Liquid-phase ethylbenzene oxidation with barium catalysts

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Introduction
Autoxidation reactions are very important milestones in the development of new petrochemical processes. These kinds of reactions use the most abundant and cheapest oxidant that minimizes the production and use of pollutants. As these reactions follow a complexe radical mechanism, it is difficult to reach high selectivity at high conversion levels. The development of catalytic systems that allows obtaining good yields could be a great challenge in the “green chemistry”.
Ethylbenzene hydroperoxide (EBHP) is prepared by the liquid-phase oxidation of ethylbenzene (EB) with molecular oxygen, and this process requires a specific catalyst to obtain high selectivity levels. The aim of this work is to study the oxidation of ethylbenzene to yield ethylbenzene hydroperoxide in the presence of minute amounts of barium oxide.

Results and Discussion
A 150 ml thermostatable glass cylindrical vessel provided with a glass stirrer and a gas inlet system, a type K thermocouple and a reflux condenser cooled by water was used for the experiments. Temperature was controlled by a heating circulator, the stirrer was powered by a variable speed engine and gases were fed to the reactor through mass flow controllers. In order to avoid the formation of explosive gas mixtures, an inert gas stream (N_2) is introduced at the upper side of the reactor, keeping the concentration of O_2 at low values (≤8%). In a typical oxidation run, 50 g of EB containing about 0.4 wt% of EBHP and the amount of barium oxide designed for the experiment were charged to the reactor, and temperature and stirring speed were set constant (typically 403 K and 1000 rpm). Once the temperature was constant, gas flow was set and kept constant during the experiment. Aliquots were taken at 0, 60, 120, 180 and 240 min of reaction, the total amount extracted was less than 10% of total mixture inside the reactor. The concentration of EBHP was measured by standard iodometric titration. Other products were analyzed by gas chromatography.
Firstly, the effect of barium oxide concentration was studied in the range 0.5-32 ppm. Figure 1 shows the relationship between EBHP yield and barium concentration. For higher barium concentrations, lower EBHP productions are obtained; yield was increasing for lower concentrations of catalyst, reaching a maximum for 1 ppm of barium oxide.
Figure 1. Variation of EBHP yield at different concentrations of barium oxide.

The effect of partial pressure of oxygen on ethylbenzene conversion and hydroperoxide selectivity was also studied. The concentration of oxygen in fed gas was varied between 21 and 70 %; the results are compiled in Table 1. An enhancement in the EB conversion and EBHP yield was detected for higher oxygen concentrations. In parallel, a remarkable decrease in the EBHP selectivity is observed upon increasing oxygen concentration. These results indicate that a careful control of the catalyst concentration and reaction variables is essential to maximize EBHP production.

Table 1. Reaction results with different oxygen partial pressures (t = 240 min)

<table>
<thead>
<tr>
<th>%O₂</th>
<th>EBHP wt %</th>
<th>%Selectivity to EBHP</th>
<th>%Conversion to EB</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>3.70</td>
<td>80</td>
<td>4.0</td>
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<td>40</td>
<td>4.59</td>
<td>55</td>
<td>5.9</td>
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<tr>
<td>70</td>
<td>5.48</td>
<td>34</td>
<td>11.7</td>
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</tbody>
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References
1. C.-Y. Wu, H. E. Swift, J. E. Bozik, (Gulf Research & Development Company) US Pat No 4,158,022 (1979)