PHOTOCATALYTIC REACTIONS ON OXIDE SEMICONDUCTORS

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ABSTRACT

This thesis describes some photocatalytic reactions on oxide semiconductors. The first part (Part A) of the thesis deals with reactions of photocatalytic oxidation and photocatalytic reduction of molecular nitrogen and the second part (Part B) is on photocatalytic degradation of organic contaminants in water by using immobilized semiconductor based catalysts.

Nitrogen fixation by photocatalysis is a promising method and the question of increasing the quantum yield deserves more attention. Essentially the presence of a sacrificial electron donor (acceptor) in the solution enhances hydrogen photogeneration from water, which, however, is not generally helpful in improving the ammonia production rates. The presence of electron donors in the solution completely suppresses ammonia production where the dissolved sacrificial agent interferes with chemisorption of nitrogen on the surfaces of the catalyst. Introducing a water insoluble solid where the sacrificial agent is "bonded" to the active catalyst can solve this problem. If holes are

transferred to the solid sacrificial agent, reduction of nitrogen will be enhanced. It was observed that N_2 photoreduction with hydrous Fe_2O_3 can be enhanced by incorporating vanadium(III) hydroxide, which acts as a hole scavenger.

The other essential factor for nitrogen reduction is chemisorption of nitrogen at the catalyst surface. After experimenting with a large number of materials, it was observed that the hydrous oxides of iron(III) and samarium(III) are more effective photocatalysts for nitrogen reduction than TiO_2 or its doped forms. Presumably, these hydrous oxides chemisorb nitrogen more strongly than TiO_2. By a coprecipitation technique, it is possible to make composite catalyst particles consisting of two components, where one component is the sacrificial agent. When hydrous ferric oxide ($Fe_2O_3.nH_2O$) is incorporated with a strong reducing agent [e.g., the hydrous oxide of V(III)], $Fe_2O_3.nH_2O$ gets partly reduced to iron(II) hydroxide which inactivates the catalyst. However, samarium(III) hydrous oxide ($Sm_2O_3.nH_2O$) resists reduction by vanadium(III) hydrous oxide, and a coprecipitate containing hydrous oxides of V(III) and Sm(III) can be readily prepared. As expected, N_2 photoreduction occurs at a rate much higher than in other systems reported in the literature.

The photocatalytic degradation of organic compounds is an important branch of the broader subject of photocatalysis. Heterogeneous photocatalysis is capable of destroying many organic pollutants in aqueous media enabling the reduction of pollutants to very low concentrations. Wide band gap semiconductor materials such as TiO_2 are

widely used for this purpose as they produce highly potent oxidants (holes) at the semiconductor surface. The technical limitation of separating the dispersed unsupported catalyst has led to a search for inert supports for easy removal of the catalyst. Therefore this study's aim was to find an effective substrate for binding TiO_2 particles.

It was observed that polythene film is an effective and cheap substrate for holding TiO_2 particles and that TiO_2 in such films are photocatalytically active. As a model system, degradation of phenol (a parent substrate of a variety of pollutants) in the presences of TiO_2 coated polythene was studied. The immobilized catalyst is approximately 1.33 times less effective than the freely suspended catalyst . The reason for the discrepancy is more likely related to the availability of active sites on the catalyst surface.

The immobilization treatment generally lowers the activity of the catalyst. Therefore, attempts were made to increase the efficiency, possibly by size quantization. Transparent TiO_2 thin films prepared on glass substrates via the sol-gel method were photocatalytically active without any corrosion. As an example, mineralization of carbofuran was tested and total mineralization was obtained.

As the above immobilized catalysts can photocatalytically mineralize organic pollutants, photocatalytic degradation of textile dye wastes (a multi-component system) using the above immobilized catalysts was studied as an attempt to establish a viable water purification technique. Of the two catalysts, TiO_2 coated on glass plates was more active. The major drawback of the catalyst was the requirement of UV irradiation for decontamination of water. TiO_2 coated polythene films were more suitable of the two catalysts as it would be used even under sunlight. Therefore water decontamination with these films would be a good alternative for potential applications.