STUDY OF ACTIVE CARBON NICKEL CATALYSTS IN PRESENCE OF AIR BY MODIFIED DTA CURVES

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DTA and TG curves from investigations on the oxidation of active carbon—nickel catalysts in a static air atmosphere with a derivatograph were used to construct modified DTA curves, the $\Delta T/m_R$ plots (where $m_R$ is the reactive mass of the sample). The $\Delta T/m_R$ plots in the range from 200 to 850° led to the finding that the oxidation process is a two-stage reaction. In the diffusion region the reaction depends on the pore volume with pore radii from 75 to 7500 nm. The variations in the ignition temperature with the nickel content of the samples are presented.

It has been established that the presence of catalytic impurities in carbon accelerates the rate of the oxidation reaction. Consequently, this implies changes in the ignition temperature of the carbon. As pointed out by Dollimore and Jones [1], the ignition temperatures of carbons decrease with increase of the impurity content. This may be used to measure the reactivity of carbon. It is obvious that ignition results from the oxidation reactions occurring in the lower range of temperature. Generally, the mechanisms of these reactions depend on the carbon reactivity, the natures and reactivities of the catalytic impurities, the natures of the bonds between the carbon and the inorganic species, and the porous structures of the samples.

In the present paper, thermal studies of active carbons impregnated with various amounts of nickel have been carried out in terms of the oxidation reaction in the temperature range from 20 to 1000°. The usefulness of the $\Delta T/m_R$ curves for the investigation of the active carbon — nickel catalysts in the presence of air has been considered.

Experimental

Active carbon (after activation by steam) produced by the Polish firm ZEW Racibórz (the trade-name of the product is Depolaryt D) was sieved and the fraction ranging in particle size from 75 to 250 μm in diameter was chosen. The active carbon was next divided into four groups: A-6/2, A-6/2-1, A-6/2-2 and A-6/2-3. Sample A-6/2 was subjected directly to the process of secondary activation, in contrast to the remaining samples, which were impregnated with aqueous solu-

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Table 1

Chemical compositions of the samples corresponding to the exothermic DTA maximum $T_{\text{max}}$ and the ignition temperature $T_i$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Nickel content, wt%</th>
<th>Ash, wt%</th>
<th>Elemental analysis, wt%</th>
<th>DTA exotherm, $T_{\text{max}}$ °C</th>
<th>Ignition temp., $T_i$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-6/2</td>
<td>0.00</td>
<td>7.9</td>
<td>91.0 0.95 1.00 0.53 6.5</td>
<td>550</td>
<td>430</td>
</tr>
<tr>
<td>A-6/2-1</td>
<td>1.03</td>
<td>8.9</td>
<td>92.85 0.85 1.03 0.44 4.8</td>
<td>530</td>
<td>400</td>
</tr>
<tr>
<td>A-6/2-2</td>
<td>2.74</td>
<td>10.6</td>
<td>92.65 0.90 1.05 0.54 4.9</td>
<td>490</td>
<td>370</td>
</tr>
<tr>
<td>A-6/2-3</td>
<td>5.25</td>
<td>14.2</td>
<td>91.1 1.17 1.11 0.52 6.1</td>
<td>440</td>
<td>340</td>
</tr>
</tbody>
</table>

Tensions of Ni(NO$_3$)$_2$·6 H$_2$O before the activation process. The aqueous solutions contained different amounts of the nickel salt (Table 1). All air-dried samples were activated in a stationary bed with carbon dioxide at 600° for 2 hours. The physicochemical properties of the samples after the process of activation are listed in Tables 1 and 2. The total porosity of each sample was determined by means of the helium adsorption method. The volume distribution of the pores and the mercury porosity in the radius range from 7.5 to 7500 nm were determined with a Carlo-Erba Ag-65 mercury porosimeter. For the reasons considered in the earlier papers [2, 3] the pore size ranges studied were divided into three groups, involving the following pore radii:

- $7.5 \text{ nm} \leq r_1 < 75 \text{ nm}$
- $75 \text{ nm} \leq r_2 < 750 \text{ nm}$
- $750 \text{ nm} \leq r_3 < 7500 \text{ nm}$

Before the measurements mentioned above, the samples were dried at 105°.

Table 2

Porosity data on the samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Helium porosity, $V_{\text{He}}$ cm$^3$/g</th>
<th>Mercury porosity, $V_{\text{Hg}}$ cm$^3$/g</th>
<th>Pore radius range</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.5–75 nm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$V_i$ cm$^3$/g</td>
</tr>
<tr>
<td>A-6/2</td>
<td>0.223</td>
<td>0.105</td>
<td>0.020</td>
</tr>
<tr>
<td>A-6/2-1</td>
<td>0.200</td>
<td>0.069</td>
<td>0.025</td>
</tr>
<tr>
<td>A-6/2-2</td>
<td>0.201</td>
<td>0.087</td>
<td>0.017</td>
</tr>
<tr>
<td>A-6/2-3</td>
<td>0.292</td>
<td>0.170</td>
<td>0.019</td>
</tr>
</tbody>
</table>

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