PHOTOCHEMICAL NITROGEN FIXATION REACTIONS ON SEMICONDUCTOR SUSPENSIONS AND COLLOIDS

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Abstract

This thesis describes attempts to develop improved semiconductor based catalysts for the photosynthesis of ammonia from dinitrogen and water. Attempts were made to understand the mechanistic aspects, reasons for catalyst poisoning and to improve the adsorption of nitrogen on these catalysts.

It was found that of the different forms of hydrous ferric oxides, only the yellow brown form is active in the photoreduction of dinitrogen. Furthermore with this system small amounts of nitrate were also found which increased with time. The eventual photooxidation of the nitrogen molecule was an interesting finding. When the wine red sol form of hydrous ferric oxide was loaded into montmorillonite clays such as Fuller's earth, an enhancement in the ammonia yield was observed with a concomittant decrease in the yield of nitrate. Coating of the gelatinous hydrous ferric oxide with other metals or doping with other metal ions decreased the activity of the catalyst.

It was found that titanium dioxide doped with magnesium ions at 500°C is an efficient catalyst for photochemical ammonia synthesis. In this case the catalyst with magnesium doping at the surface seems to be effective while higher temperatures which produce magnesium titanates are not active.

The kinetics of the photooxidation of ammonia to nitrite was studied in detail. The results indicate that (a) the

reaction takes place under UV irradiation and in alkaline solutions only (b) the orders of the reaction with respect to ammonia and hydroxyl ions are 1 and 0.5 respectively (c) oxidation to nitrate takes place without a semiconductor while in the presence of a semiconductor the nitrite is further oxidized to nitrate.