Determination of Acid-Base Properties of Silicas by Inverse Gas Chromatography: Variation with Surface Treatment

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The specific component of the free energy of adsorption, \(-\Delta G_A^D\), of untreated crystalline and fused silica, and four types of silane coupling agents-treated fused silicas, were estimated by the inverse gas chromatography (IGC) method, using the adsorption of several polar and non-polar probes on their surfaces at various measuring temperatures. The acid-base properties of the untreated and surface-treated silicas were quantified by their \(K_A\) and \(K_D\) parameters, reflecting the ability of the surface to act as an electron acceptor and donor, respectively. Acidic components were detected on the untreated crystalline and fused silica surfaces, but the surface properties of the fused silicas surface-treated with \(\gamma\)-glycidoxy propyl trimethoxysilane (GMS) and \(\gamma\)-amino propyl triethoxysilane (AES) were slightly basic, and those of the fused silicas surface-treated with \(\gamma\)-methacryloxy propyl trimethoxysilane (MTMS) and \(\gamma\)-mercaptopropyl trimethoxysilane (MCMS) were amphoteric. [doi:10.2320/matertrans.MER2007076]

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Keywords: Inverse gas chromatography (IGC). Specific component of the free energy of adsorption (\(\Delta G_A^D\)). Enthalpy of specific adsorption (\(\Delta H_A^{SP}\)). Surface acid-base characteristics.

1. General

1.1 Introduction

In the first paper of this series we described the surface properties of untreated silicas and silane coupling agents-treated silicas in terms of their dispersive force parameters, as determined by inverse gas chromatography (IGC).

However, it is clear that the full description of the surface properties can only be achieved with the use of the acid-base interaction parameters. Acid-base interactions are important components of polar forces and play a significant role in the adhesion of inorganic fillers to organic polymers. This paper describes the investigation of the acid-base characteristics of the same samples in order to complete the previously defined characterization of their surface properties.

Finally, we calculate the values of various parameters -the specific component of the free energy of adsorption (\(\Delta G_A^{SP}\)), the enthalpy of specific adsorption (\(\Delta H_A^{SP}\)), the electron acceptor index (\(K_A\)), the electron donor index (\(K_D\)) and \(S_C\) (\(K_D/K_A\)) - in order to examine the possible differences in the acid-base properties of untreated and silane coupling agents-treated silicas.

1.2 Theory of inverse gas chromatography (IGC)

For a test substance, the free energy of adsorption, \(\Delta G_A\), is the sum of the energies of adsorption attributable to the dispersive and specific interactions. The adsorption of non-polar probes such as n-alkanes occurs through dispersive interactions, whereas for polar probes both London and acid-base interactions, whereas for polar probes both London and acid-base interactions, whereas for polar probes both London and acid-base interactions.

In this study, we used the model of Donnet et al., because the injected probe is in the gaseous state. In this model, \(\Delta G_A\) is given by the following expressions:

\[
\begin{align*}
\Delta G_A &= -\Delta G_A^D + \Delta G_A^{SP} \\
&= \ln(V_N + C) \\
&= [K \cdot (h_{VS})^{1/2} \cdot \alpha_{OS} \cdot (h_{VL})^{1/2} \cdot \alpha_{OL}]
\end{align*}
\]

where \(\Delta G_A^D\) and \(\Delta G_A^{SP}\) are the dispersive and specific components of the free energy of adsorption, respectively. The value of the constant, \(C\), in expression (2) depends on the arbitrarily chosen reference state of the adsorbed molecule. In expression (3), \(K\) is a constant, \(h_{VS}\) and \(h_{VL}\) are the ionization potentials of the interacting materials, and \(\alpha_{OL}\) is the deformation polarizability of the molecules. Subscripts \(S\) and \(L\) refer to solid and liquid, respectively. In the case of n-alkanes, \(\Delta G_A\) is equal to the free energy of adsorption corresponding to the dispersive interactions, \(\Delta G_A^D\), only, i.e., \([-\Delta G_A^D]\) = 0 in expression (3). The term \([K \cdot (h_{VS})^{1/2} \cdot \alpha_{OS}]\) is characteristic of a given solid surface and is related to \(\Delta G_A^D\). Consequently, \([RT \ln(V_N + C)]\), between an adsorbate and an adsorbent, appears as a linear equation of the parameter \([K \cdot (h_{VS})^{1/2} \cdot \alpha_{OS}]\), while \([K \cdot (h_{VL})^{1/2} \cdot \alpha_{OL}]\) becomes the slope of the linear equation. Polar testing probes [Lewis acids and bases, e.g. chloroform (CHCl₃) and tetrahydrofuran (THF)] have their corresponding \([-\Delta G_A]\) values above the reference line. The vertical distance between the n-alkane plot and the data for the polar probe of interest produces the \([-\Delta G_A^{SP}]\) value.

The examination of the temperature dependence of \(\Delta G_A^{SP}\) enables the determination of the enthalpy of specific adsorptions, \(\Delta H_A^{SP}\) :2)

\[
\Delta H_A^{SP} = \frac{\partial(\Delta G_A^{SP}/T)}{\partial(1/T)}
\]

The enthalpy of specific adsorptions between the examined surface and the test solutes may be correlated with the acid-base properties of both species by using either Drago’s equation or the following equation:2)

\[
-\Delta H_A^{SP} = K_D \times AN + K_A \times DN
\]
electron acceptor and donor, respectively, and the ratio \( K_D/K_A (S_C) \) describes the character of the surface (acidic or basic).

\( K_D \) and \( K_A \), determined according to the method using Gutmann’s AN values in equation (5), are expressed in different units, *i.e.*, in order to obtain both sides of eq. (5) in the same units, \( K_D \) must be in kJ·mol\(^{-1}\) while \( K_A \) has to be dimensionless. Therefore, evaluation of conclusions from their ratio must be treated with caution, since the value of \( K_D/K_A \) remains unclear. Further discussion will be based only on the values of \( K_D, K_A \) and \( S_C \) determined according to the method using the Riddle-Fowkes AN\(^* \) values\(^4 \) in eq. (5).

The procedure described above has been used for the characterization of silicas, modified silicas, oxides, various minerals and solid polymers.\(^5 \)–\(^14 \)

2. Experimental

2.1 Materials

Natural crystalline and fused silicas were used in this work. Four types of silane coupling agents were used in the adsorption experiment. The chemical names and experimental conditions of the silane coupling agents are shown in Table 1. We used methanol and distilled water as the solvent and acetic acid as the catalyst for the hydrolysis of the silane coupling agents.

<table>
<thead>
<tr>
<th>Table 1 Chemical names and experimental conditions of the silane coupling agents.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Expressions in this paper</strong></td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td>MTMS</td>
</tr>
<tr>
<td>GMS</td>
</tr>
<tr>
<td>MCMS</td>
</tr>
<tr>
<td>AES</td>
</tr>
</tbody>
</table>

We used a homologous series of n-alkanes - hexane \((C_6H_{14})\), heptane\((C_7H_{16})\), octane\((C_8H_{18})\) - as the non-polar probes, and benzene\((C_6H_6)\), chloroform\((CHCl_3)\), carbon tetrachloride\((CCl_4)\), nitromethane\((CH_3NO_2)\), ethyl acetate \((CH_3COOC_2H_5)\) and THF\((C_4H_8O)\) as the polar probes for the IGC experiment.

2.2 Adsorption experiment

The experiment designed to modify the fused silica surface was performed as follows: The solvent \((100 \text{ mL})\), silane coupling agents \((1.0 \text{ g})\) and fused silica \((30 \text{ g})\) were stirred by a magnetic bar stirrer for an hour and then separated into solid and liquid components by a centrifugal separator. A suitable amount of acetic acid specially was added before stirring in accordance with the type of silane coupling agents to obtain a reasonable pH value, because the pH value is the most important factor in the hydrolysis of silane coupling agents. The conditions used in the adsorption experiment are shown in Table 1. The separated fused silicas were then dried for 8 hours at 105°C. The various samples, viz. the untreated crystalline and fused silicas, and the fused silicas surface-treated with MTMS, GMS, MCMS and AES, were prepared in this way for the IGC study at infinite dilution.

2.3 IGC experimental conditions

Since the particle size of the silica was too small to make chromatographic supports, silica disks were prepared by compression of the powders in an IR die, under a pressure of \(10^8 \text{ Pa}\). The disks were then hand-crushed and sieved to select the fraction of particles having diameters between 250 and 425\(\mu\)m. Particles of the correct size were introduced into a stainless steel column, 50 cm long and 3.17 mm in diameter. Approximately 1 g of each sample was used as the filling of the chromatographic column. Each column, filled with the sample, was conditioned at 200°C for 24 hours to remove any impurities in it. The IGC measurements were performed with a Hewlett Packard 6890 GC system, equipped with a highly sensitive flame ionization detector (FID). The carrier gas was nitrogen \((N_2)\) and the flow rate was 10 mL/min. The temperature of the IGC measurement was varied from 90 to 160°C. Very small amounts of the probes were injected using the following stratagem: 1 to 5 \(\mu\)L of the probe was introduced via a septum into a 1 L flask, which was flushed with \(N_2\), after which about 0.3 mL of the diluted probe was
injected into the GC system. We referred to the CRC Handbook of chemistry and physics for the physical and chemical properties of the probes.

3. Results and Discussion

We evaluated the $-\Delta G^{SP}_A$ values for the various samples by the well-established IGC method. Figs. 1 to 3 display the variation of $[RT \ln V_N]$ vs. the characteristic, $[(h\nu L)^{1/2} \cdot \alpha_{OL}]$, for each probe used to evaluate the $-\Delta G^{SP}_A$ values of the untreated crystalline silica, fused silica and MTMS-treated fused silica by expression (3), respectively. The $[RT \ln V_N]$ values of the n-alkanes used as nonpolar probe vary linearly with their characteristic, $[(h\nu L)^{1/2} \cdot \alpha_{OL}]$, and the $[RT \ln V_N]$ values for the polar probes of interest are above the reference line, as shown in these figures. The vertical distance between the n-alkane plot and the $[RT \ln V_N]$ value for the polar probe

$$\Delta G^{SP}_A = \frac{\alpha_{OL}}{C_0} \cdot \frac{RT \ln V_N}{C^{3/2} m^2 V^{1/2}}$$
corresponds to the $-\Delta G_{SP}^A$ value. The $-\Delta G_{SP}^A$ values of the silicas were computed at various measuring temperatures between 90 and 160°C.

The calculated values of $-\Delta G_{SP}^A$ are presented in Table 2. The values of $-\Delta G_{SP}^A$ decreased with increasing measuring temperature for all of the samples, except in a few cases where $-\Delta G_{SP}^A$ increased slightly. In addition, the range of IGC measuring temperature differs according to the type of silica, i.e., the range of temperature suitable to measure their surface characteristics differs, because their surface characteristics are not the same. However, the effect of the measuring temperature on the values of $K_A$ and $K_D$ could be ignored, because it did not affect the computation of their acid-base surface characteristics using these parameters. That is, the $K_A$ and $K_D$ parameters are unconcerned in the measuring temperature.

Figures 4 to 6 display the variation of $[-\Delta G_{SP}^A / T]$ with the inverse of the absolute temperature. In these figures, $-\Delta H_{SP}^A$ is the slope of the line obtained from expression (4). The values of $-\Delta H_{SP}^A$ calculated in accordance with the above method are presented in Table 3. The $K_A$ and $K_D$ parameters were calculated using these $-\Delta H_{SP}^A$ values.

Gutmann’s AN and DN and Riddle-Fowkes’ AN* numbers of the interested polar probes, as well as their acid-base properties, are reported in Table 4. We chose to use Riddle-Fowkes’ AN* numbers in units of kcal·mol$^{-1}$ instead of Gutmann’s AN numbers. Expression (5) becomes

![Figures 4 to 6](image_url)

Table 3 The specific components of the enthalpy of adsorption, $-\Delta H_{SP}^A$, of polar probes on the untreated and surface-treated silicas.

<table>
<thead>
<tr>
<th>Probe</th>
<th>$-\Delta H_{SP}^A$ (kJ·mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Untreated crystalline silica</td>
</tr>
<tr>
<td>Benzene</td>
<td>25.48</td>
</tr>
<tr>
<td>Chloroform</td>
<td>7.57</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>8.64</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>40.29</td>
</tr>
<tr>
<td>THF</td>
<td>26.67</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>26.83</td>
</tr>
</tbody>
</table>
Table 4 The acid-base properties of the polar probes.

<table>
<thead>
<tr>
<th>Probe</th>
<th>$AN(%)$</th>
<th>$AN^*$ (kcal·mol$^{-1}$)</th>
<th>$DN$ (kcal·mol$^{-1}$)</th>
<th>$DN/AN^*$</th>
<th>Specific character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>8.2</td>
<td>0.17</td>
<td>0.1</td>
<td>0.5882</td>
<td>Acid</td>
</tr>
<tr>
<td>Chloroform</td>
<td>23.1</td>
<td>5.4</td>
<td>0</td>
<td>0</td>
<td>Acid</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>8.6</td>
<td>0.7</td>
<td>0</td>
<td>0</td>
<td>Acid</td>
</tr>
<tr>
<td>Nitromethane</td>
<td>20.5</td>
<td>4.3</td>
<td>2.7</td>
<td>0.6279</td>
<td>Acid</td>
</tr>
<tr>
<td>THF</td>
<td>8.0</td>
<td>0.5</td>
<td>20.0</td>
<td>40</td>
<td>Base</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>9.3</td>
<td>1.5</td>
<td>17.1</td>
<td>11.4</td>
<td>Base</td>
</tr>
</tbody>
</table>

Table 5 The acid-base properties of the untreated and surface-treated silica surfaces.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$K_A$</th>
<th>$K_D$</th>
<th>$S_C = K_D/K_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated crystalline silica</td>
<td>3.04</td>
<td>0.33</td>
<td>0.109</td>
</tr>
<tr>
<td>Untreated fused silica</td>
<td>3.19</td>
<td>0.30</td>
<td>0.094</td>
</tr>
<tr>
<td>MTMS-treated fused silica</td>
<td>0.31</td>
<td>0.42</td>
<td>1.355</td>
</tr>
<tr>
<td>GMS-treated fused silica</td>
<td>0.52</td>
<td>1.25</td>
<td>2.404</td>
</tr>
<tr>
<td>MCMS-treated fused silica</td>
<td>0.51</td>
<td>0.39</td>
<td>0.765</td>
</tr>
<tr>
<td>AES-treated fused silica</td>
<td>0.19</td>
<td>0.94</td>
<td>4.947</td>
</tr>
</tbody>
</table>

\[
-\frac{\Delta H^*_A}{AN^*} = K_A \frac{DN}{AN^*} + K_D \tag{6}
\]

where the $[-\Delta H^*_A/AN^*]$ values of the polar probes varied linearly with their $[DN/AN^*]$ values. Figure 7 displays the variation of $[-\Delta H^*_A/AN^*]$ vs. $[DN/AN^*]$ of the polar probes on the six types of silica. The slopes of each line correspond to the $K_A$ values, and the intercept values of the Y-axis correspond to the $K_D$ values. The values of $K_A$ and $K_D$ evaluated in accordance with the above method are presented in Table 5.

In this paper, we excluded benzene and carbon tetrachloride in the reference line used to evaluate the $K_A$ and $K_D$ parameters, as shown in Fig. 7, because their values calculated from expression (6) deviated from the reference line. The cause of the deviation cannot be explained by enthalpic effects, but rather are attributable to the particular behavior of their molecules. Similar observations, such as negative values of $-\Delta G^*_A$ for benzene and carbon tetrachloride, have been reported in other studies. Hence, we evaluated the $K_A$ and $K_D$ parameters using only the values of chloroform, nitromethane, ethyl acetate and THF, without those of benzene and carbon tetrachloride.

It has already been proved that the surface property of synthetic silica is acidic. If we inquire into the $S_C$ values shown in Table 5, the results suggest that untreated natural crystalline and fused silica are also acidic. However, the $S_C$ values of the fused silicas surface-treated with all four silane coupling agents were shifted in the basic direction. While the $S_C$ values of the fused silica surface-treated with MTMS and MCMS became slightly basic, their acid-base properties were considered to be close to amphoteric. It has already been proved that the acid-base property of MTMS-treated synthetic silica is amphoteric. However, the acid-base properties of the fused silica surface-treated with GMS and AES were considered to be slight basic. That is, the fused silicas surface-treated with GMS and AES were suitable for basic polymers, and the fused silicas surface-treated with MTMS and MCMS were suitable for both acidic and basic polymers.

4. Conclusions

In this work, we used the well-established IGC method to evaluate the acid-base properties of untreated crystalline and fused silica, and fused silicas surface-treated with MTMS, GMS, MCMS and AES. By using n-alkanes and polar solutes as probes, the $-\Delta G^*_A$ values were determined from the plots of $[RT \ln V_N]$ vs. $[(Nh_L)^{1/2} \cdot \alpha_{el}]$ of the solutes. The values of $-\Delta H^*_A$ were determined from the temperature dependence of $-\Delta G^*_A$. These values were found to correlate with Gutmann’s electron donor numbers, $DN$, and the new electron acceptor numbers, $AN^*$, introduced by Riddle-Fowkes in units of kcal·mol$^{-1}$, i.e., in the same units as the donor numbers. The present study produced the following conclusions:

1. The acid-base properties of the above samples were characterized by means of two parameters describing their acidity ($K_A$) and basicity ($K_D$) in consistent units. The results suggested that the acid-base properties of the untreated crystalline and fused silicas are acidic.
2. The acid-base properties of the fused silicas surface-treated with GMS and AES are considered to be slight basic, while those of the fused silicas surface-treated with MTMS and MCMS are considered to be amphoteric.
(3) The fused silicas surface-treated with GMS and AES are suitable for basic polymers, and the fused silicas surface-treated with MTMS and MCMS are suitable for both acidic and basic polymers.

REFERENCES