Liquid-phase hydrodechlorination of CCl₄ in a medium of ethanol with co-production of acetal (1,1-diethoxyethane) and diethyl carbonate

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Catalytic hydrodechlorination (HDC) of CCl₄ in gas phase seemed to be a useful method for the disposal of this ozone-depleting compound [1-3], however, an obstacle in practicing HDC of CCl₄ in a large scale is the difficulty in controlling reaction temperature due to a large exotherm of the reaction. In principle, liquid phase reactions have the advantages of more facile control of reaction temperatures, and then problems of local hot-spots and catalyst fouling are less significant. Gomez-Sainero, et al. [3,4] showed the reactivity of CCl₄ itself (without solvent) in the liquid phase HDC over some supported metal catalysts and they have finally recommended palladium supported on carbon as the best catalyst. In this study, the palladium catalysts grafted to montmorillonite (Pd/Mont) were prepared by ion exchange of H-montmorillonite with (CH₃CN)₂PdCl₂ [5]. We investigated a reaction system that gives not only the HDC of CCl₄ but also co-production of DEC and DEE with the presence of oxygen.

Results and Discussion

The conversion of CCl₄ and C₂H₅OH as well as product distribution over Pd/Mont with time on stream are shown in Figure 1. The selectivity to CHCl₃ from the reaction of CCl₄ increased with time on stream and vice versa for C₂ compounds, but the conversion of CCl₄ showed steady value after around 12 h. This could be mainly from catalyst deactivation due to the strong adsorption of the generated chlorine sources on active sites and the water generated could inhibit further conversion of CCl₄ (Run 3).

![Graphs showing conversion of CCl₄ and C₂H₅OH and product distribution over Pd/Mont.](image)

The conversion of C₂H₅OH approached the steady values after 15 h reaction possibly due to reverse reactions of products formed with C₂H₅OH. To correlate catalytic activity...
change with the states of supported palladium, X-ray photoelectron spectroscopy (XPS) of the fresh Pd/Mont and the used ones are also investigated. The changes in oxidation states of supported palladium after reaction could be the main reason for the variation of selectivity to CHCl₃ and C₂ compounds with time on stream (Figure 1(a)). This is in line with the previous observations [3,4] and the activity changes in HDC of CCl₄ were correlated with the oxidation states of grafted palladium in liquid-phase system.

Table 1. Conversion and products distribution on 2.8wt%Pd/Mont catalyst

<table>
<thead>
<tr>
<th>Run</th>
<th>Effects</th>
<th>Conv. of CCl₄</th>
<th>Product distribution (mole %)</th>
<th>Conv. of C₂H₅OH</th>
<th>Product distribution (mole %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>CHCl₃</td>
<td>C₂H₄Cl₄₄⁺ a</td>
<td>C₂Cl₄b</td>
</tr>
<tr>
<td>1</td>
<td>-</td>
<td>43.5</td>
<td>93.3</td>
<td>1.3</td>
<td>5.4</td>
</tr>
<tr>
<td>2</td>
<td>O₂</td>
<td>36.7</td>
<td>91.9</td>
<td>2.5</td>
<td>5.6</td>
</tr>
<tr>
<td>3</td>
<td>H₂O</td>
<td>36.3</td>
<td>88.5</td>
<td>1.9</td>
<td>9.6</td>
</tr>
<tr>
<td>4</td>
<td>H₂O₂</td>
<td>21.1</td>
<td>79.7</td>
<td>2.6</td>
<td>17.7</td>
</tr>
</tbody>
</table>

Reaction conditions: T = 323 K; P(H₂) = 3 MPa; CCl₄ = 64.5 mmol; n-undecane = 1.3 mmol; catalyst = 0.1 g; reaction for 12 h. a C₂Cl₄ and C₂HCl₃ were the main products. Run 2: Effect of O₂ (P = 0.1 Mpa); Run 3: Effect of H₂O (H₂O/C₂H₅OH = 0.2); Run 4: Effect of H₂O₂ (H₂O₂(30wt% in H₂O)/C₂H₅OH =1.0). Abbreviation: DEE = 1,1-diethoxyethane; AA = acetaldehyde; EVE = ethyl vinyl ether; DEC = diethyl carbonate.

During the hydrodechlorination with C₂H₅OH, generation of DEC was observed. We thought that dissolved oxygen might be involved in this reaction. To prove this hypothesis, air was intentionally introduced at the beginning of the reaction (Run 2). When a small amount of air (P(O₂) = 0.1 MPa) was added at the beginning of the reaction, the formation of diethyl carbonate was greatly enhanced without significant effect on hydrodechlorination of CCl₄. The molecular oxygen in air could accelerate the formation of DEC by the oxidative cleavage of C=C double bonds in EVE precursors and the subsequent addition of ethoxy group. The real oxidizing agent may be hydrogen peroxide generated in-situ on the transition metal by the reaction of dihydrogen and dioxygen [6,7]. When hydrogen peroxide (30wt%H₂O₂ balanced with H₂O) was added at the beginning of reaction (Run 4), the formation of DEC was also greatly enhanced. Catalytic hydrodechlorination of CCl₄ over supported Pd in the presence of ethanol gives not only the selective synthesis of CHCl₃, but also co-production of valuable diethyl carbonate and 1,1-diethoxyethane (acetal). The formation rate of DEE was influenced by the acidity of catalysts and that of DEC was affected by the in-situ generated chlorine-containing intermediate as well as oxidative cleavage of its C=C group by in-situ generated H₂O₂.

References