



SILICA GEL SUPPORTED TITANIUM DIOXIDE PHOTOCATALYST FOR METHYL ORANGE PHOTOREDUCTION

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Abstract- TiO₂ based photocatalysis has been widely investigated and has vital applications in energy and environmental remediation processes. In this connection research is being conducted in the zone of supported TiO₂ based photocatalysts for development of visible light induced photocatalytic material. A series of materials were synthesized including zeolite based composite photocatalyst, N-doped mesoporous titania and investigated for dye degradation followed by hydrogen generation. Current research trend is towards supported photocatalyst therefore silica gel supported TiO₂ photocatalyst was designed and developed also compared with alumina based photocatalyst. From the experimental data it was found that Silica based system has edge over the other synthesized photocatalysts with effective dye degradation of about 9.61 mg of MO reduced per g of TiO₂ (0.508 mg of MO reduced per g of TiO₂ for Degussa P-25). MO photoreduction is 19 times higher as compared to benchmark material Degussa P-25. Results well illustrate the formation of high dispersed metal oxide on silica framework.

Keywords- Supported photocatalyst, noble metal, methyl orange, hydrogen

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Introduction

Titanium dioxide is by far the most stable, non corrosive and non toxic semiconductor photocatalyst [1]. It is widely used and reported due to its unique photocatalytic nature. It has been used extensively in other applications like cosmetics, paints [2], photoelectrodes, surface coating, water spitting[3], organic pollutant degradation[4] etc. It also acts as, antialgal [5] antibacterial [6-7], anti-fungal and deodorizing agent. In spite of all these properties, the photocatalytic activity of TiO₂ is limited due to fast recombination of photo generated electrons and holes, low surface area while there is a significant activity in the ultra violet light. Many attempts have been made in order to i) improve the surface area, ii) to minimize the recombination reaction and improve its activity in visible region of spectrum.

The surface area can be improved by supporting TiO₂ on a suitable

matrix. Mesoporous materials are suitable host as they have better surface area for effective dispersion of TiO₂ [8-9]. Attempts has been made to support TiO₂ on various matrices such as hexagonal mesoporous silica, zeolite Y [10-12], activated carbon[13], porous ceramic tube[14], glass [15] etc. Support material not only offers better surface area but also the support-TiO₂ interface provides the site for effective electron transfer.

Siliceous materials are most suitable support as they have following properties-

1. Chemically inertness
2. High surface area and
3. Transparency to UV radiations.

There are very few reports in literature mentioning the use of silica gel as a support. Ding et-al [16] reported synthesis of silica gel supported TiO₂ using chemical vapour deposition method. Silica

gel/ TiO₂ were also employed for degradation of trichloroethane (TCE) [17]. Silica gel as a support is advantageous in recovering the catalyst after completion of reaction [18]. Reports are also available for application of Silica- titania composites for removal of trace level of water pollutants [19]. CuO supported SiO₂ is reported as effective photocatalyst for degradation of methylene blue [20].

The other attempt widely being pursued is metal incorporation [21-22]. Photocatalytic response of TiO₂ can be improved by metal doping. Many reports are available in literature for metal ion loading. Supported/ unsupported TiO₂ was either loaded or doped with transition metals like Cr, V, Fe, Cu, Mn, Co, Ni, and Mo [23-24], noble metals like Pd and Pt [25], rare earth like La, Nd, Sm, Eu, Gd, and Yb [26]. Smaller metal particles deposited on TiO₂ surface exhibits more negative Fermi level shift. These Fermi levels are closer to the conduction band of TiO₂ resulting in more negative energy levels which are beneficial for reduction reaction. This improves the overall photoactivity of TiO₂.

Here TiO₂ was first supported on silica gel and then promoted with noble metals like Platinum and Ruthenium. Titania precursor was incorporated in silica gel by wet impregnation method and calcined at 500°C for developing anatase phase of TiO₂. Noble metals were loaded on supported TiO₂ by conventional wet impregnation route. Wet impregnation deposits the metal on a surface without material loss.

The synthesized photocatalyst was subjected to dye degradation under visible light irradiation. The methyl orange (MO) was completely degraded (100% photoreduction) by the as synthesized photocatalyst.

Experimental

A. Materials

The chemicals used for the synthesis were titanium (IV) isopropoxide (ACROS Organics USA), ruthenium chloride, methyl orange, ethanol and silica gel (Merck India Pvt. Ltd.) Tungsten lamps of 100, 200, and 500W were procured from Philips India Ltd, Mumbai.

B. Synthesis

a. Synthesis of Silica gel/TiO₂ (10%)

5g of silica gel was mixed with 1.779 g titanium isopropoxide to attempt the 10% loading of TiO₂. This mixture was ground thoroughly to get homogeneous mass and calcined at 500°C for 1h.

b. Synthesis of Silica gel/TiO₂ (10%)/Pt

1g of Silica gel/TiO₂ was mixed with platinum solution (0.5%w/w that is 0.005g of Pt on 1 g of Silica gel/TiO₂). This mixture was heated at 60°C with constant stirring in order to evaporate the water content. Dried mass obtained was ground thoroughly to get homogeneous mass. Silica gel/TiO₂ (10%)/Ru were also synthesized using similar method.

C. Characterization

X-ray diffraction patterns for Silica gel/TiO₂, Silica gel/TiO₂/Pt, Silica gel/TiO₂/Ru, were obtained by Rigaku Miniflex II, Desktop X-ray diffractometer with Cu K α radiations ($\lambda = 0.5405$). Specific surface area of photocatalyst was measured by N₂ adsorption / desorption at 77 K using Micrometecs USA ASAP 2000 instrument. Pore size and pore volume were analysed using Micrometecs USA ASAP 2000 Specific surface area analyser. Scanning Electron Microscopic (SEM) images were obtained on a JEOL JSM-6380A

Analytical Scanning Electron Microscope. UV-visible diffuse reflectance spectra (UV-DRS) and absorbance were obtained by Perkin Elmer Lambda 900 spectrophotometer.

D. Experimental method for photoreduction of methyl orange

Experimental set-up is similar as described in previous studies by the authors [4].

Results and discussion

A. Characterization of supported photocatalyst

XRD: The X-ray diffraction pattern for Silica gel/TiO₂, Silica gel/TiO₂/Pt, and Silica gel/TiO₂/Ru along with Degussa P25 photocatalyst is given in Fig. 1. Peaks having 2 θ value of 25.4°, 38.6°, 47.96°, 48.60° correspond with TiO₂ anatase phase.

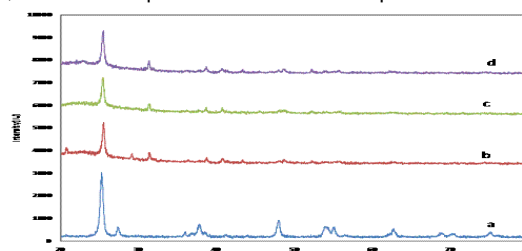


Fig: 1- XRD pattern of a) P25, b) Silica gel/TiO₂/Pt, c) Silica gel/TiO₂/Ru and d) Silica gel/TiO₂.

Surface area- Surface area is determined by BET (Brunauer-Emmett-Teller) method, Pore size distribution is estimated using BJH (Barrett-Joyner-Halenda) method. Surface area of the bare silica gel is of about 204.87m²/g with pore volume and pore size of 0.42cm³/g and 121.98 Å respectively. This confirms that the commercially available silica gel is mesoporous with high surface area. BET surface area of Silica gel/TiO₂ (190.69 m²/g), Silica gel/TiO₂/Pt (185.07 m²/g), and Silica gel/TiO₂/Ru (166.16 m²/g) is lowered due to the impregnation of TiO₂, metals onto the silica framework.

Energy-dispersive X-ray spectroscopy: EDX spectra of the photocatalyst silica gel/TiO₂/Pt and its chemical compositions are given in Fig. 2. This data states that the commercially available silica gel consists of 71 and 29 mass-percent of silica and oxygen respectively (data not shown). A spectrum reveals the presence average 8.5 mass percent of TiO₂, 0.47 mass percent of Pt in synthesized photocatalyst silica gel/TiO₂/Pt.

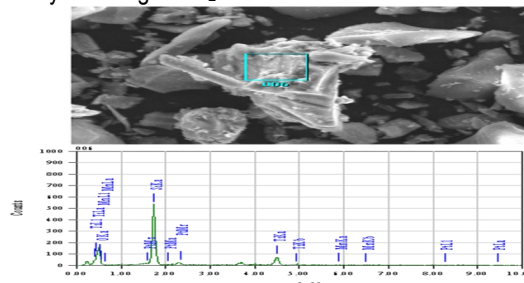


Fig: 2- EDX spectra of Silica gel/TiO₂/Pt

UV-Visible diffused reflectance (UV-DRS) spectra- UV-Visible diffused reflectance spectra of Silica gel/TiO₂, Silica gel/TiO₂/Pt, and Silica gel/TiO₂/Ru along with Degussa P25 TiO₂ photocatalyst are given in Fig. 3. The wavelength maxima observed for Silica gel/TiO₂ and Silica gel/TiO₂/Pt are 385, and 390nm respectively.

λ_{\max} values indicate that the wavelength response range for Silica gel/TiO₂/Pt is in visible region. In case of Silica gel/TiO₂/Ru, the sample is dark greyish in colour so the spectrum shows absorption for complete range of light.

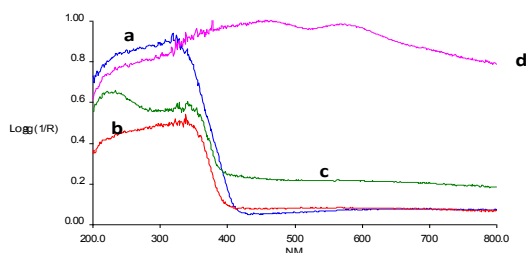


Fig 3- UV-DRS spectra of (a) Degussa P25 TiO₂ photocatalyst, (b) Silica gel/TiO₂, (c) Silica gel/TiO₂/Pt and (d) Silica gel/TiO₂/Ru.

Photoreduction of methyl orange using Supported photocatalysts

All the three synthesized photocatalyst namely Silica gel/TiO₂, Silica gel/TiO₂/Pt, and Silica gel/TiO₂/Ru along with Degussa P25 TiO₂ photocatalyst were subjected to MO photoreduction. Fig. 4 shows the comparison of supported photocatalysts. MO photoreduction was observed to be 0.508, 5.344, 8.96 and 9.615 mg of MO reduced per g of TiO₂ for Degussa P25 TiO₂ photocatalyst, Silica gel/TiO₂/Ru, Silica gel/TiO₂, and Silica gel/TiO₂/Pt respectively. The photoactivity of all the supported photocatalyst is higher as compared to the benchmark Degussa P25 TiO₂ photocatalyst. Silica gel/TiO₂/Pt shows remarkable increase in the photoactivity by a factor of 19 as compared to the Degussa P-25 TiO₂.

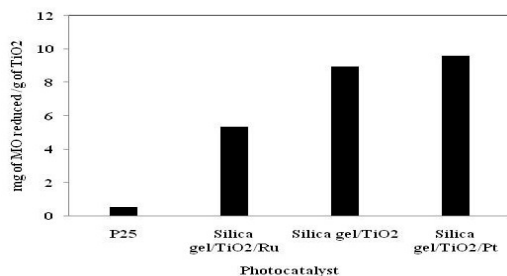


Fig 4- Comparison of MO photoreduction by P25, Silica gel/TiO₂, Silica gel/TiO₂/Pt and Silica gel/TiO₂/Ru

Conclusion

Supported photocatalyst such as Silica gel/ TiO₂, Silica gel/ TiO₂/Pt, and Silica gel/ TiO₂/Ru were synthesized with predominant anatase phase. UV-DRS spectra show that the activity of the supported photocatalyst falls in visible region. The shift in absorption maxima could be due to the presence of metal on the surface of supported photocatalysts. The photocatalytic activity of the supported photocatalyst was evaluated by carrying out the photoreduction experiments. MO photoreduction by Silica gel/ TiO₂/Pt is observed to the tune of about 9.61 mg of MO reduced per g of TiO₂.

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References

- [1] Fujishima A., Honda K. (1972) *Nature*, 238, 37-38.
- [2] Braun J.H., Baidins A., Marganski R.E. (1992) *Progress in Organic Coating*, 20, 105-138.
- [3] Chatti R. V., Dubey N., Joshi M. V., Labhsetwar N. K., Joshi P.N., Rayalu S. S., (2010) *Int. J. Hydrogen Energy*, 35, 1911-1920.
- [4] Joshi M.M., Labhsetwar N.K., Mangrulkar P. A., Tijare S.N., Kamble S.P. (2009) *Appl. Catal. A: Gen.*, 357, 26-33.
- [5] Aruoja V., Dubourguier H.C., Kasemets K., Kahru A. (2009) *Sci. of Total Environ.* 407 (4), 1461-1468.
- [6] Xu S., Shen J., Chen S., Zang M., Shen T. (2002) *J. Photochem. Photobio. B: Bio.* 67 (1), 64-70.
- [7] Linkous C.A., Carter G.J., Locuson D.B., Ouellette A.J., Slattery D.K., Smitha L.A. (2000) *Environ. Sci. Technol.* 34, 4754-4758.
- [8] Ding Z., Hu X., Yue P.L., Lu G.Q., Greenfield P.F. (2001) *Catal. Today*, 681, 73-82.
- [9] Chen Y., Wang K., Lou L. (2004) *J. Photochem Photobio A: Chem.*, 163, 281-287.
- [10] Dai Q., He N., Weng K., Lin B., Lu Z., Yuan C. (1999) *J. of Incl. Phenom. and Macrocyclic Chem.*, 35, 11-21.
- [11] Dubey N., Rayalu S.S., Labhsetwar N.K., Devotta S. (2008) *Int. J. Hydrogen Energy*, 33, 5958-5966.
- [12] Rayalu S.S., Dubey N., Labhsetwar N.K., Devotta S. (2007) *Int. J. Hydrogen Energy*, 32, 2776-2783.
- [13] Sheikh A., Al-Degs Y., Newman A., Lynch D., (2007), *Separ. and Puri. Techn. B*, 117-123.
- [14] Wang W., Irawan A., Ku Y. (2008) *Water Research*, 42 (19) 4725-4732.
- [15] Lu M., Roam G., Chen J., Huang C.P. (1993) *J Photochem Photobio A: Chem.*, 76, 103-110.
- [16] Ding Z., Hu X., Lu G. Q., Yue P.L., Greenfield P.F. (2000) *Langmuir*, 16, 6216-22.
- [17] Lim T.H., Kim S.D. (2005) *Chem. Engineering and Process*, 44, 327-334.
- [18] Aguado J., Grieken R.V., Lopez-Munoz M.J., Marugan J. (2006) *Appl. Catal. A: General*, 312, 202-212.
- [19] Byrne H.E., Mazyck D.W. (2009) *J. Haz. Mat.* 170, 915-919.
- [20] Batista A.P.L., Carvalho H.W.P., Luz G.H.P., Martins P.F.Q., Goncalves M., Oliveira L.C.A. (2010) *Environ. Chem. Lett.*, 8, 63-67.
- [21] Paola D., Marc G., Palmisano L., Schiavello M., Uosaki K., Ikeda S., Ohtani B. (2002) *J. Phys. Chem. B*, 106, 637-645.
- [22] Loosdrecht J.V., Kraan A.M., Dillen A.J., Geus J.W. (1996) *Catal. Lett.*, 4127-34.
- [23] Reddy E.P., Sun B., Smirniotis P.G. (2004) *J. Phys. Chem.* 108 (44), 17198-17205.
- [24] Wu N.L., Lee M.S. (2004) *Int J Hydrogen Energy*, 29,1601-1605.
- [25] Zou J.J., He H., Cui L., Du H.Y. (2007) *Int. J. Hydrogen Energy*, 32, 1762-1770.
- [26] El-Bahy Z.M., Ismail A.A., Mohamed R.M. (2009) *J. Haz. Mat.*, 166, 138-143.