

**PHOTOCATALYTIC NITROGEN FIXATION ON
METAL DOPED TITANIA AND OTHER OXIDES**

A Thesis presented by

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ABSTRACT

This study was undertaken for the development of semiconductor based catalysts for photochemical dinitrogen reduction. In a semiconductor, different parts of the surface form the anode and cathode. Electron-hole pairs are created on the particle which react separately on the surface and the different parts of the catalyst particle acts like microelectrodes. Therefore N_2 reduction ability of several catalytic systems was studied and the physical characterization of the catalysts was carried out.

Metal doped ($M=Ce, V$) TiO_2 powder catalysts were found to convert N_2 to NH_3 upon irradiation with a 400w medium pressure Hg Arc lamp (250-700nm). The effects of dopants such as Cerium/ Vanadium, their relative amounts, calcination temperature, duration of heating of the catalyst and pH affect the NH_3 yield.

An aqueous suspension of coprecipitated hydrous oxides of Eu(III) and Sm(III) is found to photocatalyse the reduction of N_2 to NH_3 . The activity of the complex catalyst, $Sm_2O_3 \cdot nH_2O/Fe_2O_3 \cdot nH_2O$ is higher than that of pure hydrous Ferric oxide. Sm_2O_3 also catalyses the N_2 photoreduction. The enhanced activity of this composite system is attributed to the separation of oxidation and reduction sites and chemisorption of N_2 on the reduction sites.

When composite catalyst of MoO_3/TiO_2 was irradiated with UV-Visible light TiO_2 reduces $MoO_3 \cdot H_2O$ to $MoO_{2.5} \cdot (OH)_{0.5}$. Measurement of the band position of $MoO_3 \cdot H_2O$ suggests that electron transfer from TiO_2 to MoO_3 is responsible for this reaction. The

reduced form of the Molybdenum component converts N_2 to ammonia thermally in aqueous suspensions. MoO_3/TiO_2 system gave better ammonia yield through a cyclic pathway. Irradiation over longer periods results in bronze formation and loss of catalytic activity.

A composite catalyst where Fe_2O_3 crystallites are deposited on ZnO particles was found to photogenerate NO_2^- in N_2 purged aqueous solution. Upon irradiation with UV-Visible light hydrogen is evolved concomitantly. The activity of the catalyst is attributed to the hole transfer from ZnO to Fe_2O_3 and preferential chemisorption of N_2 at the Fe_2O_3 surface.