CATALYTIC POLYMERIZATION OF OLEFINS

COMMUNICATION 7. POLYMERIZATION OF ETHYLENE OVER A NICKELOUS OXIDE - ALUMINUM SILICATE CATALYST


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It was shown previously [1] that alumina has a powerful promoting effect on a nickelous oxide - silica gel (KSK) catalyst for the polymerization of ethylene. On the other hand, various clays were investigated and found to be unsuitable as a carrier for the nickel catalyst in this reaction. It was of interest to examine the behavior of synthetic aluminum silicates in this respect.

In the literature [2] there is a description of the polymerization of ethylene in admixture with hydrogen at 40° and 20 atm over an NiO catalyst carried by a synthetic cracking aluminum silicate. The conversion of ethylene was about 97%; the yield of polymer, which contained 50% of butenes, was 325 g/liter - hr.

In the present work we studied the following samples of synthetic aluminum silicates in tablet form: a Houdry cracking catalyst (I), an analogous treating catalyst (II), and a Soviet aluminum silicate cracking catalyst (III) [3]. The physical properties and chemical compositions of these aluminum silicates have been given previously [4]. The apparatus and experimental procedure were as before [5]. The experiments were carried out at 300° with catalysts prepared both by precipitation from nickel nitrate and by impregnation with nickel formate. Each experiment, when continuous, lasted for five hours.

EXPERIMENTAL

Precipitated NiO - Aluminum Silicate (Tablet Form) Catalysts. The following catalysts were used: Catalyst 88 had a carrier of aluminum silicate I in tablet form; precipitation was carried out with aqueous ammonia from saturated nickel nitrate solution (15 ml per 10 ml of aluminum silicate). Catalyst 86 differed from Catalyst 88 only in that precipitation was carried out with potassium carbonate.

The results obtained with these catalysts at a time of contact of 11-12 seconds are given in Table 1. This table shows that with Catalyst 88, which was prepared by precipitation with ammonia, the yield of dimer averaged at 35.4% on the ethylene passed and 53.5% on the ethylene that reacted. After 15 hours of work the conversion of ethylene fell from 80% to 54%; there was a simultaneous fall in the yield of higher hydrocarbons. After regeneration in a stream of air at 450°, the catalyst worked further for 20 hours with almost the same activity, and the same regularities were observed as regards the change in the amount of ethylene that reacted and the fall in the yield of liquid condensate. Catalyst 86, prepared by precipitation with potassium carbonate, was more selective with respect to dimerization: the yield of dimer was 43.3-30.7% on the ethylene passed and 63.6-78.8% on the ethylene that reacted; the yield of higher hydrocarbons was less than in the experiments with Catalyst 88. However, after regeneration Catalyst 86 lost its selectivity. It is interesting that the yield of higher hydrocarbons was greater over a fresh catalyst and immediately after regeneration than in subsequent experiments.
Impregnated NiO - Aluminum Silicate (Tablet Form) Catalysts. Catalyst 77 had aluminum silicate I as carrier. Impregnation was carried out with a boiling 1% solution of nickel formate. Catalyst 100 differed from Catalyst 77 only in that the carrier was aluminum silicate II. Catalysts 107 and 200 were identical with the previous catalysts, but aluminum silicate III in tablet form was used as carrier; in the analogous Catalyst 99, tablets of aluminum silicate III were first ground to a powder. In the experiments with Catalyst 200 the time of contact was 6 seconds, and in work with the other catalysts the time was 11-12 seconds.

The results are presented in Table 2.

Table 2 shows that Catalyst 77 was distinguished by its good regenerability but low selectivity for the dimerization of ethylene. Catalyst 100 could also be regenerated satisfactorily. As the amount of work done by this catalyst increased, its selectivity increased. Catalyst 107 was found to be less active, poorly regenerable, and of low selectivity. The results obtained with Catalyst 99 show that the use of the carrier in powder form results in lower activity and stability. Comparison of the results of the work of Catalysts 107 and 200 shows that, with reduction of the contact time to one-half, the total conversion of ethylene is reduced by more than one half, though the yield of dimer on the amount of ethylene that reacts increases, i.e., the selectivity of the catalyst for dimerization increases. However, after the second regeneration the selectivity of the catalyst fell sharply.

The impregnated catalyst was tested in prolonged work with overnight interruptions and recirculation of ethylene, and also in prolonged uninterrupted work. All these experiments were carried out with a contact time of 9-12 seconds.

Work with Interruptions Between Experiments. Catalyst 76 was used; this differed from Catalyst 77 only in that impregnation of the aluminum silicate was with a saturated nickel formate solution. The results are shown in Figures 1 and 2. Eleven regenerations were carried out in 95 hours. During the whole working period, 365 liters of ethylene was passed and, on the average, 52.5% of this reacted. The average yield of dimer was 32.7% on the ethylene passed and 55% on the amount that reacted. The yield of higher hydrocarbons was 13.3% and 22.9%, respectively. After about 100 hours of contact the catalyst largely maintained its activity, even after the eleventh regeneration.

Experiments with Recirculation of Gas. In this series of experiments we used Catalyst 135, which is like Catalyst 77. The results obtained with this catalyst are given in Table 3. In 50 hours 99.3 liters of 99% ethylene was passed; we obtained 10.5 liters of composition

<table>
<thead>
<tr>
<th>Catalyst No.</th>
<th>Yield of butene (% on ethylene that reacted)</th>
<th>Yield of higher hydrocarbons (%)</th>
<th>Expt.</th>
<th>Catalyst</th>
<th>Catalyst used</th>
<th>Yield of higher hydrocarbons (on ethylene passed)</th>
<th>Yield of higher hydrocarbons (on ethylene that reacted)</th>
<th>Before this experiment the catalyst was regenerated in a stream of air at 450° for five hours.</th>
</tr>
</thead>
<tbody>
<tr>
<td>86</td>
<td>86</td>
<td>NiO - aluminum silicate (for cracking)</td>
<td>1</td>
<td>1 - 2</td>
<td>4 - 7</td>
<td>88,0 - 54,4</td>
<td>82,0 - 56,4</td>
<td>3,5</td>
</tr>
<tr>
<td>86</td>
<td>86</td>
<td>NiO - aluminum silicate (for cracking)</td>
<td>3</td>
<td>1 - 2</td>
<td>4 - 7</td>
<td>68,0 - 30,0</td>
<td>63,0 - 28,0</td>
<td>1 - 2</td>
</tr>
<tr>
<td>88</td>
<td>88</td>
<td>NiO - aluminum silicate (for cracking)</td>
<td>4</td>
<td>4 - 7</td>
<td>66,0 - 49,4</td>
<td>68,0 - 50,4</td>
<td>63,0 - 28,0</td>
<td>3 - 2</td>
</tr>
<tr>
<td>88</td>
<td>88</td>
<td>NiO - aluminum silicate (for cracking)</td>
<td>3</td>
<td>1 - 2</td>
<td>4 - 6</td>
<td>47,0 - 35,0</td>
<td>44,0 - 32,0</td>
<td>1 - 2</td>
</tr>
</tbody>
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