PHOTOCATALYTIC NITROGEN FIXATION

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The conversion of nitrogen to fixed forms such as ammonia and nitrate is essential for Agriculture and hence for sustaining life on Earth. At present time, the Haber process provides the major portion of fixed nitrogen while biological nitrogen fixation and electric discharges in the atmosphere provide the rest. Petroleum price increases have brought a simultaneous increase in the fertilizer prices which have adversely affected developing countries. Thus research leading to alternative nitrogen fixation pathways have assumed great economic and sociological importance.

The use of sunlight to convert nitrogen to fixed forms is an attractive method especially for the developing countries. Semiconductor catalysts are widely used for this purpose. Upon irradiation, such catalysts generate electron-hole pairs and the excited electron can be utilized for reducing nitrogen to ammonia. However, the yields in these reactions are generally very small.

Scientists have found several semiconductor oxide catalysts that help to convert nitrogen to ammonia.

Such catalysts also split water into hydrogen and oxygen. The first report on the photochemical synthesis of ammonia was in 1941 by Dhar, a prominent Indian soil scientist. He showed that river sand collected from the Jumna river in Allahabad, India converted nitrogen to ammonia upon exposure to tropical sunlight in the presence of starch or cellulose. The Western scientific community largely ignored this important discovery. It was only in 1977 that an American chemist, Schrauzer rediscovered the photosynthesis of ammonia on metal-doped rutile catalysts. He further showed that the Jumna river sands which Dhar employed was rich in rutile and this accounted for its catalytic activity.

A large number of active catalysts have been discovered. These include the metal-doped TiO_2 catalysts where the metal is iron, nickel,molybdenum, chromium etc. and metal titanates such as $BaTiO_3$, $SrTiO_3$. All these catalysts however, absorb light in the ultraviolet region. Since solar energy contains only about 5% ultraviolet light such catalysts have little practical value. Furthermore, the yields of ammonia are very small (in the microgram range) and the catalytic activity drops rapidly with time. Because of these limitations,an economically feasible catalytic system has not been developed up to the present time.

In a joint research programme on this problem between the Institute of Fundamental Studies and the Universities of Ruhuna and Peradeniya, we have developed a new catalyst which absorbs well in the visible part of the solar spectrum. It was found that hydrous ferric oxide reduced nitrogen to ammonia with better efficiency and yields compared to TiO_2-based catalysts. Even here, the catalytic activity decreases with time and this was attributed to the partial oxidation of ammonia to nitrate which in turn poisons the catalyst. Thus, we have been able to show at least one of the factors that affect efficiency. There is also a fair amount of research carried out to establish the exact mechanism of this interesting reaction and devising ways to prevent catalyst poisoning. It was found that composite catalysts containing ferric and titanium hydroxides and hydrous ferric oxides supported on clays, show enhanced activity. Further work along these areas is in progress.

If a nitrogen-fixing solar cell can be developed, one can visualize the irrigation waters going into our paddy fields running over catalyst beds exposed to sunlight. Even if the yields of ammonia are small, the enrichment of soil nitrogen may be significant over a long period.