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Visible Light Active Titania Photocatalyst Doped with Molybdneum

Chemistry

KEYWORDS : acid orange 7, anatase, sol-gel, photocatalytic activity, titania

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ABSTRACT

Mo-TiO_2 catalysts with different Mo contents (0.5–3 wt%) were prepared by the sol–gel method. X-ray diffraction pattern denoted that all catalysts are in anatase phase. The UV-Vis. diffuse reflectance spectra showed that the band gap was shifted to lower energy levels in the samples with higher Mo contents. Photocatalytic activity of the catalysts was evaluated based on the photodegradation of Acid Orange 7 in aqueous solution under visible light. The experiments demonstrated that the Mo doped titania exhibited higher visible-light activity compared to undoped one.

1 INTRODUCTION

Semiconductor photocatalysis is one of the most efficient destructive technologies among advanced oxidation processes (AOPs), since the total mineralization of most of the organic pollutants that exist in air and aqueous systems is possible. TiO_2 is of great interest due to its non-toxic nature, photochemical stability and low cost, particularly when sunlight is used as the source of irradiation [1]. Transition metals have usually been used as doping agents to obtain photocatalysts with better photoactivity. Doping of metal decreases the band gap energy and induces a red shift in the absorption spectrum, the dopant improves the TiO_2 photocatalytic activity by enhancing the absorption in visible region by the introduction of additional band in the solid [2].

In this study, Mo-doped TiO_2 photocatalysts were prepared. Molybdenum was chosen because its cationicradius Mo(VI) (0.62 A °) is similar to that of Ti(IV) (0.68 A °) and hence the Ti(IV) substitution in the titania network can be possible[2]. The catalysts were prepared by the sol–gel method using titanium isopropoxide(TTIP) and ammonium heptamolybdate tetrahydrate as starting materials. The catalysts were characterized by X-ray diffraction, BET Surface area and UV-Vis.DRS. The photocatalytic properties was evaluated by studying the degradation of Acid Orange 7(AO7) in aqueous solution.

2 EXPERIMENTAL

2.1 Preparation of photocatalysts

The metal doped photocatalysts with different metal concentrations (metal load- 0.5, 1.0, and 3.0 wt%) were prepared by the sol–gel method as follows. Titanium isopropoxide(TTIP) and ammonium heptamolybdate tetrahydrate were used as precursors. 12.5 ml of TTIP was dissolved in 25 ml of absolute alcohol with stirring for 10 minutes; then 0.25 ml of HNO_3 was added dropwise to the above solution under stirring for 30 minutes. Another solution containing metal salt in the required stoichiometry was slowly added into the above solution, stirred for two hours and the transparent sol was obtained. The gel was prepared by aging the sol for 24 hours at room temperature. The gel was dried at 60^{o}C. Before characterization, all the samples were calcined in air at 400^{o}C for 4 hours. Thus Mo doped titania catalysts (metal load- 0.5wt% (labeled as MoT1), 1.0wt% (labeled as MoT2), and 3.0 wt% (labeled as MoT3)) were prepared [3]. Pure titania catalyst (labeled asT) was also prepared to compare the results with the doped one.

2.2 Characterization

The crystal phases of the catalysts were determined by X-ray diffraction (XRD) analysis. XRD patterns of the samples were obtained using Bruker AXS D8 advance X ray diffractometer using CuKα radiation. Data were collected over the angle of 2θ between 10° to 70^{o}. Crystallite size was determined by using Scherrer's equation : D=0.9λ /β(Π/180)cosθ (1) where D is the crystallite size λ is the wavelength of X ray radiation, β is the full width of half maximum and θ is the diffraction angle. BET Surface area was measured using Micrometritics Tristar 3000 surface area analyzer. The samples were activated at 90^{o}C for 30 minutes and degassed at 350^{o}C for 4 hours. The UV- DRS were obtained in the range 300-800nm on Labomed UV VIS DOUBLE BEAM UVD 500 Spectrophotometer equipped with an integrating sphere assembly using $BaSO_4$ as reflectance standard. The wavelength at the onset of reflection was taken and band gap was calculated using the equation: Ebg=1240/λ (2). where λ is the wavelength in nanometer

2.3 Photocatalytic Activity studies

Photocatalytic activity of the prepared samples was measured by studying the degradation Acid Orange 7 in aqueous solution. The experiment was carried out using an Oriel Uniform Illuminator 150 W Xe ozone free lamp with filter. 420-630nm dichoric mirror for visible irradiation was used. The studies were carried out by taking 10 ml of 10^{-4} M solution of AO7 and 1g/L of catalyst. The solution was stirred for 30 minutes before irradiation to attain the adsorption desorption equilibrium. After photodegradation, the solution was centrifuged and recorded the absorbance wavelength of 483nm using a SPECTRASCANUV 2600 DOUBLEBEAM UV VIS spectrophotometer. The percentage degradation of dye was calculated using the equation: X= (C_o- C_t/C_o) x 100 in which X is the percentage degradation, C_t is dye concentration at time t and C_o is initial dye concentration.

3 Results and Discussion

3.1 Structure and Properties of Photocatalysts

The diffraction peak at 25.5 corresponds to anatase phase of titania. The peak positions are same and no extra peaks except for anatase TiO_2 was observed, suggesting that the structure of TiO_2 is not changed by the incorporation of molybdenum. No peak was observed for dopants, may be due to the low amount of doped molybednum so that it cannot be detected by XRD. The materials show a very high degree of crystallinity of fully anatase phase. The XRD profile of Mo doped TiO_2 catalysts are shown in Fig. 1

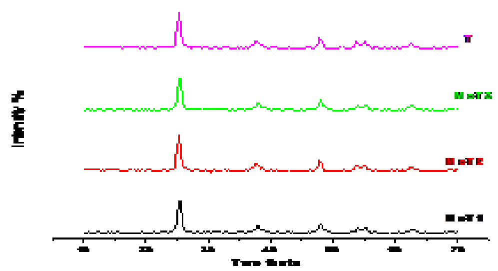

Fig.1 XRD pattern of Mo doped titania

For doped TiO_2 samples, the surface areas increase with the increase of dopant concentration up to a maximum of 1 wt % and then decreases with the increase of dopant concentration. The crystallite size and surface area of the catalysts are given in table.1

Table 1 Crystallite size and surface area of prepared catalysts

Catalyst	Crystallite size(nm)	BET surface area (m^2/g)
MoT1	9.6	69
MoT2	9.4	91
MoT3	8.7	38
T	13.4	77

Extending the absorption edge of TiO_2 to the visible region is considered as one of the main objective in this study. The UV DRS of the prepared catalysts are shown in Fig.2 The presence of a small amount of Mo in the catalyst gives rise to the red shift of its absorbance wavelength, decrease of its energy gap and increase of the utility of visible light .The band gap of MoT2 was found to be 2.57eV and for undoped titania(T) 3.18eV corresponding to a wavelength of 389nm which falls in the UV region. The absorption of visible light enhance along with the impurity concentration.

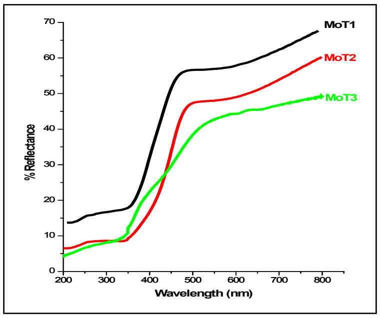

Fig.2 UV-Vis.DRS of Mo doped titania

3.2Photocatalytic Activity of the catalyst

The superior photocatalytic activity of the Mo doped TiO_2 can be demonstrated by illumination experiments in visible light irradiation. Fig.3 represents the percentage degradation of Acid Orange 7 using all ratios of Mo doped catalyst within a time of 30 minutes under visible light irradiation. The superior photocatalytic activity of doped samples can be related to their absorption spectra presented in Fig. 2, because Mo doped TiO_2 showed stronger absorption in visible range compared to the pure TiO_2. Apart from band gap narrowing, one possible reason for this photocatalytic activity enhancement of Mo-TiO_2 is the good surface area with fully anatase phase. It can also be attributed to the efficiency of dopant to prevent charge carrier recombination. The highest visible light activity was shown by MoT2 prepared with 1wt% of Mo. Even though MoT3 showed large visible light absorption its visible light activity is very low. When the concentrations of dopant ions are above the optimum ratio, the dopant atoms become the recombination centres [4]. The existence of the optimum value can be associated with the amount of active sites on TiO_2. These active sites however will be easily blocked if the amount of dopants is above the optimum value.

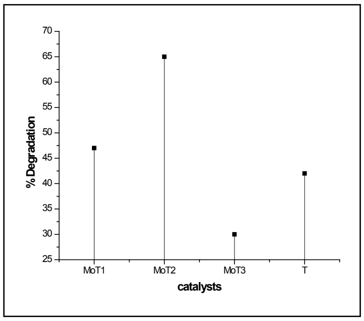

Fig.3 % Degradation of Acid orange 7 using different catalysts

Irradiation time 30 minutes; Amount of catalyst 1g/L; Dye concentration 10ml 10^{-4}M

This result clearly shows that doping increase the photocatalytic activity of TiO_2 in visible light and also shows the possibility of utilizing sunlight for photodegradation. It was also observed that no decolorization of the solution was achieved in the absence of light, indicating that the decolorization process is photo-induced. The blank experiments conducted in the absence of photocatalyst, did not result in any measurable degradation of Acid Orange7.

4 Conclusion

Visible-light-active Mo doped TiO_2 photocatalyst was synthesized by sol gel method. Mo doped TiO_2 exhibited stronger absorption in the visible light range with a red shift in the band gap transition. All TiO_2 catalysts showed entire anatase phase and MoT2 with optimum dopant content shows significantly high photocatalytic activity for the degradation of Acid Orange 7in aqueous solution under visible light irradiation.

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