Photocatalytic reduction of nitrite and nitrate ions over oxide (ZnO, ZrO₂ and Fe₂O₃) semiconductors

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The photocatalytic reduction of nitrite and nitrate ions to ammonia has been studied over ZnO, ZrO₂, Fe₂O₃ and Fe₃O₄ oxide semiconductors. Many parameters such as the position of the conduction band edge of the semiconductor, the metal-semiconductor junction, light absorption capacity of the semiconductor, adsorption of the reagent species and pH of the medium used influence the yield of ammonia and hence one cannot a priori predict the relative activity of these systems on the basis of band edges alone. The resulting photoactivity is a balance of the above said factors some of which play contrasting roles.

The electrochemical reduction of nitrite and nitrate ions have been reported in acidic media but only a few investigations on the photocatalytic reduction of nitrite and nitrate ions in neutral media have been so far performed. The photoassisted reduction of nitrite anions to ammonia was first reported by Halmann and Zuckerman in aqueous solution. The photocatalytic reduction of nitrite to ammonia in alkaline medium has been studied by Kudo et al. in the presence of water decomposition using SrTiO₃, TiO₂ and WO₃ semiconductors.

We have studied the photocatalytic reduction of nitrite and nitrate ions over ZnS, CdS and TiO₂ catalysts. The purpose of the present study is to examine a number of functional variables affecting the photocatalytic reduction of nitrite and nitrate ions over other typical oxide based systems, especially that of ZnO, ZrO₂, Fe₂O₃ and Fe₃O₄, as the efficiencies of these oxides towards the photodecomposition have been examined in the past and to examine whether one can rationalise their relative efficiencies with any of the fundamental characteristics of the systems considered.

Materials and Methods
Metallisation of semiconductors by photodeposition method was carried out in the presence of methanol. In a typical preparation procedure, about 1-1.5 g of the accurately weighed semiconductor was added to 20 ml of doubly distilled water containing appropriate concentration of the noble metal chloride. Irradiation was carried out using a Xe lamp (Oriel Corporation, USA) for 2-4 h. Argon gas was bubbled through the solution during irradiation. After irradiation, the catalyst was filtered, washed several times with distilled water and dried in an air oven before use.

α-Fe₂O₃ was obtained after 24 h hydrolysis of Fe(NO₃)₃·9H₂O at 333 K. The colloidal solution was boiled and allowed to settle. The precipitate obtained was filtered, washed, dried in an air oven at 383 K overnight and calcined at 693 K for 4 h. Another catalyst sample was prepared in a similar manner, except that the colloidal solution obtained was allowed to age for 12 h.

Fe₃O₄ was prepared by boiling ferrous ammonium sulphate with concentrated nitric acid and 6N ammonia was added at 333 K. The resultant colloidal solution was boiled for some time and then allowed to age for 12 h. The precipitate obtained was filtered, washed, dried in an air oven at 383 K overnight and calcined at 693 K for 4 h.

The bulk metal content of the catalysts were analyzed by inductively coupled plasma atomic emission spectra (ICPAES) after extraction from the catalyst by boiling in aqua regia.

X-ray diffractograms were obtained for the powdered samples with a Philips diffractometer (Philips Generator, Holland; Model PW 1130) using a Ni filtered CuKα radiation (λ = 1.5418 Å) for all the samples.

The surface area of the samples was measured by N₂ adsorption at 77 K using the dynamic BET method using a Carlo Erba (Model 1800) sorptometer. The samples were outgassed in an evacuation chamber to a pressure of 10⁻³ atm. at 393 K prior to adsorption.
A Hitachi spectrophotometer (Model 150-20) equipped with an integrating sphere was used to record the diffuse reflectance spectra of the samples.

The photocatalytic experiments were performed in an all glass static system at ambient temperature and atmospheric pressure. In all the experiments, 100 mg of the freshly prepared catalyst and 20 ml of the appropriate solution (sodium nitrite and sodium nitrate of appropriate concentration for nitrite and nitrate reduction) was taken in a double walled cylindrical pyrex glass reactor. The reactor was equipped with water circulation in the outer jacket in order to maintain a constant temperature as well as for infrared filtering. The reaction mixture was stirred at a constant speed during illumination by a magnetic stirrer. The suspension was irradiated using a 450 W Xe lamp (Oriel Corporation, USA). Argon gas was purged when nitrite (nitrate) solutions were illuminated. Before starting the illumination, the reaction mixture was stirred for half an hour in the dark. After irradiation the solution was centrifuged to remove essentially all the catalyst and the centrifugate was analyzed for ammonia. Ammonia was estimated by the indophenol-blue method and nitrite by modified by Griess method. No significant amount of other products was detected.

Results and Discussion

The anodic decomposition potential of ZnO, namely + 0.43 V vs SCE is more negative than the potential of the photogenerated holes in the valence band of the ZnO (+ 2.7 V vs SCE at pH = 13). As a consequence, ZnO can react with the photogenerated holes giving Zn(II) ions and oxygen

\[
\text{ZnO} + 2h^+ \rightarrow \text{Zn}^{2+} + \frac{1}{2} \text{O}_2
\] ...

Thus, the presence of a sacrificial agent is necessary to prevent the photocorrosion of ZnO.

The X-ray diffraction shows all the ZnO catalysts to be in the hexagonal phase. The Pt/ZnO catalyst showed an additional peak with \( d = 2.269 \) Å which can be ascribed to metallic Pt. The characteristics of various ZnO catalysts are given in Table 1.

The diffuse reflectance spectra of the metallised ZnO catalysts are shown in Fig. 1. It is observed that on metallisation, the visible light response of the photocatalysts is increased. In the case of Rh loaded ZnO, an almost steady absorption in the visible region is observed when compared with other metallised catalysts.

The ZnO catalysts were evaluated for the photocatalytic activity. The optimum concentration of nitrite in the experimental study was determined to be 10 ppm. When no sacrificial agent was employed no ammonia was detected. Among the sacrificial agents employed only sulphite and sulphate were found to be effective. The data generated for the photocatalytic reduction of nitrite are given in Table 1. From the data given in Table 1 it is clear that the yield of ammonia is

![Fig. 1—Diffuse reflectance spectra of ZnO catalysts](image)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Metal content (wt%)</th>
<th>Phase</th>
<th>Surface area (m²/g)</th>
<th>Yield of ammonia (μmol) from reduction of nitrite</th>
<th>Yield of ammonia (μmol) from reduction of nitrate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SO₄⁻</td>
<td>SO₄⁻</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.08</td>
<td>0.12</td>
</tr>
<tr>
<td>Pt</td>
<td>0.98</td>
<td>ZnO(hexagonal)</td>
<td>14.0</td>
<td>0.08</td>
<td>0.12</td>
</tr>
<tr>
<td>Ru</td>
<td>0.99</td>
<td>ZnO(hexagonal) + Pt</td>
<td>4.5</td>
<td>0.5</td>
<td>0.49</td>
</tr>
<tr>
<td>Rh</td>
<td>1.0</td>
<td>ZnO(hexagonal)</td>
<td>5.9</td>
<td>0.19</td>
<td>0.22</td>
</tr>
<tr>
<td>Pd</td>
<td>1.02</td>
<td>ZnO(hexagonal)</td>
<td>11.8</td>
<td>0.65</td>
<td>0.69</td>
</tr>
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</table>

N.D.—Not detected

Table 1—Characteristics and photocatalytic activities of ZnO systems for the reduction of nitrite and nitrate

Reaction conditions for the reduction of nitrite and nitrate are: 10 ml of 10 ppm nitrite or nitrate, 10 ml of 50 ppm of sacrificial agent (only sulphite in the case of nitrate reduction), 2 h irradiation, 100 mg catalyst
independent of the nature of the sacrificial agent used. The photocatalytic reduction of nitrate to ammonia was evaluated on the metallised ZnO catalysts and the results obtained are given in Table 1.

The order of activity among the metal loaded ZnO was found to be Rh > Pd > Ru > Pt. Diffuse reflectance spectral studies show that the absorption in the visible region was in the order Pd > Ru > Pt > Rh. Photocorrosion studies also indicate that the nature of the sacrificial agent does not influence the activity. The results of the photocorrosion studies are given in Table 2. In the absence of any sacrificial agent, the decomposition of ZnO is favoured in preference to oxidation of water since the photogenerated holes have a higher potential for oxidizing the former. Thus, the need for a sacrificial agent arises. Indeed, no ammonia was detected when no sacrificial agent was employed.

The equilibrium dark adsorption of nitrite was determined and it was found that there is no linear relationship between the yield of ammonia and the amount of nitrite adsorbed on the catalysts.

ZrO₂ catalyst

Attempts have been made to use ZrO₂ as a catalyst for various reactions both in the form of a single oxide as well as in ternary systems and interesting results have been reported. Another added advantage of zirconia is that it is stable under irradiation conditions and has a highly negative flatband potential. Hence it was of interest to investigate the photocatalytic properties of ZrO₂ based semiconductors.

All the catalysts show only the monoclinic phase of ZrO. The characteristics of ZrO₂ catalysts are given in Table 3.

The optical behaviour of ZrO₂ suspensions showed that the absorbance of the bare ZrO₂ semiconductor (Fig. 2) is more in the UV region 200-250 nm compared to the metallised ZrO₂ semiconductor. The metallised ZrO₂ catalysts show an almost constant absorption in the visible region from 400-600 nm. The photocatalytic reduction of nitrite and nitrate ions to ammonia was evaluated over ZrO₂ based semiconductors and the results are given in Table 3. The metallised semiconductors exhibited lower activity compared to ZrO₂ itself. The barrier of ZrO₂-metal junction is high compared to that of other semiconductor-metal systems such as TiO₂-metal and it is presumed that the electron in the ZrO₂ can thus scarcely migrate to metal. The reason why the activity was not improved by loading metal can be explained in terms of the barrier height of the semiconductor-metal (Schottky) junction.

### Table 2—Photocorrosion studies of ZnO catalysts

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Zinc concentration (µ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ppm NO⁻, no sacrificial agent</td>
<td>23.9</td>
</tr>
<tr>
<td>10 ppm NO⁻, 50 ppm SO²⁻</td>
<td>1.09</td>
</tr>
<tr>
<td>10 ppm NO⁻, 50 ppm SO²⁻</td>
<td>1.63</td>
</tr>
<tr>
<td>10 ppm NO⁻, 50 ppm SO²⁻</td>
<td>1.65</td>
</tr>
</tbody>
</table>

### Table 3—Characteristics and photocatalytic activities of ZrO₂ systems for the reduction of nitrite

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal content (wt%)</th>
<th>Surface area (m²/g)</th>
<th>Yield of ammonia (µ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂⁻ → NH₃</td>
<td>NO₃⁻ → NH₃</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.1</td>
<td>22.7</td>
<td>1.02</td>
</tr>
<tr>
<td>Pt/ZrO₂</td>
<td>0.99</td>
<td>24.5</td>
<td>0.19</td>
</tr>
<tr>
<td>Ru/ZrO₂</td>
<td>1.01</td>
<td>22.2</td>
<td>0.28</td>
</tr>
<tr>
<td>Rh/ZrO₂</td>
<td>1.01</td>
<td>24.0</td>
<td>N.D.</td>
</tr>
<tr>
<td>Pd/ZrO₂</td>
<td>1.01</td>
<td>35.0</td>
<td>0.40</td>
</tr>
</tbody>
</table>

N.D.—Not detected

The equilibrium dark adsorption of nitrite on ZrO₂ based catalysts was evaluated. No linear correlation was observed between the amount of nitrite adsorbed and the yield of ammonia.

Iron oxide catalysts

The photoassisted electrolysis of water on α-Fe₂O₃ has been extensively studied in the last few years. Although stable to photocorrosion, the flatband potential of Fe₂O₃ lies positive to the hydrogen evolution potential and hence there would be a need for a bias voltage. In the present study Fe₂O₃ and
Table 4—Precursors used, phases obtained and photocatalytic activity of iron oxide catalysts

<table>
<thead>
<tr>
<th>Precursor used</th>
<th>Designation</th>
<th>Phase</th>
<th>Surface area (m²/g)</th>
<th>Yield of ammonia (µ mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(NO₃)₃ and NH₃, no aging</td>
<td>FO-1</td>
<td>α-Fe₂O₃</td>
<td>45.8</td>
<td>NO₂ → NH₃: 0.25, NO₃⁻ → NH₃: 1.43</td>
</tr>
<tr>
<td>Fe(NO₃)₃ and NH₃ 12 h aging</td>
<td>FO-2</td>
<td>Fe₂O₃</td>
<td>24.6</td>
<td>NO₂ → NH₃: 0.82, NO₃⁻ → NH₃: 1.70</td>
</tr>
<tr>
<td>FAS and NH₃, 12 h aging</td>
<td>FO-3</td>
<td>Fe₃O₄</td>
<td>13.7</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

Table 4: Precursors used, phases obtained and photocatalytic activity of iron oxide catalysts

Reaction conditions: 20 ml of 10 ppm nitrite (nitrate), 2h irradiation, 100 mg catalyst

Fe₃O₄ catalysts were tested for the photocatalytic reduction of nitrite and nitrate ions. α-Fe₂O₃ was prepared by the procedure described in ref. (13) and designated as FO-1. The effect of aging was also studied and the catalyst thus aged was designated as FO-2. Fe₂O₃ (designated as FO-3) was prepared as discussed earlier. The precursors used and the phases obtained are given in Table 4.

From the data given in Table 4, it is clear that the iron oxide phase and surface area are influenced by the nature of precursor used and the aging conditions employed.

The diffuse reflectance spectra of the iron oxide catalysts are given in Fig. 3. From Fig. 3, it is evident that an increase in absorbance of the α-Fe₂O₃ (FO-2) catalyst is noted over the whole wavelength domain, indicating that lower energy transitions than that of the bandgap play a larger role. Therefore, this catalyst is expected to exhibit higher activity compared to other catalysts.

The following conclusions can be drawn from the present investigation:

1) The absolute positions of the band edges of the semiconductor normally should influence the activity of the semiconductor. According to this expectation the expected activity order for the title reaction would be ZrO₂ > ZnO > Fe₂O₃. However, the observed activities of these oxide systems do not correspond to this expectation indicating that the positions of the
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Conduction band edges alone is not controlling the reaction.

(2) It is possible to design photoelectrochemical cells in which photosensitive semiconductor electrodes are replaced by a suspension of the same powder material to enable one type of the photoproduced charges to be collected by colliding with a fixed electrode.

(3) A higher efficiency can be realized in such photoelectrochemical cells by virtue of the separation of the oxidizing and reducing functions.

References