PROTON DONOR ABILITY OF SURFACE HYDROXY GROUPS FROM THE IR SPECTRA OF HYDROGEN-BONDED COMPLEXES

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The influence of the strength of N-bases on the shift of $\nu$(OH) in hydrogen-bonded complexes upon adsorption on the surface of a decationized zeolite, phosphates and aerosil differing in the proton donor ability of surface hydroxy groups has been investigated. It is shown that the acid-base properties of the adsorbent-adsorbate pair produce additive influence on the above frequency shifts. A method for the determination of the proton donor ability of surface hydroxy groups (in terms of $pK_a$) from the IR spectra of hydrogen-bonded complexes is suggested.

As known /1/, during the formation of complexes with a hydrogen bond in homogeneous media the frequency of stretching vibrations of the proton donor groups decreases. The shift is determined by the proton donor and proton acceptor ability of the components participating in complex formation /2/. One may suppose that on the catalyst surface the strength of hydrogen bonds of adsorbed bases with hydroxy groups will be mainly determined by these factors.

IR adsorption spectra of the catalyst hydroxy groups have been studied during the adsorption of numerous N-bases of different strength. The proton donor ability of hydroxy groups on the surface of aerosil ($\nu = 3740 \text{ cm}^{-1}$), decationated zeolite
HNaY ($v = 3650$ cm$^{-1}$), aluminium, ferric and zirconium phosphates ($v = 3670$ cm$^{-1}$) have been examined. The procedure is described in Ref. [3].

During the adsorption of bases on the catalyst surface, complexes with different perturbations of the initial hydroxy groups are formed. In several cases the valence band of the proton donor groups $v$ (OH) is shifted towards the overtones of deformational vibrations of the hydroxy group. Fermi resonance with these result in the appearance of single components in the region from 1700 to 3000 cm$^{-1}$ [3-5]. In this case the position of the adsorption band of perturbed hydroxy groups is determined by the center of gravity of all the components ($v_{cg}$). It should be noted that for several strong bases the hydrogen-bonded molecular surface complexes are detectable only at lower temperatures, since at room temperature complete proton transfer (see, e.g., pyridine adsorption [3]) takes place.

Experimental data are shown in Fig. 1. The relative shift of the vibration frequency of surface OH-groups involved in molecular complex formation ($A v/v = \frac{v - v_{cg}}{v}$) depends linearly on the strength of the adsorbed base ($pK_a$):

$$A v/v = a + b pK_a$$

with the following constants:

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>a</th>
<th>b</th>
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<tbody>
<tr>
<td>Aerosil</td>
<td>0.145 ± 0.004</td>
<td>0.0096 ± 0.0007</td>
</tr>
<tr>
<td>Phosphates</td>
<td>0.263</td>
<td>0.0101</td>
</tr>
<tr>
<td>Zeolite</td>
<td>0.301 ± 0.004</td>
<td>0.0090 ± 0.0007</td>
</tr>
</tbody>
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The proportionality factor $b$ is essentially the same for all the adsorbents, and the different nature of catalysts is reflected only in the value of parameter $a$, which should be noted that for several strong bases the hydrogen-bonded molecular surface complexes are detectable only at lower temperatures, since at room temperature complete proton transfer (see, e.g., pyridine adsorption [3]) takes place.

The linear dependence between $A v/v$ and $pK_a$ shows that in the adsorbed state the relative strength of N-bases is similar to that in aqueous solution. The data