The first application of illuminated ferrofluid towards catalytic photoreduction of nitrogen by visible light

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The photoreduction of \( \text{N}_2 \) to ammonia at a turnover rate of 0.03 mole of \( \text{NH}_3 \) gm\(^{-1}\) hr\(^{-1}\) using ferrofluid as a catalyst is described. The product quantum yield of the formation of ammonia is 0.02.

A ferrofluid contains tiny magnetic particles of magnetite (\( \text{Fe}_3\text{O}_4 \), \( \text{Fe}_2\text{O}_3 \)) with diameter 100 Å colloidally dispersed in a carrier liquid such as water, hydrocarbon diester etc. Aggregation of the particles is prevented by coating each particle with an appropriate surfactant such as, oleic acid. Under these conditions the number density of the particle is very large (10\(^{23} \text{/m}^3 \)). Under the action of the external magnetic field such fluids exhibit saturation magnetisation ranging between 5 and 500 gauss. Ferrofluids exhibit many novel phenomena, and are used in many devices including semiconductors. Compared to other disciplines of science and technology much less work has been carried out on the applications of ferrofluid in chemistry. The ferrofluid material \( \text{Fe}_3\text{O}_4 \) is of special interest because of its relation to famous Haber-Bosch synthesis for \( \text{NH}_3 \), where \( \text{Fe}_3\text{O}_4 \) in KOH is used as a catalyst. We have earlier reported the use of \( \text{Fe}_2\text{O}_3 \) in the photodecomposition of water. A few reports indicate the possibilities of reduction of nitrogen to \( \text{NH}_3 \) when nitrogen-purged solutions containing hydroxous ferric oxide \( [\text{Fe}_2\text{O}_3(\text{H}_2\text{O})] \) or \( \text{Fe}_2\text{O}_3 \) doped with TiO\(_2\) particulate system are irradiated with UV-visible light at 595 nm. However, the direct use of \( \text{Fe}_2\text{O}_4 \) or ferrofluid has not been made earlier for this purpose. In view of our continued interest in the synthesis of ammonia under ambient conditions by photochemical route we found that colloidal particles of ferrofluid work as a good catalyst for photoreduction of \( \text{N}_2 \) upon irradiation with visible light. This report presents the first example of chemical application of ferrofluid towards catalysis of \( \text{N}_2 \) reduction by water base ferrofluid.

**Experimental**

Photocatalytic reduction of \( \text{N}_2 \) to \( \text{NH}_3 \) was conducted in a flat faced pyrex glass cell. The commercially available ferrofluid (FW 40 Matsomoto, Japan) of particle density 1.359 g/ml was further diluted to 43 \( \mu \text{g/ml} \) with distilled water and used as a catalyst in this study. The ferrofluid (25 ml) was taken in the cell and CO\(_2\)-free \( \text{N}_2 \) was bubbled through the system at a constant rate (25 ml/min) to ensure saturation of dissolved nitrogen at any instant. During the reaction nitrogen was dispersed uniformly by stirring the reaction mixture. The entire reaction mixture was irradiated with a 250 watt xenon lamp at 484 nm. At time intervals chosen, aliquots were withdrawn and analysed for \( \text{NH}_3 \) spectrophotometrically using Nessler’s reagent. The gaseous products (\( \text{H}_2 \) and \( \text{O}_2 \) also generated in the system due to photodecomposition water) were analysed by gas chromatographic method (Shimadzu GC-9A).

**Results and discussion**

The build up curve for ammonia with time of irradiation is shown in Fig. 1. A total of 150 \( \mu \text{ mole} \) of \( \text{NH}_3 \) is produced during 5 hr of photolysis at 25 to 30 \( \mu \text{ mole hr}^{-1} \). Taking into consideration the density of \( \text{Fe}_3\text{O}_4 \) particles in ferrofluid used in this study (43 g/ml), a turnover rate of 30 mmole of \( \text{NH}_3 \) per gram of catalyst per hour was obtained.

No \( \text{NH}_3 \) was formed when the experiments were conducted in the absence of either \( \text{N}_2 \) or ferrofluid or light. In the absence of nitrogen photolysis of water occurred to give \( \text{H}_2 \) and \( \text{O}_2 \) in a 2:1 mole ratio.

When the experiment was carried out in the presence of \( \text{N}_2 \) the amount of \( \text{O}_2 \) produced by photolysis remained unchanged, but the yield of \( \text{H}_2 \) was largely inhibited and instead of \( \text{H}_2 \), \( \text{NH}_3 \) was formed. The amount of \( \text{O}_2 \) analysed during the reaction was about 0.7 mole per mole of \( \text{NH}_3 \) produced, which is in accord with the stoichiometry given by Eq. (1).

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\text{N}_2 + 3\text{H}_2\text{O} \xrightarrow{\text{hv}} 2\text{NH}_3 + 1.5 \text{O}_2
\]
The proton (H⁺) and N₂ are both chemisorbed in the same site on the surface of the ferrofluid. In the absence of N₂, evolution of H₂ takes place, but the presence of N₂ electron transfer to the partially activated surface adsorbed N₂ results in the cleavage of N–N bond and formation of NH₃. In the absence of light the activation of N₂ does not proceed sufficiently to form NH₃. This requires in the famous Haber-Bosch process optimum temperature of 250° and a pressure of 400 atmosphere.

**References**