

Photocatalysis Approach for Energy and Environmental Challenges at Indian Institute of Chemical Technology, Hyderabad, India

V. Durga Kumari *, M. Subrahmanyam, M.V. Phanikrishna sharma, J. Krishna Reddy, K. Lalitha
Catalysis and Physical Chemistry Division

Indian Institute of Chemical Technology, Hyderabad 500607, India

ABSTRACT

The R & D developments in several aspects of catalysis area require cleaner and clean up technologies. Catalysts are used for energy conversion and to convert environmentally hazardous materials into harmless compounds. This presentation reviews the work currently under exploration at IICT that illustrates the perspective of photocatalyst technologies for solving energy and environmental issues for providing sustainable development. Studies on development of photocatalytic materials for degradation of phenolic wastes, common industrial effluent, H-acid, Calmagite (an azodye), Isoproturon (herbicide) and for E-coli disinfection are highlighted. Materials like Natrotantite, Ce-modified zeolites, Ag₂O/TiO₂, CuO/TiO₂ and C,N-doped TiO₂ are designed and evaluated for photocatalytic splitting of water for generation of hydrogen energy. Furthermore, potential applications of photo catalysts in the chemical synthesis of N-containing heterocyclic compounds like pyrazines and piperazines which are useful intermediates in the synthesis of various drugs, perfumes, herbicides and dyes are new interesting aspects in the presentation. Thus the present review describes the emerging trends in using photocatalysts for energy and environmental applications.

INTRODUCTION

Though TiO₂ in anatase form is the best photocatalyst reported so far, poor adsorption properties lead to great limitation in exploiting the photocatalyst to the best of its photoefficiency. The other problem with the semiconductor photocatalyst is the faster electron-hole recombination that results in decreased photo-efficiency. Several attempts have been made to improve the photo efficiency of titania by adding adsorbents like silica, alumina, zeolites, clays and active carbon. This addition is expected to induce synergism as the pollutants are adsorbed prior to photodegradation making the process more facile. Supported TiO₂ is commonly reported to be less photoactive due to the interaction of TiO₂ with the support during the thermal treatments. A method of supporting TiO₂ on zeolites without losing the photoefficiency of TiO₂ and the adsorption properties of the support is the important aspect while preparing zeolite based photocatalysts. Synergistic effects were also evidenced when mixtures of TiO₂ and adsorbents like active carbon were employed for photooxidation. TiO₂ based zeolites are extensively prepared, characterized and evaluated in this laboratory for the degradation of phenolic waste and also for the synthesis of N-heterocyclics using both UV and solar irradiation. TiO₂ and TiO₂ supported zeolites are also drawn into thin films using acrylic emulsions as binder and applied for large scale applications for treating common industrial effluent containing dye and drug intermediates. TiO₂ is also supported on mesoporous materials like Al-MCM-41 and SBA-15 for treating pesticide containing wastewater in order to achieve higher degradation rates. Ce and Bi modified zeolites are showing photocatalytic properties in

water splitting reaction and photodegradation of phenol. Whereas Fe modified zeolites are heterogenised photo-fenton catalysts used in phenol degradation. Ce modified Al-MCM-41 is also used as support to disperse TiO_2 wherein Ce ion is stabilized in lower oxidation on photoirradiation acting as electron acceptor and minimizing the electron-hole recombination. TiO_2 is also sensitized by doping metal ions as well as nonmetals to obtain visible light activity. Thus $\text{Ag}_2\text{O}/\text{TiO}_2$, CuO/TiO_2 and C, N-doped TiO_2 are established for water splitting to generate hydrogen using solar energy. Natrotantite which is normally synthesized in solid state at very high temperatures was attempted in hydrothermal conditions and established for structure and as a water splitting catalyst under UV irradiation. TiO_2 supported on pumice stone, H β and hydroxy apatite (HAP) are evaluated for disinfection of water. The materials prepared, characterized and evaluated as photo catalyst for energy and environmental applications are summarized below and their fine tuning and development for specific applications is a continuous study in this laboratory.

DISCUSSION

Photocatalysts developed for the degradation of organic wastes

Bi-ZSM-5 : This catalyst is prepared by impregnation of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ over HZSM-5 zeolite. Isolated Bi_2O_3 particles are present over the support with interaction. The adsorption properties of the support and the increased band gap of interacted bismuth resulted in enhanced activity of Bi-ZSM-5 catalysts in the photodegradation of phenol under UV light [1].

Sm³⁺ doped Bi₂O₃ : Sm³⁺ doped Bi_2O_3 photo catalyst is prepared by hydrothermal process. DRS showed a large decrease in the band gap from 2.85 to 2.1 eV. The low band gap energy, high surface area and decreased rate of e^-/h^+ recombination by Sm doping increased the photocatalytic activity of the catalyst in the degradation of methylene blue under solar light. The decreasing order of the activity under solar irradiation is: Sm^{3+} doped $\text{Bi}_2\text{O}_3 > \text{TiO}_2 > \text{Bi}_2\text{O}_3$ [2].

Ce-Al-MCM-41 : Ce-Al-MCM-41 is prepared by the impregnation of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ over Al-MCM-41. Cerium ion in interaction with Al-MCM-41 is in +3 oxidation state and showing the higher photocatalytic activity compared to pure ceria. Ce^{3+} on irradiation generates electrons that participate in effective photodegradation of phenol under UV light [3].

TiO₂/Ce-Al-MCM-41 : $\text{TiO}_2/\text{Ce-Al-MCM-41}$ composite is prepared by solid state dispersion of P-25 (TiO_2) over Ce-Al-MCM-41. The Ce^{4+} ion formed on photoexcitation of Ce^{3+} ion, traps the electron of TiO_2 and minimizes the e^-/h^+ recombination over titania. The synergism resulted in enhanced activity of the composite catalyst for the degradation of phenol under UV light [4].

Nano C, N doped TiO₂ : Mesoporous nano C, N doped TiO_2 is prepared by the hydrolysis of titanium isopropoxide. Pyridine is used as the source of C and N doped in to the TiO_2 lattice. Pyridine developed the selective linkage of Ti-O-N in C, N doped- TiO_2 evidenced by the IR and XPS techniques. The catalysts show high visible light activity for the degradation of 4-nitro phenol and MB under solar light [5].

TiO₂ /HZSM-5 Acrylic films : These films are made with a proprietary binder using a spray technique onto an inert support. HZSM-5 zeolite is immobilized in a stable polyacrylic film. It is an economical, practical and promising method to immobilize photocatalysts for the elimination

of xenobiotic pollutants from wastewaters. TiO₂/HZSM-5 films are showing higher activity compared to TiO₂ under UV light [7].

Fe (III)-HY : Fe (III)-HY catalysts are simply prepared by impregnation method. IR, DRS and XPS studies confirm the redox states of Fe before and after the reaction. No leaching of Fe from the solid catalyst into the solution is detected by AAS. Heterogeneous Fe (III)-HY is more efficient compared to homogenous Photo-Fenton system that can be applied at pH>3 [8]. The catalyst is showing good activity with a minimum concentration of H₂O₂ and Fe for the degradation of phenol under UV light [8].

TiO₂ and TiO₂-AE film : TiO₂ slurry and TiO₂-AE film are coated on a cuddapah flat stone support and used in the degradation of H-acid. The catalyst is stable and showing enhanced activity that recommended for large scale continuous operation [9].

TiO₂ Suspension : Commercial TiO₂ samples are used in suspensions and evaluated for the degradation of orange red. P-25 suspension is showing higher activity compared to PC 50, PC 100 and PC 500 TiO₂ [10].

Photocatalysts developed for water splitting

Ag₂O/TiO₂ : This catalyst was prepared by impregnation method. XRD and TEM show fine dispersion of silver on TiO₂. XPS establishes the interaction of silver with TiO₂. DRS shows a red shift of 50 nm in the absorption band edge of titania making the catalyst visible sensitive. H₂ production about 145 μmol h⁻¹g⁻¹ cat is observed with pure water. In 5% aqueous methanol the H₂ production is around 3350 μmol h⁻¹ g⁻¹ cat. Continuous H₂ production is observed due to the reversibility in the redox properties of silver ion (Ag⁺ + e⁻ ↔ Ag). [11]

CuO/TiO₂ : This catalyst was prepared by impregnation method. XRD shows fine dispersion of Cu on TiO₂ surface. DRS shows a shoulder in the absorption edge of TiO₂. XPS results indicate the interaction of Cu with TiO₂. H₂ production about 581 μmol h⁻¹g⁻¹cat is observed in pure water. In 5% aqueous methanol the hydrogen production observed is around 19117 μmol h⁻¹ g⁻¹ cat. [12]

C, N-doped TiO₂ : This catalyst was prepared by hydrolysis method. A single crystalline anatase phase is observed by XRD. N₂ adsorption measurements show that catalysts are mesoporous with high surface area. Ti-O-N and Ti-C bonds are confirmed by XPS studies. C, N doped TiO₂ with oxynitride linkages are showing shift in the band gap towards the visible region. H₂ production about 700 μmol h⁻¹ g⁻¹ cat is observed in nano TiO₂ catalyst in 10% aqueous methanol. In C,N-doped TiO₂ catalyst the rate of hydrogen production is around 3400 μmol h⁻¹ g⁻¹ cat. Improvement in activity is observed for C, N doped TiO₂ catalyst compared to nano TiO₂ due to C doping into TiO₂ lattice and the incorporation of N preferentially into interstitial positions of the titania lattice. [13]

Natrotantite (Na₂Ta₄O₁₁) : This catalyst was prepared by hydrothermal synthesis. Nano crystalline natrotantite is observed in ethanol washed sample. Mesoporous and crystalline samples resulted during the high temperature calcinations. Nano and mesoporosity of the sample are confirmed by TEM and N₂-adsorption studies. H₂ production of 14.10 μmol h⁻¹g⁻¹cat is observed in pure water. In presence of methanol the H₂ production reached 83.30 μmol h⁻¹g⁻¹cat. In high temperature calcined samples, 7.40 μmol h⁻¹g⁻¹cat of H₂ was produced. This work

highlights the preparation of nano crystalline Natrotantite through surfactant assisted hydrothermal synthesis at low temperatures [14].

Ce-modified Zeolites : These catalysts were prepared by impregnation method. XPS of Ce-zeolites with low Ce content shows strong interaction between zeolites and cerium and most of the cerium is in Ce^{3+} state. The rate of H_2 production over Ce- MCM-41, Ce-Al-MCM-41, Ce-HY, Ce-HZSM-5 is 1416, 651, 121 and $231\mu\text{mol h}^{-1}\text{g}^{-1}\text{cat}$ respectively. With increasing Al content the activity decreased as Al traps the excited electrons. The photo irradiation of Ce^{3+} species generates electrons and forms redox couple Ce^{+3}/Ce^{+4} ($Ce^{3+} + hv \rightarrow Ce^{4+} + e^-$) [15].

Photocatalysts developed for pesticide degradation

TiO₂/HY : HY zeolite with Si/Al ≈ 2.6 and surface area of $340\text{ m}^2\text{g}^{-1}$ is used as a support. TiO₂ is dispersed over it by SSD method. 10 wt% loading of TiO₂ is found to be optimum for the degradation of isoproturon. TiO₂/HY shows decreased surface area of $130\text{ m}^2\text{g}^{-1}$. The SEM-EDAX data proved that nearly 9.8 % TiO₂ is present on the surface of HY. Isoproturon is completely degraded with in 120 min with the rate of $5.95\text{ E-}06$ and nearly 80% mineralization was observed with in 5h over 1 gL^{-1} catalyst amount. [16]

TiO₂/H-MOR : H-MOR zeolite with SiO₂/Al₂O₃ ≈ 20 and surface area of $440\text{ m}^2\text{g}^{-1}$ is used as a support. TiO₂ is dispersed over it by SSD method. 15 wt% TiO₂ loading is found to be optimum for this study and its surface area is $352\text{ m}^2\text{g}^{-1}$. Isoproturon is completely degraded within 45 min with the rate of $1.16\text{E-}05$ and ~87% mineralization was noted within 5h over 1.5 gL^{-1} catalyst amount [17].

TiO₂/AlMCM-41 : Al-MCM-41 with Si/Al ≈ 15.5 and surface area of $1124\text{ m}^2\text{g}^{-1}$ is prepared by hydrothermal synthesis using a template and all TiO₂ loadings over the support are prepared by SSD method. 10wt% loading was to be found optimum for this study and the catalyst is having surface area of $742\text{ m}^2\text{g}^{-1}$. Isoproturon is degraded completely with in 90 min with the rate of $6.79\text{E-}06$ and ~88% mineralization was observed within 5h over 1 gL^{-1} catalyst amount. [18]

TiO₂/PNS : Porous nano silica (PNS) material with a surface area of $153\text{ m}^2\text{g}^{-1}$ is prepared by salt mediated synthesis and over this material TiO₂ is finely dispersed by SSD method. Only 5wt% of loading found to be optimum and having surface area of $115\text{ m}^2\text{g}^{-1}$. XRD of PNS is showing clearly the low angle with mesoporous range and these are confirmed by N₂ adsorption-desorption studies and TEM. Isoproturon is completely degraded with in 90min with the rate of $7.88\text{E-}06$ and ~81% mineralization was occurred within 5h over 1 gL^{-1} catalyst amount. Optimum catalyst amount for this reaction is 3 gL^{-1} and its rate is $2.12\text{E-}05$. Also technical Pirimicarb is degraded within 60 min in the same conditions. Commercial pesticides Imidacloprid and Phosphamidon were also checked for degradation in the same conditions and were found to degrade with in 240 and 120 mins respectively. [19]

TiO₂/SBA-15 : SBA-15 with a surface area of $624\text{ m}^2\text{g}^{-1}$ is prepared by hydrothermal synthesis and TiO₂ is dispersed over it by SSD method. 10 wt% loading of TiO₂ was found to be optimum for this reaction and its surface area is $432\text{ m}^2\text{g}^{-1}$. XRD is showing clearly the low angle (100, 110 and 200 planes) with mesoporous range and it is supported by TEM and N₂ adsorption-desorption studies. Isoproturon is degraded with in 30min at a rate of $1.88\text{E-}05$ and ~91% mineralization was observed with in 5h (completely mineralized in 9h) over 1 gL^{-1} catalyst amount. Technical Pirimicarb was degraded within 45 min in the same conditions. Commercial

pesticides Imidacloprid and Phosphamidon were degraded under the same conditions within 180 and 60 mins respectively. Consortium of pesticides (Isoproturon 20 ppm, Imidacloprid and Phosphomidon each 15 ppm) total 50 ppm are successfully degraded within 90 min. [20]

Industrial Effluent Treatment

TiO₂ : In this study photo catalytic de-colorization and mineralization of common industrial effluent is obtained with TiO₂ photo catalyst using solar light illumination. Also solar photo catalytic coupled biological treatment of N-containing organic compounds in wastewater are tested successfully for pyrazinamide drug manufacturing effluent [21,22]

Photocatalytic disinfection of water

TiO₂ over pumice, H β and HAP : Disinfection and detoxification are illustrated in our recent work [23] using TiO₂ over pumice stone, H β [24] and hydroxyapatite [25]. These are taken as supports for TiO₂ and used for treatment of bacterial inactivation (E coli), which are commonly existing in real waters and also different organic pollutant degradations like acid orange-7, resorcinol, 4,6 dinitro-o-cresol, 4-nitrotoluene-2-sulfonic acid, isoproturon are performed [23] The water that was passed through the pumice stone supported reactors demonstrated strong bactericidal ability as well as detoxification affects by showing reduction in TOC, extent of decrease in color over treatment period. The photo catalytic deactivation of total E coli by solar light has been also attempted for real river waters. The technical feasibility and performance of photo catalytic effects of TiO₂ coatings over pumice stone in continuous reactor processes studied proved to improve the potability of drinking water collected from real waters.

Photocatalytic organic synthesis

TiO₂ over Zeolites : Also several N-heterocyclic compounds like dihydropyrazine (DHP), trans-1,4,6,9-tetraazabicyclic[4.4.0] decane (TAD), 2-methyl-quinoxaline (2-MQ), quinoxaline (Q), 2-methyl pyrazine (2-MP) and piperazine (P) have been synthesized in artificial UV light and solar light using TiO₂/Zeolite as photocatalyst [26-28].

CONCLUSIONS

This paper describes some of the existing photocatalysts developed in our laboratory. Although new catalysts are greatly needed in various areas, it is not easy to realize those specific catalysts due to severe requirements for the catalytic performance. The design of photo active sites, making them more visible light absorption thin film materials for large scale water treatment are some of the potential areas for the development with high efficiency and long sustainability. The technologies for the wastewater applications or organic synthesis or fuel production either using artificial or solar light, will compete in the market to develop more precise material preparation methods.

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