Effect of Mode of Preparation of Zinc Oxide on its Photocatalytic Activity

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The photoinduced catalytic activities of zinc oxide samples, prepared by the decomposition of the nitrate, carbonate, oxalate and hydroxide, for the formation of peroxide in the presence of isopropanol have been compared. The differences in activities are rationalised on the basis of the differences in surface area and the nature of adsorbed decomposition products present on the zinc oxide.

**TABLE 1 — COMPARISON OF CATALYTIC ACTIVITIES OF DIFFERENT ZINC OXIDE PREPARATIONS**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
<th>Peroxide formed (meq/litre)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO (M &amp; B)</td>
<td>4.81</td>
<td>4.17</td>
</tr>
<tr>
<td>ZnO-C</td>
<td>2.89</td>
<td>1.72</td>
</tr>
<tr>
<td>ZnO-O</td>
<td>2.90</td>
<td>1.84</td>
</tr>
<tr>
<td>ZnO-H</td>
<td>0.70</td>
<td>0.61</td>
</tr>
<tr>
<td>ZnO N</td>
<td>&lt;0.10</td>
<td>0.61</td>
</tr>
</tbody>
</table>

*After 3 hr.

Zinc oxide is known to catalyse the oxidation of various aliphatic alcohols under stimulation by light, yielding the corresponding carbonyl compounds and hydrogen peroxide. There are reports in the literature on the reactions of amides and amines under similar conditions. The effects of solvents, temperature and intensity and wavelength of light in these reactions have been extensively studied. X-ray studies and electron-microscopic studies show that the features of zinc oxide depend upon its mode of preparation. Studies on dehydrogenation of isopropanol and decomposition of methanol on zinc oxide under non-photochemical conditions have revealed that the catalytic activity of zinc oxide in such reactions is sensitive to the method of preparation. This paper presents results of studies on the dependence of the photoinduced catalytic activity of zinc oxide on the method of preparation.

**Materials and Methods**

Various zinc oxide samples were obtained by decomposing different zinc compounds prepared starting from zinc nitrate. Zinc nitrate was prepared by dissolving reagent grade ZnO (May & Baker) in concentrated HNO₃ (AR, BDH). ZnCO₃, Zn(OH)₂, and Zn₂C₃O₆ were precipitated by treating Zn(NO₃)₂ with the corresponding ammonium salt solutions. The precipitates were washed with water, dried in an oven at 110°C and decomposed by heating in a muffle furnace at 550°C for 6 hr. The samples are labelled as ZnO-C (prepared from carbonate), ZnO-O (from oxalate), ZnO-H (from hydroxide) and ZnO-N (from nitrate). In addition to these samples, ZnO (M & B) was also used for comparison.

Surface areas of these samples were determined by the BET method using nitrogen as the adsorbate. The experimental set up used has been described earlier.

**Results and Discussion**

The catalytic activities of the different samples were compared on the basis of the amount of peroxide formed in each case after 3 hr of irradiation using for each experiment 0.5 M solution (35 ml) of isopropanol (BDH, AR) in water and the sample (1 g). The data are given in Table 1. None of the samples prepared was as active as ZnO (M & B). This sample has the largest surface area. In the same way ZnO-C and ZnO-O having nearly the same surface area were found to have almost the same catalytic activity. No difference in activity was observed between ZnO-H and ZnO-N despite the difference in their surface areas. However, both these samples have very low surface areas. These observations suggest that while surface area may be a factor that controls the net amount of peroxide formed in this reaction, change in catalytic activity is not commensurate with change in the surface area.

At λ≈3650 Å, ZnO is known to catalyse the formation as well as the decomposition of peroxide in aqueous solutions. The amount of peroxide estimated at any time would thus be the net amount at that time. In order to check whether the rates of decomposition of peroxide are different on these samples, an aqueous solution of H₂O₂ of known concentration was taken and the rates of disappearance of H₂O₂ with the different samples of ZnO measured. The results obtained indicated that the catalysts efficient for the formation of hydrogen peroxide were efficient for its decomposition also.

It has been shown by Zawadski et al. that zinc oxide prepared by the decomposition of ZnCO₃ always contains adsorbed CO₂. The probability of small amounts of surface carbonate being present in zinc oxide samples treated with CO₂ has also been indicated. Experiments with added ZnCO₃ showed...
considering the effect of various species adsorbed on the surface ZnCO3. Following the procedure of Atherton et al.,14 the adsorbed CO2 was removed from ZnO-C sample by passing dry O2 followed by moist O2 over the catalyst at 400°C. This sample, expected to be free of CO2, showed less activity (~15% less) than the original untreated sample. There was no detectable reduction in the catalytic activity of ZnO-N subjected to a similar treatment supporting the attribution of a beneficial role to surface carbonate in ZnO-C. If the adsorption of water from the moist bed gases are promoting the reaction to some extent. In ZnO-N, if NO3- is assumed to be present, it might be due to the presence of adsorbed CO2 in them. These adsorbed gases do not affect the reflectance.

All these observations may be understood by considering the effect of various species adsorbed on the samples during their formation from the corresponding compounds. CO2 is the only gaseous product of Zn2C2O4. CO2 is also formed along with CO2, due to the incomplete elimination of water during the preparation of ZnO-H, surface water in the form of OHads or H2Oad may be present. OHads is capable of decomposing the peroxide formed by the reaction:

\[
\text{H}_2\text{O}_2 + \text{H}_2\text{O}_{\text{ad}} \rightarrow \text{H}_2\text{O}_{\text{ad}} + \text{HO}_2^\cdot
\]

H2Oad reduces the number of sites available for the alcohol. In fact water added to the system reduces the amount of H2O2 formed, supporting this conclusion.

Recently Carniso et al.,18 have suggested that the difference in the catalytic activity of different ZnO preparations is due to the difference in their morphological conditions and consequent changes in the surface Zn/O ratio. Their results are however on doped ZnO samples. While in the samples of ZnO considered here, morphological factors might have an influence on the activity, it must be in addition to the influence of the surface carbonate.

The effects of these adsorbed gases or ions can be explained by considering the following possibilities: (i) The adsorbed species may be trapping the holes produced on illumination, thereby inhibiting the electron-hole recombination. This tends to increase the efficiency of the catalyst by inhibiting the deactivation mode. (ii) The first step of the reaction is the heterolytic splitting of the C-H hydrogen of the alcohol adsorbed on the surface. This is favoured when C-H hydrogen is lost as H+ readily, if the conjugate base of a weak acid is present on the surface of ZnO. CO3- being an ion of this kind, enhances the C-H rupture process. Thus in the case of ZnO-C and ZnO-O the adsorbed gases promote the reaction. In ZnO-N, if NO3- is assumed to be present, it being a weak base does not accept a proton so easily. Instead it competes with the alcohol for the surface sites. This may be a reason for the lower activity of ZnO-N.

It is clear that a low surface area results in reduced catalytic activity, since the number of sites available for occupation by the alcohol are reduced. However, in ZnO-C and ZnO-O the loss of activity is more than compensated for inherent inefficiencies if removed by the adsorbed gases and these adsorbed gases are promoting the reaction to some extent. Hence the loss of catalytic activity is not proportionate to the reduction in surface area.

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References