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Photocatalytic Degradation of Methyl orange over Cobalt – Titanium Mixed Oxides

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ABSTRACT

The combined effect of Co and Ti oxides on the photodegradation of methyl orange dye were investigated and, the performance was compared with individual single metal oxides. Influence of preparation method on the formation of mixed oxide photocatalyst and their photoactivities was also studied. Mixed oxides of Co and titanium were prepared by different methods such as hydrothermal, sol-gel, and their mixed route. Crystallographic and physical states of Co and TiO_2 were examined by using XRD and FTIR analysis. Among the different synthetic methods engaged in the present study, hydrothermal preparation method was found to be the most effective in developing cobalt/titanium single metal oxide as well as mixed metal oxide photocatalysts

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INTRODUCTION

Among the different types of pollutants, dyes are unavoidable and, treatment of industrial dye effluents is very important for environmental safety. Treatment of these toxic dye effluents over TiO_2, the most common photocatalyst, is getting significance because of its interesting properties in addition to low cost, chemical stability and non-toxicity (Wang, Z., *et al*., 2002; Shchukin, D.G., D.V. Sviridov, 2006; Zhang, R., I. Ga, Q. Zhang, 2004; Richardon, S., *et al*., 1996). Due to its specific band gap, TiO_2 semiconductor under UV irradiation has been extensively studied in the heterogeneous photocatalytic process (Wang, S., S. Zhou, 2010). Metal doping and fabrication of mesoporous structure on TiO_2 is highly important in improving the photocatalytic activity of TiO_2[(Wu, J.C.S., C.H. Chen, 2004; Colon, G., *et al*., 2006; Colmenares, J.C., *et al*., 2006; Tayade, R.J., *et al*., 2006). In addition to metal ion doping, the formation of mixed oxides of TiO_2 with other semiconductor metal oxides also have significant role in developing photocatalysts.

Various methods are available for the preparation of metal oxides. Formation of homogenous structured nanomaterial gave attention to the wide application of sol - gel method in preparation of composite oxides (Li, Z., *et al*., 2005). Hydrothermal synthesis is applied for the preparation of nanocrystalline inorganic materials (Byrappa, K., M. Yoshimura, 2001). In hydrothermal method, material synthesis is done under high pressure and temperature conditions. As a result, dissolution and crystallization of specific materials occurs, so generating characteristic diversity in material properties at the nano-scale (Lorturn, P., *et al*., 2008).

Here, we report the synthesis of nanocrystallineanatase TiO_2 based materials by the sol gel, solvothermal and a mixed method from titanium isopropoxide as the precursor for TiO_2. Mixed oxides of Co and TiO_2 were prepared by the same methods, and studied the combined effect of oxides of Co as well as TiO_2 on photodegradation of pollutants. Methyl orange (MO) was selected as a model organic pollutant and its degradation was studied in the presence of prepared catalysts in acidic, neutral and basic solutions under UV illumination.

Experimental Procedure:

Sol gel method: To prepare Co- TiO_2 mixed oxide photocatalyst, Titanium (IV) isopropoxide (Sigma Aldrich) as TiO_2 precursor and cobalt nitrate hexahydrate (Hamburg chemical GmbH) as Co source were used.18.6 ml Titanium (IV) isopropoxide was hydrolyzed in 221.7 ml water containing 1.8 ml HNO_3 and stirred continuously at room temperature to form highly dispersed sol. To the stable sol, calculated amount of cobalt

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nitrate solution was added to get the required Co loading of 50%. The sol was aged for 48 hours, then concentrated at 60˚C and dried at 110˚C for 12 hours. Calcined at 500 ˚C for 5 hours.

Hydrothermal method: A mixture of 50 ml ethanol and 50 ml water containing required amount of cobalt nitrate were added to a solution of 9 ml Titanium isopropoxide in 41 ml ethanol and stirred vigorously for 4 h. Then it treated hydrothermally at 80˚C for 48 hours. Filtered the precipitate, washed and dried at 100˚C for 12 hours. Ground into fine powder and calcined for 5 hours at 500˚C.

Two-step method: The sol obtained by the above sol gel method was then hydrothermally treated under the same condition used for hydrothermal method.

TiO_2 without Co was also prepared by the above three methods for comparison. Details of the prepared system are given in Table1.

The photocatalytic activity of the prepared systems was evaluated by degrading MO, by using a Rayonet type Photoreactor with UV light having 16 tubes of 8W (Associate Technica, India). The MO concentration was analyzed using colorimeter (Microprocessor photo colorimeter model 1312) at a wavelength of 464 nm, whereas in acidic medium it was measured at 506 nm. Degradation of 5mg/L MO with 4g/L catalyst was performed for 6 h with different systems. Optimization studies were done by varying the catalyst weight, dye concentration, irradiation time to get best system.

Table 1: Letters C indicates Co, T stands for TiO_2, H implies solvothermal and S means sol gel

NAME OF SYSTEM	DESIGNATION
CTH	Co- TiO_2 by hydrothermal
CTS	Co- TiO_2 by sol gel
CTSH	Co- TiO_2 by sol gel and hydrothermal method
TH	TiO_2 by hydrothermal
TS	TiO_2 by sol gel
TSH	TiO_2 by sol gel and hydrothermal

RESULTS AND DISCUSSION

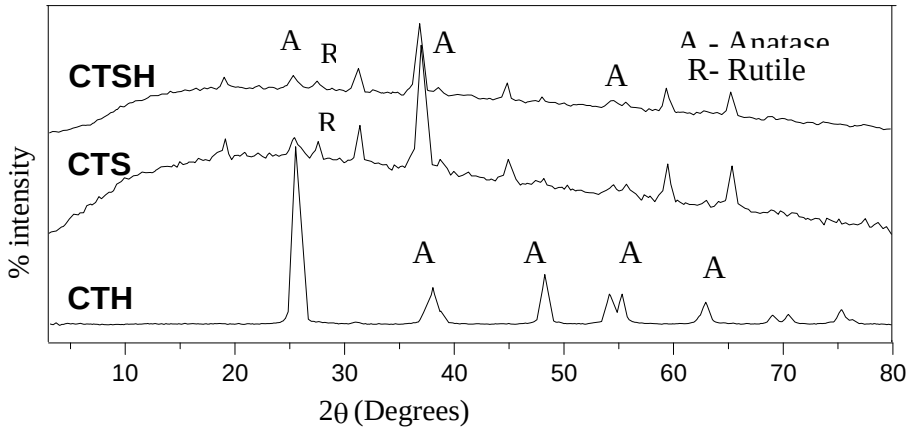

Fig.1: XRD patterns of prepared samples

XRD patterns of the samples were recorded for 2θ between 3 to 80˚ on a Bruker AXS D8 Advance diffractometer employing a scanning rate of 0.02˚/S with Cu Kα radiation (λ=1.5418). Fourier Transform-Infrared spectral analysis was done on a thermo scientific NICOLET 6700 apparatus in the region of 400-4000 cm^{-1}.

The phase characterization of different samples was investigated by XRD and is shown in Fig. 1. It is clear from the figure that CTH is mostly composed of anatase phase. No peak of rutile phase was observed in CTH. Whereas, a small peak of rutile phase was observed at 27.4° in CTS and CTSH systems. Moreover, it is worth noting that no peaks corresponding to cobalt oxides were observed in CTH sample which implies well dispersion of Co.

Photocatalytic Activity:

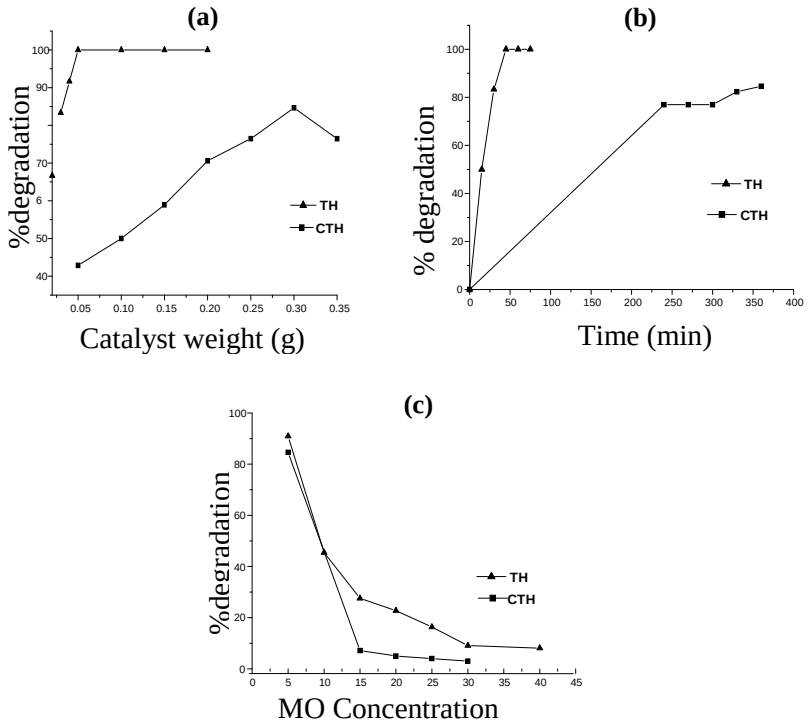

Fig. 2: (a)Effect of catalyst weight (b) Effect of time (c) Effect of concentration

Effect of catalyst concentration:

Photocatalytic efficiency increases with an increase in catalyst concentration and then decreases after a certain catalyst dosage. After reaching a maximum at 6g/L catalyst weight, there occurs a decreasing trend in the photocatalytic efficiency. Further increase in photocatalyst dosage after 6g/L may increase the opacity of solution, and thereby decreasing the penetration of light inside the solution and as a result, a consequent decrease in the photodegradation of MO was observed (Maruthamuthu, P., *et al*., 1989). Thus an optimum catalyst concentration has to be maintained (Herrmann, J.M., 1995) at 6g/L to ensure total absorption of photons for efficient photodegradation of MO over present CTH catalyst. But when we use TiO_2 prepared by hydrothermal method without any introduction of Co, 1g/L of catalyst was found to be enough to remove 100% MO within a short interval of 45 min. This shows that presence of Co decreases the activity of pure TiO_2.Fig. 2(a) shows the effect of catalyst weight on the photoactivities of CTH and TH.

Effect of Time:

Fig.2 (b) illustrates the influence of time on the degradation experiments under visible light irradiation. Degradation studies were conducted with 6g/L of CTH system and the absorbance measurements were done at various times and the percentage degradation was calculated. Increase in irradiation time increases the number of photons absorbed by photocatalyst, which further enhances the photocatalytic activity of semiconductor, resulting in high photodegradation rate. Degradation studies with the CTS and CTSH catalysts were very low compared to CTH. In the case of TH, TSH and TS with 1g/L catalyst dosage, degradation became 50% after 15 min and increased to 100% after 45 min of reaction time for TH.

Effect of initial MO concentration:

The influence of initial MO concentration on the photodegradation is shown in Fig.2(c). MO photodegradation decreases linearly with increase in the initial concentration of MO. While measuring the influence of initial concentration of dye on the photoactivity of catalysts, the other two parameters time (6h for CTH and 45min for TH) and catalyst concentration (6g/L for CTH and 1g/L for TH) were kept constant. As the catalyst dosage was maintained constant, the active sites available remained constant. Therefore with increase in MO molecules for the same number of active sites and time, there observed a decrease in the percent degradation rate.

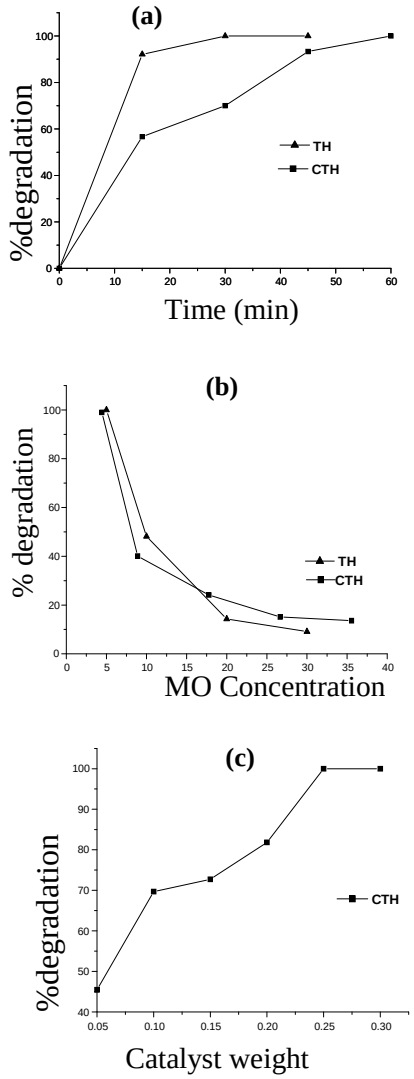

Fig. 3: Effect of pH (a) Time optimization(b)MO concentration(c)Catalyst weight optimization

Influence of pH Value on The Dye Degradation:

Fig. 3 shows the pH-dependent photocatalytic activities of CTH and TH under UV light irradiation. Due to the variation of surface charge properties of the photocatalyst under different pH values, absorption behavior of a dye on a catalyst surface changes. Adsorption of anionic dyes like MO was favored in acidic solution and hence the attack by positive holes or hydroxyl radicals upon photoexcitation increases (Hu *et al*., 2006). Here the single (TH, TS and TSH) and mixed oxide (CTH, CTS and CTSH) systems showed excellent activity in acidic pH whereas in basic pH, there occurred diminishing activity. At pH 3, the optimum time for Co containing systems reduced from 6 h to 1 h giving 100% conversion.

Effect of Preparation Methods:

The effects of preparation methods on photodegradation of MO under optimized reaction condition were plotted in Fig. 4. (a) and (b). Among three methods selected, solvothermal method is found to be the best in providing photocatalytic activity to both single and mixed oxides.

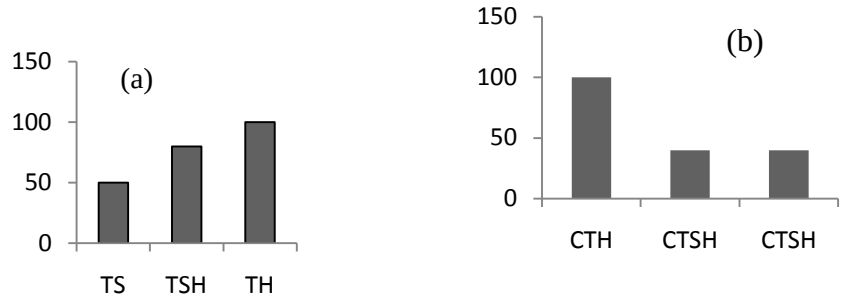

Fig. 4: Effect of preparation methods(a).single metal oxides (b) Mixed oxides

Conclusions:

A comparison of sol gel, solvothermal, and their mixed routes on the preparation of Co - TiO_2 mixed oxides and TiO_2 without Co were investigated in the photodegradation of MO. In the neutral solution, Co containing systems prepared by solvothermal method provided a maximum degradation for 6 h run, whereas the corresponding systems prepared by sol gel and mixed route was not much effective in MO photodegradation. The effect of pH on the degradation of MO showed higher percentage degradation at lower pH (pH3).Over single TiO_2 system prepared under hydrothermal conditions 100% dye degradation was achieved within 30 min. In the present study, hydrothermal method was found as an outstanding method preparation of TiO_2 based photocatalyst.

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