# Photo-oxidation of nitrogen to nitrite using a composite $ZnO-Fe_2O_3$ catalyst

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#### Abstract

A composite catalyst, in which  $Fe_2O_3$  crystallites are deposited on ZnO particles, is found to photogenerate  $NO_2^-$  in nitrogen-purged aqueous solution. Hydrogen is evolved concomitantly. The effectiveness of the catalyst is attributed to hole transfer from ZnO to  $Fe_2O_3$  and preferential chemisorption of nitrogen at the  $Fe_2O_3$  surface.

### 1. Introduction

The photofixation of nitrogen is one of the most attractive ways to use solar energy. Although the quantum yields are far below the practical level, several reports indicate the detection of ammonia in irradiated, nitrogen-purged aqueous suspensions of semiconductor particles [1-9]. The electron and hole transfer reactions leading to the formation of ammonia are

$$N_2 + 6H^+ + 6e^- \longrightarrow 2NH_3 \tag{1}$$

$$3H_2O + 6h^+ \longrightarrow \frac{3}{2}O_2 + 6H^+$$
<sup>(2)</sup>

 $N_2 + 3H_2O \longrightarrow 2NH_3 + \frac{3}{2}O_2 \qquad \Delta G \approx 678 \text{ kJ}$  (3)

Oxygen from eqn. (3) is rarely detectable owing to the formation of peroxo complexes [10].

In aqueous nitrogen-purged dispersions of semiconductor catalysts, oxidative fixation of nitrogen can also occur via the reactions

$$6H_2O + 6e^- \longrightarrow 3H_2 + 6OH^-$$
(4)

$$N_2 + 4H_2O + 6h^- \longrightarrow 2NO_2^- + 8H^+$$
(5)

 $N_2 + 4H_2O \longrightarrow 3H_2 + 2HNO_2 \qquad \Delta G \approx 538 \text{ kJ}$  (6)

With catalysts such as TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>, the predominant nitrogen fixation mode [1–9] is eqn. (3), whereas ZnO [11] produces mostly NO<sub>2</sub><sup>-</sup> possibly via eqn. (6). We have found that in a composite catalyst, in which Fe<sub>2</sub>O<sub>3</sub> crystallites are in contact with ZnO, the oxidative fixation of nitrogen occurs at an enhanced rate compared with pure ZnO. Nitrogen is more strongly chemisorbed in Fe<sub>2</sub>O<sub>3</sub> than in ZnO and hole

transfer from ZnO to  $Fe_2O_3$  in the composite system is responsible for the more efficient oxidation of nitrogen.

## 2. Experimental details

The composite catalyst ZnO-Fe<sub>2</sub>O<sub>3</sub> was prepared as follows. ZnO (10 g) was mixed with a few millilitres (measured quantity) of 0.1 M FeCl<sub>3</sub> solution. The paste was dried at 100 °C, ground and heated in air at 1000 °C for 2 h. The sample was allowed to cool, washed with water and dried at 100 °C. X-ray diffractometry (Shimadzu X-ray diffractometer XD-7A) revealed the presence of ZnO and  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Photolysis experiments were carried out in a photochemical reactor (500 ml), with a water-cooled (26 °C) cylindrical quartz jacket, housing a 400 W medium-pressure mercury lamp. The catalyst (200 mg) suspended in 350 ml of water (pH adjusted with NaOH) was rapidly purged with nitrogen (99.99%) for approximately 30 min to remove dissolved oxygen. The lamp was switched on and a slower purging rate (10 ml min<sup>-1</sup>) was



Fig. 1. Time variation of the  $NO_2^-$  yield during photolysis of nitrogen-purged aqueous suspensions (pH 11) of  $ZnO-Fe_2O_3$  composite catalyst (a) and pure ZnO (b). Inset: schematic diagram showing the structure of the composite  $ZnO-Fe_2O_3$  particle.

maintained. Control experiments were also run with the lamp switched off and with argon purging with the lamp switched on.

Aliquots of solution drawn from the reactor at different time intervals were tested for nitrite (azo dye test), nitrate (cadmium reduction followed by azo dye test) and ammonia (indophenol blue method). In another experiment, solutions initially purged with nitrogen and argon were irradiated, and hydrogen in the atmosphere of the reactor was monitored by gas chromatography (Shimadzu GC-9A gas chromatograph, molecular sieve 5A column, thermal conductivity detector). For comparison, experiments were also performed using pure ZnO instead of the composite catalyst.

# 3. Results and discussion

Figure 1 illustrates the time development of  $NO_2^-$  concentration during photolysis ( $NO_3^-$  and  $NH_3$  were not detected). Compared with pure ZnO, the composite catalyst gives a high yield of  $NO_2^-$ . Furthermore, with  $ZnO-Fe_2O_3$ , the  $NO_2^-$  concentration in the photolysed solution continues to increase for longer durations of irradiation.



Time/h

Fig. 2. Time variation of the hydrogen yield in the photolysis of nitrogen-purged (a) and argonpurged (b) aqueous suspensions (pH 11) of the composite  $ZnO-Fe_2O_3$  catalyst. Inset: relative band positions of ZnO and  $Fe_2O_3$ .

The rate of photogeneration of  $NO_2^-$  initially increases with an increase in pH and then decreases; the optimum pH value is approximately 11. The catalyst is most active when the Fe<sub>2</sub>O<sub>3</sub> content is approximately 0.12%. Figure 2 illustrates the time dependence of hydrogen photogeneration from nitrogen- and argon-purged catalyst suspensions. It is interesting to note that the former generates more hydrogen.

The enhanced activity of the composite catalyst can be understood as follows. Our method of preparation is expected to yield ZnO particles deposited with crystallites of Fe<sub>2</sub>O<sub>3</sub> (inset, Fig. 1). Nitrogen is preferentially chemisorbed on the Fe<sub>2</sub>O<sub>3</sub> surface. The relative band positions of ZnO and Fe<sub>2</sub>O<sub>3</sub> (derived from the literature values [12]) are indicated in the inset of Fig. 2. It is clear that the transfer of photogenerated holes from ZnO to Fe<sub>2</sub>O<sub>3</sub> is energetically favoured compared with electron transfer from ZnO to Fe<sub>2</sub>O<sub>3</sub>. As nitrogen is chemisorbed on Fe<sub>2</sub>O<sub>3</sub>, the nitrogen oxidation reaction (eqn. (5)) occurs at the surface of the Fe<sub>2</sub>O<sub>3</sub> crystallites. The concomitant electron transfer reaction (eqn. (4)) occurs at the ZnO surface (inset, Fig. 1). The reason why the hydrogen yield is higher in nitrogen-purged solutions (compared with argon-purged solutions) is also understood. The faster removal of holes in the presence of chemisorbed nitrogen facilitates the electron transfer reaction (eqn. (4)).

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