PHOTOFIXATION OF DINITROGEN ON SEMICONDUCTOR CATALYSTS

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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 polymeric hydroxo iron species adsorbed bentonite is more active in the photoreduction of dinitrogen compared to the hydrous ferric oxide. Furthermore, with this system small amounts of nitrate were also formed, which increased with time. The catalyst is also active in generating hydrogen from water while oxygen is also evolved under long time irradiation. The platinization of the catalyst or the addition of inorganic ions and also sacrificial organic reagents did not have any significant enhancement of the NH_3 yields. Dehydration of the catalyst also denatures its catalytic properties. It was observed that the band gap of polymeric hydroxo iron species is higher than that of hydrous ferric oxide.

The titanium dioxide doped with ruthenium at 1000°C was found to be an active catalyst for the photooxidative nitrogen fixation. In this case the catalyst with ruthenium doping at higher temperatures seems to be effective, while catalysts prepared at lower temperatures,which produce oxide mixtures are not active.

The yellow form of WO_3 can be reduced to blue form of tungsten oxide by TiO_2 upon irradiation. The chemical reduction of nitrogen to ammonia can be carried out, by using this reduced form of tungsten oxide. The optimum conditions for the aqueous phase

reaction was found to be 15% (w/w) of WO_3 doped TiO_2 at 250°C for 2 hours in pH 6 suspension. In the gas-solid phase, more ammonia is produced compared to the aqueous suspension of the same system. It was also observed that ammonia oxidation in the gas-solid phase is significantly lower than that for aqueous suspension.