Effect of acidity on the hydroxylation of benzene and toluene

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Abstract: This research studies effect of acidity of solution on two reactions. That is hydroxylation of benzene and toluene by hydrogen peroxide using the catalyst titanium silicalite-1 modified with metallic cobalt in the ratio Si/Co 150. The catalyst are prepared by hydrothermal method. The reaction is carried out at reaction temperature 70 °C and 90 °C in a stirred slurry reactor. Toluene solubility in water was also studies. It is found that adding hydrochloric acid can increase toluene solubility rate and concentration in water. This is the reason why during the catalytic activity testing of hydroxylation of toluene it was found that the reaction added with hydrochloric acid has higher conversion than reactions which no acid. In addition, the addition of hydrochloric acid significantly increases the formation of benzaldehyde due to the decrease self decomposition of hydrogen peroxide before reacting with toluene. For the catalytic activity testing of hydroxylation of benzene, it was found that the reaction added with hydrochloric acid has lower formation of phenol than the reaction which no acid. This result shown that the addition of acid inhibits the hydroxylation at the aromatic ring.

Key Words: Hydroxylation / benzene / toluene / TS-1

INTRODUCTION

Nowadays, Cresol is an organic compound which has a methyl group substituted onto the benzene ring of a phenol molecule. There are three forms of cresols that are only slightly different in their chemical structure: ortho-cresol (o-cresol), meta-cresol (m-cresol) and para-cresol (p-cresol). Cresol have a wide variety of uses including the manufacture of synthetic resins, tricresyl phosphate, salicylaldehyde and herbicides. Cresol solutions are used as household cleaners, disinfectants and important chemical raw material. At present, cresol is mainly produced from the methyl alkylation of phenol process which produces a mixture of anisol and mixed cresol. The several steps in reaction is the disadvantage of this process and cumenehydroperoxide is unstable, its may be danger for process.

Benzaldehyde is a chemical compound consisting of a benzene ring with an aldehyde substituent. It is the simplest representative of the aromatic aldehydes and one of the most industrially used members of this family of compounds. At room temperature it is a colorless liquid with a characteristic and pleasant almond-like odor. Benzaldehyde is an important component of the scent of almonds. It is used in manufacturing of benzoic acid, pharmaceuticals and dyes, as a solvent for oils, cellulose acetate and nitrate. Benzaldehyde can be obtained by many processes. Presently liquid phase chlorination or oxidation of toluene is among the most used processes. The disadvantages of this route are (i) the reaction consists of two steps, (ii) the use of light to activate the chlorination reaction, and (iii) the formation of by product. The direct oxidation of toluene also possesses the disadvantage of the over oxidation of toluene to benzoic acid.

It can be obviously seen from the above paragraphs that there is no common production step between the production of cresols and benzaldehyde. In our previous researches (Rojarek Passasadee, 2008 and Pattaraporn Harnvanich, 2008), however, it is found that the reaction between toluene as reactant and H₂O₂ as oxidant can produce either benzaldehyde or cresols or both by using an appropriate catalyst. The catalyst found to have the above property is TS-1 and TS-1 modified with a suitable second metal. For example, if TS-1 is modified by adding Co (Co-TS-1), cresol will become the prominent product. The advantage of the new route is only one process is required for the production of cresols or benzaldehyde and the reaction complete in only one step. The only thing has to be changed is the catalyst used. This offers process flexibility.
This process, however, still has a drawback that is the conversion is rather low. A possible cause is \( \text{H}_2\text{O}_2 \) decomposes rather than reacting with toluene and the low solubility of toluene in water. It is widely known that in an acidic solution, \( \text{H}_2\text{O}_2 \) decomposes slower than in a neutral or a basic solution. This research, therefore, studies the effect of acidity of solution on the reaction between toluene or benzene and hydrogen peroxide over TS-1 catalyst.

2. MATERIAL AND METHODS

2.1. The preparation of the Co-TS-1 catalyst

The Co-TS-1 catalyst is prepared by a hydrothermal method using sodium silicate solution as Si source, titanium (IV) butoxide 97% as Ti source and Cobalt nitrate as promoter. The atomic ratio of silicon/titaniuim is 150. A glass container contains mixture of precursors of TS-1 or modified TS-1 is placed in a stainless steel autoclave. Further details of the preparation of the mixture of precursors are described elsewhere (Rojarek Passassadee, 2008 and Pattaraporn Harnvanich, 2008). The atmosphere in the autoclave is replaced by nitrogen gas and pressurized up to 3 kg/cm² gauge. Then, the autoclave is heated from room temperature to 180 °C and kept at this temperature for 3 days, followed by cooling the mixture to room temperature in the autoclave. The obtained product crystals are washed with de-ionized water decreased pH from about 12 to 7 by centrifugation in order to remove chloride out of the crystals. Then the crystals are dried in an oven at 110 °C for at least 24 h. The dry crystals are calcined in an air stream at 550 °C and held at that temperature for 7 h, by heating them from room temperature to 550 °C at a heating rate at 10 °C/min. The calcined crystals are finally cool down to room temperature. Then the obtained Co-TS-1 are placed into a round bottom flask filled with 5 M of HNO₃ aqueous solution. After reflux at 80 °C for 3 h, the treated catalyst is filtered, washed with distilled water until pH 7, dried at 110 °C and calcined again at 540 °C for 7 h in static air.

2.2. Experimental

The hydroxylation of toluene and benzene with \( \text{H}_2\text{O}_2 \) (30 wt% in water, Merck) is carried out in a 250 ml, paraffin oil jacketed, three-necked, glass flask fitted with a condenser and a mechanical stirrer placed in a stirring block heater, see Figure 2.2.1. The reaction is performed at atmospheric pressure. Typically, 1 g of catalyst is used with toluene and \( \text{H}_2\text{O}_2 \) at a molar ratio equals to 1 to 1 with 90 ml or 120 ml of water which acts as solvent. If x ml of 0.1 M HCl, the volume of water used will be reduced to 90-x ml or 120-x ml. An experiment using NaCl solution instead of HCl is also performed to determine whether the effects come from the presence of \( \text{H}^+ \) or Cl. To carry out the reaction, the catalyst and water, used for dispersing the catalyst are added into the reactor. Then the reactor temperature is raised to 90 °C and kept at this temperature for 1 hour in order to drive out gases in pores of the catalyst. Then 1 ml of toluene is added into the reactor. 1 ml of \( \text{H}_2\text{O}_2 \) is slowly injected dropwise (0.1 ml per 12 min) into the reactor. The overall reaction time (counts from the first drop of \( \text{H}_2\text{O}_2 \) is added) in 2 hours. The reaction was stopped by removing the reactor from the oil bath and put into an ice bath. After that 50 ml of ethanol is added into reactor to homogenize the aqueous phase and the organic phase. The reaction products are analyzed by a gas chromatograph equipped with a FID detector (SHIMADZU GC9A).

![Figure 2.2.1. The hydroxylation reactor](image)

Calculations of %\( \text{H}_2\text{O}_2 \) converts to organic products, productivity and %selectivity of each product are carried out using the following equation:

\[
\text{The percentage of } \text{H}_2\text{O}_2 \text{ converts to product } = \frac{\text{overall mole of product}}{\text{mole of } \text{H}_2\text{O}_2} \times 100
\]

\[
\text{The percentage of productivity } \text{Productivity of benzaldehyde} = \frac{\text{mole of benzaldehyde}}{\text{weight catalyst(\text{g})} \times 120 \text{ min} \times 10^{-6}} \times 100
\]

The productivity of o-cresol and p-cresol can be calculated using the equation of the productivity of benzaldehyde but the mole of o-cresol and p-cresol is used instead of the mole of benzaldehyde.

\[
\text{The percentage of product selectivity } \text{Selectivity of o - cresol} = \frac{\text{mole of o - cresol}}{\text{overall mole of product}} \times 100
\]

Similarly, the %selectivity of o-cresol and p-cresol can be calculated using the equation %selectivity of benzaldehyde but the mole of o-cresol and p-cresol is used instead of the mole of benzaldehyde.

3. RESULTS AND DISCUSSION

3.1. The effect of acidity on hydroxylation of toluene and benzene

Table 3.1.1. shows the percentage of \( \text{H}_2\text{O}_2 \) conversion for the reaction of toluene with HCl and without HCl, and with NaCl at reaction temperature 90 °C. Since the conversion of \( \text{H}_2\text{O}_2 \) when no HCl is added and when NaCl is added is about the same, and lower than when HCl is added, it can be concluded that the presence of \( \text{H}^+ \) in the aqueous phase enhance the progress of the reaction. Cl does not take any role during the reaction.
Table 3.1.1. Percentage of H$_2$O$_2$ converts to product at 90 °C used Co-TS-1(150) catalyst for each solution.

<table>
<thead>
<tr>
<th>Solution</th>
<th>HCl 10 ml</th>
<th>NaCl 10 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>0.38</td>
<td>2.24</td>
</tr>
<tr>
<td>0.33</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1.2. Productivity and selectivity at 90 °C used Co-TS1 catalyst.

<table>
<thead>
<tr>
<th>Product of catalyst</th>
<th>Productivity (µmoles/min)</th>
<th>% Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzaldehyde</td>
<td>0.09</td>
<td>54.94</td>
</tr>
<tr>
<td>o-cresol</td>
<td>0.22</td>
<td>17.54</td>
</tr>
<tr>
<td>p-cresol</td>
<td>0.24</td>
<td>33.91</td>
</tr>
</tbody>
</table>

Table 3.1.2 shows the percentage of productivity and selectivity for the reactions of toluene with HCl, without HCl, and with NaCl at reaction temperature 90°C. It is found that in the reaction without acid, the productions of both o-cresol and p-cresol are higher than benzaldehyde. But when the solution is added with hydrochloric acid, the benzaldehyde production increases while the cresol productions decrease. Therefore, at this step it can be concluded that the acidity of the solution promotes the oxidation at the methyl group attached to the ring.

In order to identify the role of H$^+$ on the reaction at the ring, another set of reaction is carried out using benzene instead of toluene. The results are reported in Table 3.1.3. The results show that the percentage of H$_2$O$_2$ conversion for the reaction with acid is lower when no acid is added. Thus, it can be concluded that the present of H$^+$ inhibits the direct insertion of –OH group to the ring.

Table 3.1.3. Percentage of H$_2$O$_2$ converts to product at 70 °C used Co-TS-1(150) catalyst.

<table>
<thead>
<tr>
<th>Solution</th>
<th>HCl 18 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>4.15</td>
</tr>
<tr>
<td>3.44</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1.4 shows the percentage of productivity and selectivity for the reactions of toluene with acid at reaction temperature 70 °C, the total volume of aqueous phase is 120 ml (water 96 ml + 0.1 M HCl 24 ml). It is found in this case that the production of both o-cresol and p-cresol are still lower than benzaldehyde. While the production of benzaldehyde is higher than the production of benzaldehyde at reaction temperature 90 °C and added 0.1 M HCl 10 ml. This experiment suggests that the toluene molecules directly involve in the reaction may be the toluene molecule already dissolved into the aqueous phase. It is suspected that the presence of HCl in the aqueous phase may increase the concentration of toluene in the aqueous phase. In order to test this hypothesis, an additional experiment, solubility of toluene in an acidic aqueous is carried out.

Table 3.1.4. Productivity and selectivity at 70 °C used Co-TS1 catalyst.

<table>
<thead>
<tr>
<th>Product of catalyst</th>
<th>HCl 24 ml</th>
<th>Productivity (µmoles/min)</th>
<th>% Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzaldehyde</td>
<td>0.90</td>
<td>92.49</td>
<td></td>
</tr>
<tr>
<td>o-cresol</td>
<td>0.02</td>
<td>1.89</td>
<td></td>
</tr>
<tr>
<td>p-cresol</td>
<td>0.05</td>
<td>5.62</td>
<td></td>
</tr>
</tbody>
</table>

3.2. Toluene solubility in water

Figure 3.2.1 shows the toluene solubility in water with and without 0.1 M HCl. The results show that adding HCl can increase the solubility of toluene in water. When increase the volume of water in the reaction, it is found that percentage of H$_2$O$_2$ converts to organic products and the productivity and selectivity are increased. Since toluene molecules can be converted into products must be the toluene molecules dissolved already dissolved into the aqueous phase, the increase amount of toluene dissolved into the aqueous phase means that higher conversion can be achieved. This is the reason why the reaction added with hydrochloric acid has higher conversion than the reaction which no acid.

4. CONCLUSION

This research has found that the proton (H$^+$) really affects the reaction between toluene and hydrogen peroxide because the acidity of the solution promotes the oxidation at the methyl group attached to the ring. For the reaction between benzene and hydrogen peroxide, the presence of H$^+$ inhibits the direct insertion of –OH group to the ring. It can be summarised that the presence of H$^+$ in the aqueous phase containing H$_2$O$_2$ can enhance the oxidation of the alkyl group attached to the aromatic ring. At the same time, the direct insertion of –OH group to the aromatic ring is inhibited.

From the result of toluene solubility in water and the hydroxylation reaction of toluene with hydrochloric acid
which the increase in the volume of water it can be concluded that the higher amount of toluene dissolved into the aqueous phase, the higher amount of organic products formed.

5. REFFERENCE