Photocatalytic Behaviour of Metal doped Titanium Dioxide

Studies on the Photochemical Synthesis of Ammonia on Mg/TiO₂ Catalyst Systems



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ABSTRACT

Magnesium doped titanium dioxide was found to convert nitrogen to ammonia upon UV irradiation. The effects of magnesium dopant level, calcination temperature, duration of heating of the catalyst and pH affect the ammonia yield. The optimum conditions were 2-4% magnesium doping level and heating of the catalyst at 500° C for 2 h.

Keywords: magnesium/titania, ammonia synthesis, photocatalysis, catalyst preparation (metal doping)

INTRODUCTION

Metal ion doping of TiO_2 has been investigated as a possible way to improve the efficiency of TiO_2 catalysts for the photosplitting of water [1] and also for the photoreduction of nitrogen to ammonia [2]. Doping with a metal ion of different valence is known to alter the catalytic properties of a semiconductor

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[3]. This can also improve the adsorption properties of the catalyst and extend the absorption of light to the visible region. In our efforts to optimize the photoreduction of nitrogen to ammonia on semiconductor surfaces, we have studied the $Mg^{2+}-TiO_2$ system which exhibits enhanced photocatalytic effects compared to TiO_2 alone [4]. The efficiency of this catalyst was found to depend on the level of Mg^{2+} doping, mixing temperature and the duration of heating of the sample.

EXPERIMENTAL

Preparation of the catalyst

 TiO_2 powder (BDH) was first suspended in distilled water and the calculated amount of MgSO₄·7H₂O (AR grade) was added. After stirring for 24 h, the mixture was evaporated to dryness and the samples for this study were obtained by heating at different temperatures for varying periods of time in air. The catalysts so obtained were characterized by X-ray powder diffraction on a Shimadzu XD7A powder diffractometer. Particle size analyses were carried out on a Horiba particle size analyzer using the sedimentation technique.

Irradiation procedure

All irradiations were carried out using a 400 W medium pressure Hg arc lamp. The lamp is housed in an immersion well type quartz reactor with an inner water cooled jacket. The lamp produces $>5 \times 10^{19}$ photons/s/cm². An amount of 0.200 g of the catalyst suspended in 300 ml of double distilled water was irradiated under a slow stream of purified nitrogen. Control experiments were carried out under argon and in the dark. After the irradiation, the contents were treated with 10 ml of 0.10 *M* NaOH and the ammonia distilled off to a receiving flask containing 10 ml of 0.10 *M* hydrochloric acid. The ammonia in the distillate was determined by the indophenol blue method.

RESULTS AND DISCUSSION

Fig. 1 shows the effect of different Mg^{2+} doping levels on the yields of ammonia and NO_3^- obtained. The optimum yields are obtained after ca. 2 h of irradiation. The ammonia yields after 2 h were highest for a Mg^{2+} dopant level of 2-4%. A similar effect was observed by Kiwi and Graetzel [4] for hydrogen generation over Mg^{2+} doped TiO₂ catalysts. At higher levels of magnesium doping, we observed that the Mg^{2+} initially added is not wholly incorporated into the TiO₂ structure as seen from the determination of Mg^{2+} in the actual catalyst samples using atomic absorption spectrometry. X-ray powder diffraction patterns of the catalyst doped up to 8% did not exhibit any evidence of



Fig. 1. Variation of the ammonia yields with time at different magnesium dopant levels (doping temperature 500° C, doping time 2 h).



Fig. 2. Variation of the ammonia yield with time at different pH values (doping temperature 500 °C, dopant level 2%, doping time, 2 h).

titanate formation. Particle size analysis on the catalyst with optimal activity (2% dopant level, heated at 500 °C for 2 h) showed that the average particle diameter is 0.64 μ m compared to undoped TiO₂ (0.57 μ m). The respective surface areas are 2.384 m² g⁻¹ (Mg/TiO₂) and 2.622 m² g⁻¹ for undoped TiO₂.

The effect of pH on this reaction was also studied. The results (Fig. 2) show that the yields of ammonia increase with increase in pH. At higher pH values more NO_3^- is also produced. The optimum temperature and the duration of heating was found to be 500°C and 2 h respectively (Figs. 3 and 4). Higher temperatures and higher periods of heating cause titanate formation and hence decreased activity. Furthermore the diffusion of Mg^{2+} into the TiO₂ lattice appears to be detrimental to its catalytic activity.

 TiO_2 can accommodate massive defect levels especially at the surface. The alteration of catalytic properties in a semiconductor by doping catalysts with ions of different valency was first observed by Verwey et al. [3]. Thus Li⁺ and Mg^{2+} doping of TiO_2 leads to enhanced water photocleavage under UV irradiation [4,5]. Doping with Mg^{2+} creates a narrower depletion layer width, which affects the rate of band bending. This would allow electron tunneling to proceed more easily at the interphase, thereby enhancing electron transfer. This hypothesis could explain the enhanced yields of ammonia observed in the above system. Our yields are significantly higher than those observed by Schrauzer and Guth [2] with other metal doped TiO_2 catalysts fired at 1000°C.



Fig. 3. Variation of the ammonia yield with time at different catalyst doping temperatures (dopant level 2% pH = 10, doping time 2 h).



Fig. 4. Variation of the ammonia yield with time at different doping times (dopant level 2%, pH=10, doping temperature 500 °C).

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