

A NOVEL PHOTOCATALYST FOR THE PHOTOREDUCTION OF  
WATER TO HYDROGEN AND NITROGEN TO AMMONIA

J.M.S. Bandara\*, O.A. Illeperuma\*\*,\*\*

\*Institute of Fundamental Studies, Kandy.

\*\*Dept. of Chemistry, University of Peradeniya.

Photoreduction of  $H_2O$  to  $H_2$  and  $N_2$  to  $NH_3$  are two important photochemical processes taking place on irradiated semiconductor. Although the yields observed in these light driven reactions are small, their practical utility is significant.

$MnO(OH)_2$  is a Mn(IV) which is obtained by oxidizing hydrous manganous oxide with  $H_2O_2$ . Photochemical properties of this interesting compound have not been previously reported. With our previous observations of efficient nitrogen reduction to  $NH_3$  combined with the reduction of  $H_2O$  to  $H_2$  on certain hydrous metal oxides<sup>1,2</sup>. We have now investigated the above compound for possible photocatalytic activity. Although  $MnO(OH)_2$  by itself is only feebly active for  $N_2$  fixation, its activity can be enhanced considerably upon loading with hydrous ferric oxide. At an optimum loading concentration of 15% of  $Fe(OH)_3$  on  $MnO(OH)_2$  nearly  $80 \mu mol l^{-1}$  of  $NH_3$  are obtained after 6h of irradiation. This is far greater than the yields of  $NH_3$  with individual hydrous oxides or iron and manganese (ca.  $15 \mu mol l^{-1}$ ). After 6h, the yields initially decrease, but continue to increase after about 12h of irradiation.

Photoreduction of water to hydrogen under  $N_2$  and Ar show that around  $883 \mu l$  of  $H_2$  are evolved after 12h of irradiation under Ar while 800 are evolved under  $N_2$ . Under sacrificial conditions in the presence of ethanol nearly  $25,000 \mu l$  of  $H_2$  are evolved under irradiation.

Possible reasons for the enhanced activity of this composite catalyst are (a) increased adsorption of  $N_2$  on the hydrous Mn(IV) oxide and (b) separation of oxidation and reduction sites of  $H_2O$  manganese and iron centers respectively.

- References: 1. Tennakone K., Wickremanayake, S., Fernando, C.A.N. Illeperuma, O.A., & Punchedewa S. J.C.S. Chem. Commun. (1987) 1278.  
2. Tennakone K., Illeperuma, O.A., Bandara, J.M.S., Thaminimulla, C.T.K. (submitted for publication).