2. By x-ray diffraction analysis it was found that the crystalline structure of high-silicon zeolites NaM and superhigh-silicon zeolites scarcely changes under the reaction conditions. There are thus new prospects for the preparation of new effective catalysts for the synthesis of carboxylic acids by carbonylation of olefins.

LITERATURE CITED


SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN IN THE PRESENCE OF Co CATALYSTS CONTAINING HIGH-SILICON ZEOLITES

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Cobalt catalysts on carriers are used as catalysts in the Fischer-Tropsch synthesis [1-5].

We studied the synthesis of hydrocarbons from CO and H2 in the presence of Co catalysts based on high-silicon zeolites of the pentasil type, obtained by using cobalt carbonate or carbonyl.

EXPERIMENTAL

All the carriers used for the preparation of the catalysts were first calcined for 5 h at 450°C. Some of the catalysts were prepared by mixing freshly prepared Co carbonate with the carrier in a ratio of 1:2. These catalysts were reduced for 4 h in an H2 current at 450°C, and at a bulk speed (b.s.) of 100 h-1. The carbonyl catalysts were prepared by impregnating the carrier with a dicobalt octacarbonyl Co2(CO)8 solution in n-hexane. The catalysts were then transferred in an Ar current into the reactor of a flow-type catalytic apparatus, and were treated in an H2 current (b.s. 25 h-1), while the temperature was raised from 25 to 150°C at a rate of 1 deg/min.

The synthesis of the hydrocarbons was carried out in a flow-type catalytic apparatus under the following conditions: CO:H2 = 1:2, 170-200°C, b.s. = 100 h-1. The liquid products were analyzed by GLC, and the heating was programmed from 60 to 250°C (10 deg/min). Column: 3% atalgione L on chromosorb P (3 mm × 3 m), katharometer.

The chemisorption of CO was studied by pulse chromatography method [6], and the forms of adsorption of CO were studied by the procedure described in [7].

DISCUSSION OF RESULTS

Table 1 shows that for the contacts not containing MgO, at 190°C, the contraction of the synthesis-gas (40%) and the total yield of the products (49 g/nm3) are practically independent of the zeolite modulus, but the ratio of the liquid and gaseous products are thus not equal. Thus, with increase in the modulus from 42 to 109, the yield of liquid hydrocarbons decreases by a factor of 2, and the yield of the gaseous reaction products almost doubles.
TABLE I. Dependence of Activity of Mix Type Co Catalysts in Synthesis of Hydrocarbons from CO and H₂ on Carrier Used (H₂:CO = 2:1, b.s. 100⁻¹, atmospheric pressure)

<table>
<thead>
<tr>
<th>Carrier</th>
<th>T., °C</th>
<th>Contraction, %</th>
<th>Yield of hydrocarbons, g/nm³</th>
<th>Yield of liquid hydrocarbons, %</th>
<th>Yield of gaseous hydrocarbons, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentasil-42</td>
<td>240</td>
<td>71</td>
<td>110</td>
<td>65</td>
<td>45</td>
</tr>
<tr>
<td>Pentasil-66</td>
<td>240</td>
<td>52</td>
<td>43</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>Pentasil-109</td>
<td>240</td>
<td>39</td>
<td>28</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td>Pentasil -42 + 3% MgO</td>
<td>190</td>
<td>51</td>
<td>141</td>
<td>124</td>
<td>17</td>
</tr>
<tr>
<td>Pentasil -42 + 6% MgO</td>
<td>190</td>
<td>60</td>
<td>178</td>
<td>172</td>
<td>6</td>
</tr>
<tr>
<td>Pentasil -42 + 12% MgO</td>
<td>190</td>
<td>88</td>
<td>145</td>
<td>139</td>
<td>6</td>
</tr>
</tbody>
</table>

Fig. 1. Influence of temperature on the total yield of products in the synthesis of hydrocarbons from CO and H₂ on mix type Co catalysts:
1) Co-(pentasil-42 + 6% MgO);
2) Co-pentasil-42.

At 240°C, with increase in the zeolite modulus, as at 190°C, the content of liquid and gaseous hydrocarbons decreases.

The introduction of MgO into the composition of the catalyst at 190°C leads, as shown in Table I, to an appreciable increase in the activity of the catalysts of the Fischer-Tropsch synthesis, prepared by the mixing method. The most active catalyst is that containing 6% of MgO in the composition of the carrier. It should be noted that for all MgO-containing catalysts, the yield of liquid hydrocarbons is higher than the yield of gaseous reaction products. At 240°C, the introduction of MgO into the composition of the catalyst scarcely changes the total yield of the hydrocarbons, but also at this temperature the maximal amount of liquid hydrocarbons is formed on a contact containing 6% of MgO in the composition of the carrier. It should also be noted that the introduction of MgO leads to a decrease in the optimal temperature of the synthesis (see Fig. 1). The products obtained on the catalysts studied contain C₁₋C₂₂ hydrocarbons. With increase in the MgO content, the yield of the light fractions of the liquid (C₅₋C₆) hydrocarbons decreases (see Table 2), and the yield of heavy oil (>C₆) increases. Thus, on a catalyst containing 12% of MgO in the composition of the carrier, the liquid fractions with a chain length of >C₆ comprise 57%. At 240°C, on the mix type Co catalysts, aromatic hydrocarbons are formed in a maximal yield (7%) on a catalyst not containing MgO. With increase in the amount of MgO in the composition of the catalyst, the fraction of the aliphatic hydrocarbons in the reaction products increases appreciably. The aromatic hydrocarbons (9%) are also formed under the conditions of hydropolymerization of ethylene initiated by small amounts of CO at 310°C, on similar catalysts.