Selective synthesis of p-ethylphenol by gas phase ethylation of phenol.

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Introduction

P-Ethylphenol (p-EP) is raw material for the production of p-vinylphenol, which is a valuable chemical used in resins preparations, synthesis of pharmaceuticals and dyes. p-EP is commercially produced by ethylbenzene sulfonation followed by alkaline fusion using corrosive acids and bases. This process poses serious environmental concerns because of the generation of significant amount of wastes. Therefore, the development of an alternative route for obtaining p-EP becomes highly desirable. Ethylphenols can be obtained by gas phase phenol alkylation with ethanol. In fact, the selective synthesis of o-ethylphenol and 2,6-diethylphenol by alkylation of phenol with ethanol using SiO₂-Al₂O₃ and Fe₂O₃ catalysts has been already reported [1]. p-Selective alkylation of phenol with ethanol has been claimed on pore size tailored HZSM5 zeolite at 673 K and phenol/ethanol ratio of 2, however the highest p-EP yield obtained was less than 7% [2]. In this work we studied the gas phase ethylation of phenol on zeolites HZSM5 and HMCM22 in order to obtain higher yields of p-ethylphenol and thus developing a technological alternative route for the efficient production of p-EP.

Materials and Methods

Commercial HZSM5 (Zeocat Pentasil PZ-2/Si, Si/Al = 20) and zeolite HMCM22 (Si/Al=15) prepared in our laboratory were used. Zeolite surface areas and total density of de acid sites were similar for both catalysts; however, the Brønsted (B) to Lewis (L) ratio for HMCM22 was about three times higher than the B/L ratio for HZSM5.

Table 1. Characterization of catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>S BET (m²/g)</th>
<th>Mean pore size (Å)</th>
<th>TPD NH₃ (µmol/g)</th>
<th>IR of pyridine (Area/g)</th>
<th>L Sites</th>
<th>B Sites</th>
<th>B/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>HZSM5</td>
<td>350</td>
<td>5.1x5.5; 5.3x5.6</td>
<td>475</td>
<td>341</td>
<td>337</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>HMCM22</td>
<td>400</td>
<td>4.0x5.5; 4.1x5.1</td>
<td>470</td>
<td>176</td>
<td>560</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>

Reactants conversions and selectivities values obtained at times zero and 3 h are given in Table 2. Phenol conversion was similar on both catalysts and decreased with time on stream. At time zero only ethylphenols and dialkylated products from C-alkylation of phenol were formed, but with the progress of the reaction the S BET (from O-alkylation) increased at expenses of the ethylphenols. A remarkable difference in ethylphenols distribution was observed. In fact, on...