Catalytic distillation for ethyl acetate synthesis using microfibrous-structured Nafion-SiO$_2$/SS-fiber solid acid packings

Tao Deng, Yakun Li, Guofeng Zhao, Zhiqiang Zhang, Ye Liu and Yong Lu*
<table>
<thead>
<tr>
<th>Coating composition(^a)</th>
<th>Total loading (wt%)</th>
<th>IEC (mmol g(^{-1}))(^b)</th>
<th>1 h ultrasonic concussion (mmol g(^{-1}))</th>
<th>2 h ultrasonic concussion (mmol g(^{-1}))</th>
<th>3 h ultrasonic concussion (mmol g(^{-1}))</th>
<th>4 h ultrasonic concussion (mmol g(^{-1}))</th>
<th>5 h ultrasonic concussion (mmol g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nafion</td>
<td>10.7</td>
<td>0.09</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Nafion/SiO(_2)</td>
<td>17.5</td>
<td>0.07</td>
<td>0.03</td>
<td>0.01</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Nafion/TEOS</td>
<td>25.3</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
<td>0.07</td>
</tr>
</tbody>
</table>

\(^a\) The coating solution were 5 wt\% Nafion polymer dispersion, SiO\(_2\) sol-gel in 5 wt\% Nafion polymer dispersion and TEOS in Nafion polymer dispersion with the same Nafion:additives weight ratio of 2:1.

\(^b\) The ion-exchange capacity (IEC) was used to represent the catalyst acid capacity.
Figure S1. Effect of reboiler temperature (duty) on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: molar feed ratio of acetic acid to ethanol = 1:1, reflux ratio = 2.5, WHSV = 0.3 h⁻¹, molar ratio of acetic acid to ethanol in the flask = 1.2:1, catalyst amount = 8.5 mmol H⁺.
Figure S2. Effect of molar ratio of acetic acid to ethanol on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: reboiler temperature = 220 °C, reflux ratio = 2.5, WHSV = 0.3 h⁻¹, molar ratio of acetic acid to ethanol in the flask = 1.2:1, catalyst amount = 8.5 mmol H⁺.
Figure S3. Effect of WHSV on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: reboiler temperature = 220 °C, reflux ratio = 2.5, molar feed ratio of acetic acid to ethanol = 1.2:1, molar ratio of acetic acid to ethanol in the flask = 1.2:1, catalyst amount = 8.5 mmol H⁺.
Figure S4. Effect of reflux ratio on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: reboiler temperature = 220°C, molar feed ratio of acetic acid to ethanol = 1.2:1, WHSV = 0.5 h⁻¹, molar ratio of acetic acid to ethanol in the flask = 1.2:1, catalyst amount = 10.5 mmol H⁺.
Figure S5. Effect of amount of the catalyst on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: reboiler temperature = 220 °C, reflux ratio = 2.5, WHSV = 0.5 h⁻¹, molar feed ratio of acetic acid to ethanol = 1.2:1, molar ratio of acetic acid to ethanol in the flask = 1.2:1.
**Figure S6.** Effect of molar ratio of acetic acid to ethanol in the flask on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour. Reaction conditions: reboiler temperature = 220 °C, molar feed ratio of acetic acid to ethanol = 1.2:1, reflux ratio = 2, WHSV = 0.5 h⁻¹, catalyst amount = 10.5 mmol H⁺.
Figure S7. The stability test with structured catalyst on the purity of ethyl acetate at the top (A) and bottom (B) of the column for every 1 hour in five consecutive batch experiments. Reaction conditions: reboiler temperature = 220 °C, molar feed ratio of acetic acid to ethanol = 1.2:1, reflux ratio = 2, WHSV = 0.5 h⁻¹, catalyst amount = 10.5 mmol H⁺, molar ratio of acetic acid to ethanol in the flask = 1:1.2.