Copper containing mixed oxides for catalytic oxidation of toluene and phenol in solid-liquid phase

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The YBa2Cu3O7-δ and its precursors (YCu2O3 and BaCuO2) have been used as catalysts for toluene and phenol oxidation in solid-liquid phase. It has been observed that the oxide without Cu(III) content and without alkaline earth metal, Y2Cu2O5, have low activity for the decomposition of H2O2 and high activity for these oxidation reactions. Maximum toluene conversion (25.9%) has been observed when acetonitrile is used as a solvent and maximum phenol conversion (45.3%) when water is used as a solvent. Mechanism of toluene oxidation on these mixed oxides has been suggested.

Perovskite type mixed oxides have been reported to be useful as catalysts in the gas-solid phase oxidation reactions as well as dehydrogenation of methane. These oxides have also been recognised as promising catalysts for electrocatalysis and in the treatment of automotive exhausts. However, there are only a few reports on the solid-liquid phase oxidation reactions using pure metal oxides and perovskite oxides.

Ito et al. have reported the oxidation of benzene to phenol using cuprous chloride as a catalyst and molecular oxygen as the oxidant. Recent reports have indicated that TS-1, TS-2 and Ti-MCM-41 have replaced the homogeneous catalysts, but failed to be useful because of their difficult preparation procedures and slower reaction rates. Mixed oxide like BaMn12XCu5O15 has been tested for H2O2 decomposition by Das et al. and they observed that catalytic activity for H2O2 decomposition increases with increase in copper content. Sugunan and Sherly have also reported catalytic activity for La2O3 in the reduction of cyclohexanone.

In the present study, toluene oxidation on copper containing oxides gives benzaldehyde and o,p-cresols as the major products. The main interest in the oxidation of toluene is the formation of cresols. The bactericidal and fungicidal properties of cresols enable them to be used as disinfectants in soap. Cresol mixtures are also used in ore flotation.

Materials and Methods

Preparation of catalysts

The Y2Cu2O5, BaCuO2 and YBa2Cu3O7-δ compounds were prepared by high temperature solid state reaction between the constituent oxides and/or carbonates. The Y2Cu2O5 was prepared by mixing Y2O3 and CuO in acetone and the mixture was heated at 1223 K for 48 h with intermediate grinding. The BaCuO2 was prepared by mixing BaCO3 and CuO in acetone and the mixture was heated at 1073 K for 12 h and then at 1123 K for 24 h with intermediate grinding. The YBa2Cu3O7-δ was prepared by high temperature solid state reaction between the constituent oxides and/or carbonates. The fresh and the used catalysts were characterised using XRD. The surface areas of these samples were very low less than 2 m²/g and hence no reliable estimate could be made on the values.

Results and Discussion

The catalysts were characterised using XRD and cyclic voltammetry. The rate of decomposition of H2O2 on these metal oxides was studied from the volume of oxygen evolved with respect to time. XRD of these oxides were recorded to check the single phase formation using CoKα radiation. The XRD patterns of the fresh catalysts are given in Fig. 1. The XRD patterns of all the catalysts matched well with those reported by Choy et al.

The cyclic voltammograms of the samples Y2Cu2O5, BaCuO2 and YBa2Cu3O7-δ are given in Fig. 2. These voltammograms were recorded in the potential range +800 to -800 mV. The scan rate was 50 mV/s. The oxide, dissolved in formamide, was taken in an electrochemical cell consisting of three electrodes, glassy carbon (working electrode), platinum (counter electrode) and silver wire (reference electrode). The identification of peaks c1 and c2 was done by recording cyclic voltammograms of NaCuO2 and CuO. Backer et al. had synthesized...
NaCuO₂ with high Cu(III) content and reported that it can be considered as Cu(III) standard reference material. From the cyclic voltammograms, it was observed that the peaks c₁ and c₂ were due to the presence of Cu⁺⁺ and Cu⁺⁺⁺ in the corresponding systems NaCuO₂ and CuO respectively. All the catalysts gave the second reduction peak (c₃), which indicated the presence of Cu⁺⁺⁺ in all the samples. Apart from the second reduction peak, first reduction peak (c₁) also appeared for the sample YBa₂Cu₃O₇₋ₓ indicating the presence of Cu⁺⁺ apart from Cu⁺⁺⁺ in the YBa₂Cu₃O₇₋ₓ system.

**Catalytic activity and the possible mechanism of toluene oxidation**

Toluene oxidation was carried out at three different temperatures (308, 323 and 338 K) and appreciable conversion was found only above 308 K. Analysis of the product mixture showed that these catalysts (Y₂CuO₃, BaCuO₂ and YBa₂Cu₃O₇₋ₓ) promote both the side-chain oxidation (benzaldehyde as the product) and ring substitution (α, p-cresols as the product). The results on conversion and product distribution of the mixed oxides along with the data obtained for parent oxides Y₂O₃ and CuO as catalysts are given in Table 1.

It is observed that among these oxides, Y₂CuO₃ is the most active. The Y₂O₃ and BaCuO₂ did not show any activity.

The rate of decomposition of H₂O₂ was studied on these mixed oxides. The results revealed that Y₂CuO₃ decomposed H₂O₂ at a moderate rate whereas BaCuO₂ decomposed H₂O₂ rapidly thereby making oxygen unavailable for the substrate (Fig. 3).

Liu et al. have reported that the catalyst containing only Cu⁺⁺⁺ was most active for phenol hydroxylation when compared to catalysts containing both Cu⁺⁺ and Cu⁺⁺⁺ like La₀.₇Sr₀.₃CuO₃₋ₓ. In the present study, although BaCuO₂ contains Cu⁺⁺ the
presence of alkaline earth metal barium enhances the rate of decomposition of H₂O₂ thus leading to no conversion of toluene.

The results of the toluene oxidation carried out at different temperatures are given in Table 2. It is observed that, at a high temperature of 338 K, apart from benzaldehyde and o, p-cresols, a trace amount of benzyl alcohol is also obtained.

As seen from the data in Table 3, the conversion is found to be high in acetonitrile (solvent) compared to t-butanol. It is known that t-butanol can effectively trap ·OH thereby making it less available for the substrate.

Based on these results, a mechanism for toluene oxidation has been proposed as given in Scheme 1.

In the present study, it is observed that the oxide having higher valence of copper (Cu³⁺) and alkaline earth metal (barium) has high activity for the decomposition of H₂O₂ and low activity for toluene oxidation.

According to the proposed mechanism, the oxide with higher valence of copper and alkaline earth metal will promote mainly reactions (8) and (9), thereby converting H₂O₂ rapidly into oxygen without participating in the toluene oxidation. The Y₃Cu₂O₅ which contains exclusively Cu²⁺, promotes reaction (1) thus leading to the formation of benzaldehyde and o, p-cresols.

**Phenol oxidation**

The oxidation of phenol with H₂O₂ has been reported both in the homogeneous and

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**Table 2**—Effect of reaction temperature on toluene oxidation (catalyst = Y₂Cu₂O₅; solvent = acetonitrile; reaction time = 2 hr; toluene/H₂O₂ = 1; catalyst/toluene (g/g) % = 10)

<table>
<thead>
<tr>
<th>Reaction temperature (K)</th>
<th>Conversion of toluene (mole percent)</th>
<th>Conversion to (mole percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>323</td>
<td>10.2</td>
<td>7.2</td>
</tr>
<tr>
<td>338</td>
<td>25.9</td>
<td>8.7</td>
</tr>
</tbody>
</table>

**Table 3**—Effect of solvent on toluene oxidation (Catalyst = Y₂Cu₂O₅; temp. = 338 K; toluene/H₂O₂ = 1; catalyst/toluene (g/g) % = 10)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Conversion of toluene (mole percent)</th>
<th>Conversion to (mole percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>25.9</td>
<td>8.7</td>
</tr>
<tr>
<td>t-butanol</td>
<td>10.3</td>
<td>4.4</td>
</tr>
<tr>
<td>t-butane</td>
<td>3.8</td>
<td>3.8</td>
</tr>
<tr>
<td>DMSO</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

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**Scheme 1**

\[
\begin{align*}
\text{Cu}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Cu}^{3+} + \cdot\text{OH} + \cdot\text{OH}^- \\
\text{H}^+ + \cdot\text{OH}^- & \rightarrow \text{H}_2\text{O} \\
\text{H}^+ + \cdot\text{OH}^- & \rightarrow \text{H}_2\text{O} \\
\text{Cu}^{2+} + \cdot\text{OH}^- & \rightarrow \text{Cu}^{3+} + \cdot\text{OH} \\
\text{Cu}^{2+} + \cdot\text{OH}^- & \rightarrow \text{Cu}^{3+} + \cdot\text{OH}^- \\
\text{Cu}^{2+} + \cdot\text{OH}^- & \rightarrow \text{Cu}^{3+} + \cdot\text{OH}^- \\
\end{align*}
\]
It can be concluded that (i) the catalyst without \( \text{Cu}^+ \) and without alkaline earth metal, \( \text{Y}_2\text{Cu}_2\text{O}_5 \), was found to be effective for the oxidation of both toluene and phenol; (ii) the higher activity of \( \text{Y}_2\text{Cu}_2\text{O}_5 \) may be due to moderate decomposition rate of \( \text{H}_2\text{O}_2 \); (iii) XRD analysis confirmed that \( \text{Y}_2\text{Cu}_2\text{O}_5 \) retained its structure under reaction conditions, whereas \( \text{BaCu}_2\text{O}_5 \) underwent decomposition; (iv) studies on the effect of solvent on the oxidation revealed that toluene conversion (25.9%) was maximum when acetonitrile was used as a solvent, maximum phenol conversion (45.3%) was observed when water was used as a solvent and lower activity was observed when tert-butanol was used as a solvent; (v) according to the suggested mechanism, the catalyst which produces \( \cdot \text{OH} \) at moderate rate can effectively oxidise the organic substrate; and (vi) mixed oxides apart from being used as catalysts in gas-solid phase reactions, can be used as effective catalysts in solid-liquid phase.

Table 4—Phenol oxidation on pure metal oxides and mixed metal oxides (solvent = water; temp. = 338 K; phenol/\( \text{H}_2\text{O}_2 \) (mole) = 1; reaction time = 2 hr; catalyst/phenol (g/g) = 10)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion of phenol (mole percent)</th>
<th>Conversion to (mole percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CAT</td>
<td>HQ</td>
</tr>
<tr>
<td>( \text{Y}_2\text{O}_3 )</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( \text{CuO} )</td>
<td>5.2</td>
<td>3.0</td>
</tr>
<tr>
<td>( \text{Y}_2\text{Cu}_2\text{O}_5 )</td>
<td>45.3</td>
<td>23.0</td>
</tr>
<tr>
<td>( \text{BaCu}_2\text{O}_5 )</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>( \text{YBa}_2\text{Cu}<em>2\text{O}</em>{7.6} )</td>
<td>11.1</td>
<td>6.7</td>
</tr>
</tbody>
</table>

![Fig. 4—X-ray diffraction patterns of (a) fresh BaCu2O2 and (b) spent BaCu2O2](image)

Heterogeneous media. In the present study, phenol oxidation has been carried out on pure metal oxides and mixed metal oxides. As shown in Table 4, the products observed were catechol (CAT), hydroquinone (HQ) and benzoquinone (BQ). No activity was observed when acetonitrile was used as a solvent. When water was used as a solvent, \( \text{Y}_2\text{Cu}_2\text{O}_5 \) showed good activity. Among the oxides, \( \text{Y}_2\text{Cu}_2\text{O}_5 \) showed maximum catalytic activity.

XRD analysis of the spent catalysts confirmed that \( \text{BaCu}_2\text{O}_5 \) underwent decomposition under reaction conditions as shown in Fig. 4. The major phases observed were \( \text{BaO} \) and \( \text{CuO} \). XRD patterns of the used \( \text{Y}_2\text{Cu}_2\text{O}_5 \) and \( \text{YBa}_2\text{Cu}_2\text{O}_{7.6} \) catalysts did not show any additional lines, thus confirming that the structure of these catalysts is essentially retained under reaction conditions.

References