Photochemical Synthesis of Ammonia over Zeolites

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Summary Ammonia is synthesised by performing the photolysis of water and the photoreduction of nitrogen concomitantly, using titanium-exchanged zeolites in a fluidised bed reactor.

THE discovery of the photolysis of water in the presence of semiconductor materials has inspired a great deal of interest in the possibility of the conversion of solar into chemical energy. Some attempts have been made to utilise the photolysis products to carry out photoreduction reactions *in situ* over catalysts containing semiconductor materials. Schrauzer and Guth[1] reported the production of small amounts of ammonia in a batch reactor using iron-doped titanium dioxide. Augugliaro *et al.*[2] also succeeded in making ammonia in a fluidised bed reactor using similar photocatalytic materials supported on γ-alumina. In both cases the catalysts were subjected to near-u.v. irradiation.

Zeolites, with irradiation by visible light, have been shown[3,4] to be good catalysts for water splitting. Partial thermal regeneration of these catalysts is possible; however this method does not make it possible to achieve a closed photochemical cycle that harnesses visible solar energy to produce hydrogen.

We report here the production of ammonia using titanium-exchanged zeolites irradiated by visible light. The calcium ions in 5A zeolite were exchanged with titanium ions by using 30% (w/v) aqueous titanium trichloride (1 g of zeolite per 2 ml of solution). 5A zeolite beads of 1—2 mm diameter were soaked in the unstirred titanium trichloride solution for 1—3 h at room temperature. Atomic absorption studies showed that about 10 mg of titanium were exchanged per gram of zeolite. After exchange the zeolite was purple, characteristic of hexa-aquotitanium(III) ions, and the e.s.r. spectrum of Ti^{3+} in the exchanged zeolite was almost identical to that observed by Ono *et al.*[5] for Ti^{3+} in zeolite Y.

The washed catalyst was immersed in water in the reaction vessel and supported on a porous sintered disc. High-purity nitrogen was bubbled through the porous disc continuously and the catalyst was partially fluidised. The fluidised catalyst was irradiated by a 150 W lamp, and 0·35 mg of ammonia was produced per gram of catalyst per hour. The activity of the catalyst decreased after about 2 h; the deactivated catalyst was discoloured, and no e.s.r. signal of Ti^{3+} could be detected. The spent catalyst could be re-exchanged by the method used for the preparation of the fresh exchanged zeolite, and the e.s.r. spectrum again showed the presence of Ti^{3+}. The activity of the re-exchanged catalyst was higher than that of a fresh sample, the rate of production of ammonia increasing to a maximum of 0·5 mg per gram of catalyst per hour. After 3 h of operation the catalyst showed a decrease in activity, and required further replenishment with Ti^{3+}. The catalyst may be re-exchanged continuously or in batches, and so this method makes it possible to synthesise ammonia continuously. The rate of ammonia production per gram of catalyst is much higher than the rates reported so far.[1,2]

Experiments without the introduction of nitrogen showed vigorous bubbling when the catalyst is active. Analysis of the resulting gas showed that hydrogen was produced together with oxygen and nitrogen obtained from air adsorbed in the highly porous catalyst.

Small amounts of a milky precipitate were obtained in the reaction vessel, comprising titanium oxides and zeolite that had broken up. Thus there is a net loss of catalyst over a long period of time.

(*Received*, 25*th June* 1981; *Com.* 745.)

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