
<td>1.8</td>
<td>0.9964</td>
<td>0.74</td>
</tr>
<tr>
<td></td>
<td>C16</td>
<td>0.54</td>
<td>0.46</td>
<td>1.2</td>
<td>0.9948</td>
<td>0.85</td>
</tr>
<tr>
<td>5b</td>
<td>C16-SH</td>
<td>0.58</td>
<td>0.29</td>
<td>2.0</td>
<td>0.9911</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>C16-NH₂</td>
<td>0.55</td>
<td>0.10</td>
<td>5.4</td>
<td>0.9953</td>
<td>0.90</td>
</tr>
</tbody>
</table>
The acceptor–donor properties of the tested MCMs have been characterised on the basis of the recommended values of the $\frac{K_A}{K_D}$ quotient.

Figure 2. The plots for the $-\Delta H^\text{SP}_{\text{ads}}$ and $\Delta G^\text{SP}_{\text{ads}}$ parameters and the employed probes corresponding to the equations (4) and (5b) for $\Delta G_{\text{ads}}(I)$, where: 1 – ethyl acetate, 2 – diethyl ether, 3 – methylene chloride, 4 – chloroform, 5 – tetrahydrofuran, 6 – acetone, 7 - acetonitrile

Figure 3. The plots for the $-\Delta H^\text{SP}_{\text{ads}}$ and $\Delta G^\text{SP}_{\text{ads}}$ parameters and the employed probes corresponding to the equations (4) and (5b) for $\Delta G_{\text{ads}}(II)$, where: 1 – ethyl acetate, 2 – diethyl ether, 3 – methylene chloride, 4 – chloroform, 5 – tetrahydrofuran, 6 – acetone, 7 - acetonitrile

Figure 4. The temperature variation of the $\frac{K_A}{K_D}$ quotient for the C16-NH$_2$ material

As the results of the analysis, it has been found that all the tested adsorbents have acceptor properties. It seems obvious in the case of the C16 and C16-SH because of the...
strong acceptor properties of $-\tilde{Q}H$ and $-\tilde{S}H$ groups, whereas the well-founded doubts come from the values of the $\frac{K_a}{K_D}$ quotient for the $C16-N=H_2$ adsorbent.

Generally, the $\equiv Si-N = H_2$ groups are considered to be weak bases or hard bases, according to the hard and soft acids and bases (HSAB) principle, which are connected with their unshared electron pair able to accept a proton, i.e., a hard acid. The nitrogen atom of an amine group can be taken into account to be $sp^3$ hybridized with the lone pair of electrons occupying one orbital, i.e. $2s^2$. This signifies that the unshared pair of electrons is relatively exposed to Lewis acidic species.

**CONCLUSIONS**

The employed IGC method gives more plausible results taking the $-\Delta H_{ads}^{sp}$ and $\Delta G_{ads}^{sp}$ parameters into account, on the basis of which it is possible to characterize the acceptor-donor properties of the MCMs surfaces.

A good correlation between the EDX results and the IGC ones has been obtained in the case of the acceptor–donor characteristic. The combination of the IGC results with the EDX ones provides a detailed understanding of the crux of physical adsorption on the MCMs surfaces and also the chemistry of them. It is conspicuously seen, that the specific adsorbate–adsorbent interactions are strongly dependent on the percentage of elements in the surface layers of the tested MCMs.

It is necessary to work out the set of probes for these tests for an unambiguous interpretation of the acceptor-donor properties.

The $K_a$ and $K_D$ values strongly depend on the column temperatures interval at which the probes have been eluted. Employing the $DN$ and $AN$ parameters in the physicochemical calculations based on the IGC results is mandatory because their empirical values unambiguously illustrate their fundamental source in the interaction strength of lone and shared electron pairs, and they do not treat each functionality (or molecule) as being either an acid or a base, thus making allowances for amphoteric behaviour.

**Acknowledgement**

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**REFERENCES**