Photocatalytic Activity of Co:TiO$_2$ Nanocomposites and their Application in Photodegradation of Acetic Acid

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Abstract: Nanocomposites of Co:TiO$_2$ were prepared by wet chemical methods. The prepared samples were characterized by XRD, SEM, BET, FTIR and UV-Visible spectra. The XRD analysis confirmed the presence of rutile and anatase both phases were present. It is found that rutile phase was more dominant. Applying the Scherrer's calculations through which particle size was found 35 and 80 nm in case of Co:TiO$_2$ and pure TiO$_2$ respectively. SEM image of Co:TiO$_2$ and TiO$_2$ were observed and both found in nanodiamension. The photocatalytic degradation of acetic acid was done at different condition of concentration, amount of photocatalyst and type of catalyst. The effective photodegradation of acetic acid were found at low concentration and photodegradation increases with decrease the concentration of acetic acid. The prominent degradation of acetic acid was found in the presence of nanocomposites Co:TiO$_2$ as compared with TiO$_2$.

Introduction

The photocatalytic degradation (PCD) in the presence of UV-Visible and oxygen has attracted attention of researchers for remediation of hazardous pollutants in the water[1]. The advantages of PCD over conventional treatment techniques are degradation of a broad range of organic pollutants, lower cost, and mild operating conditions[2]. The TiO$_2$ catalyzed PCD of various groups of organic pollutants like alcohols, phenols, carbonyls and carboxylic compounds, aromatic, halocarbons etc. have been reported extensively[3-8].

The removal of several aliphatic carboxylic acids[9,10] as well as aromatic acids such as benzoic acid, polycarboxylic acids, salicylic acid, chlorobenzoic acids, *etc.,*[11-14] from water using TiO$_2$ catalyzed PCD has been reported. Besides this, the photocatalytic degradation of the higher aliphatic carboxylic acids such as branched C4 and C5 aliphatic acids using titanium dioxide has also been studied[15].

The present paper focus on Co:TiO$_2$ catalyzed PCD of Acetic acid and studying the influence of various parameters affecting PCD of acetic acids, *i.e*., Molecular structure on the kinetics and mechanistic pathway, the effect of initial concentration, pH, temperature, the amount of catalyst and type of catalyst[16].

Most of the researchers working on the photocatalytic degradation of organic compounds such as dyes, pesticides and aromatic compounds. The photocatalytic reactions for the degradation of trace acids, dyes and pesticides in water have been used by researchers in recent years. It is the advanced oxidation process[17] to degrade the water contaminants such as acids[18], dyes[19], pesticides[20] and non biodegradable materials[21], which exhibit chemical stability and resistance to biodegradation[22].

Most of the research is focused on the use of semiconductor materials as photocatalysts for the removal of organic and inorganic species from aqueous or gas phase[23]. Titanium dioxide (TiO_2) is the cheapest, corrosive resistant photocatalysts[24] and it have high oxidative power, stability and non-toxicity[25]. The photocatalytic reactions mostly occor under ambient conditions. Titanium dioxide (TiO_2) photocatalysed reaction, complete oxidation of the substrate into CO_2 in most cases and it is comparatively inexpensive and remains quite stable in contact with different substrate[26]. Semiconductorphotocatalytic oxidation is the best eco-friendly techniques for the removal of trace organic pollutants from wastewater.

Wolff *et al.*,[27] have examined the photocatalytic oxidation of acetic acid on TiO_2. It has been proposed that hydroxyl radicals ($^\bullet OH$) attack acetate ions mainly, at the methyl group.

$$CH_3COOH + {}^\bullet OH \rightarrow {}^\bullet CH_2COOH + H_2O \tag{1}$$
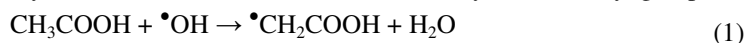
In the presence of oxygen, the radicals, thus formed react quickly with moleColar oxygen leading to the formation of $CHOCOOH$, $HOCH_2COOH$, $HOOCH_2OOCH_2COOH$, $HCHO$, and CO_2. Direct electrochemical oxidation of acetate results in the well-known Kolbe decarboxylation with the formation of a methyl radical.

Experimental

25 mL of diluted $TiCl_4$ was taken along with 1 mL of concentrated H_2SO_4 and diluted to 1 L using double distilled water. Liquor NH_3 was added drop wise to the solution so as to maintain the solution pH in the range of 7–8. The precipitate was filtered and washed free of chloride and ammonium ions. The precipitate is first oven dried at 100 ^{o}C for 12 h and grinded in a mortar. The powder obtained is then calcined at 500 ^{o}C for 4 h in a muffle furnace[28] to get TiO_2.

Synthesis of Co:TiO₂

In this study, $Co:TiO_2$ nanocomposites were prepared by the solution impregnation method. TiO_2 powder (4.5 g) was dispersed in 100 mL of the alcoholic solution of 0.1 M cobalt acetate. The dispersion was agitated continuously for 4 hour at 80 ^{o}C temperature. After the heating and agitation, the residue was removed through filtration and was sintered for 3 h in the presence of air at 400 ^{o}C by keeping it in a silica boat inside a muffle furnace. After sintering and slow anilling to room temperature, content was taken out from the furnace and was used as photocatalyst[29].

Photo-degradation studies

Photocatalysed oxidative degradation reactions of organic substrates is held lot of potential in pollution abatement as well as in synthetic Organic Chemistry. Although in the literature several photocatalyst have been cited for this purpose many of them suffer from one or more disadvantage, particularly with regard to either then being highly expensive and chemically unstable. TiO_2 is a well known semiconductor that has also been widely used as photocatalyst. In this study, to investigate the photo-degradation behavior of a prepared TiO_2 and $Co:TiO_2$ nanocomposites towards photo-degradation of acetic acid[30,31].

Result and Discussion

X-ray diffraction analysis

The Phase identification of samples was analyzed by the using x-ray diffractometer (Bruker AXS D8 Advance System, Germany). The obtained x-ray diffraction patterns of TiO_2 and $Co:TiO_2$ are shown in Figure 1. The observed XRD pattern was compared with the standard JCPDS database, suggested that, in synthesized TiO_2, major peaks at 2θ angles 25.5, 37.2,48.3 and 55.4 correspond to anatase phase, whereas major peaks at 2θ angles 26.9, 28.2, 42.6 and 54.2^0 indicate the presence of rutile phase. In case of $Co:TiO_2$ sample, the observed XRD pattern indicates not only a decrease in the peak intensity, compared to TiO_2, but even the absence of some originally observed TiO_2 peaks. This is, probably, due to the change in the crystallinity, grain fragmentation and partial amorphization, when the samples were doped by cobalt acetate[32].
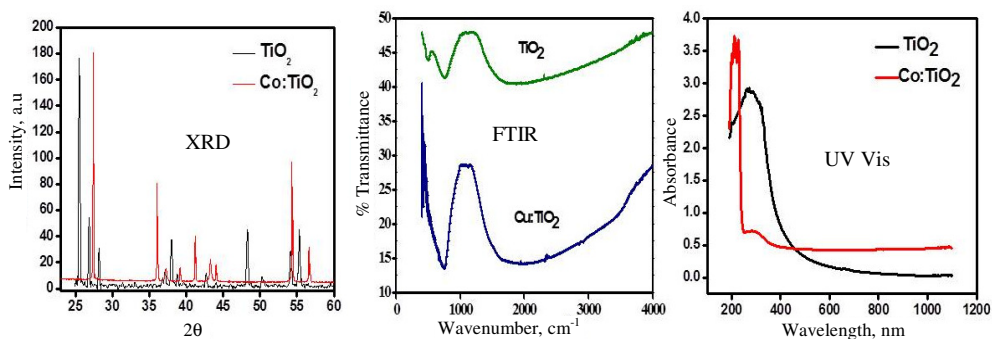
Figure 1. Observed XRD, FTIR and UV Vis spectra of (a) TiO_2 (b) $Co:TiO_2$

Determination of average size of particles/grains in samples

Utilizing the observed x-ray diffraction data of samples, Scherrer's calculations was attempted to know the average size of particles/grains in the samples. Although, Scherrer's calculations are only approximate in nature, but definitely provide a first-hand idea of the average size of the particles/ grains in the samples, which may be quite accurate, provided the size of particles/grains is below[32] 100 nm. The results of Scherrer's calculations are presented in Table 1. The results suggest the average size of the particles/grains in the samples lying in nm range.

Table 1. Average size of particles/grains in the samples of TiO_2 and $Co:TiO_2$

Sample	Particle size from Scherrer's calculation *(nm)
TiO_2	100
$Co:TiO_2$	35

FT-IR spectroscopy

FT-IR spectra of undopped and 10.0% Co doped TiO_2 samples (Figure 1) show peaks corresponding to stretching vibrations of the O-H and bending vibrations of the adsorbed water molecules around 3750 cm^{-1} and 2319 cm^{-1}, respectively. The broad, intense band below 497, 604 and 645 cm^{-1} is due to Ti-O-Ti vibrations. The shift to the higher wave numbers and the sharpening of the Ti-O-Ti band (Figure 1) may be due to decrease in size of the catalyst nanoparticles. In addition, the surface hydroxyl groups in TiO_2 increase with the

increase of co loading, which is confirmed by an increase in intensity of the corresponding peaks. The FT-IR spectra show strong band at 757 cm^{-1} corresponds to the vibration of Co-O bond and it is confirmed the penetration of cobalt in Titania[32].

UV-Vis spectroscopy

The absorption spectrum of TiO_2 consists of a single broad, intense absorption between 250 to 300 nm due to the charge-transfer from the valence band to the conduction band[33]. The undoped TiO_2 showed absorbance in the shorter wavelength region while $Co:TiO_2$ results showed a blue shift in the absorption onset value in the case of Co added Titania (Figure 1). The impregnation of Co ions into TiO_2 could shift its optical absorption edge from uv into UV-Visible light range[34]. Aqueous suspensions of the samples were used for the u absorption studies. The blue shift that is observed in the absorption spectra with the decrease in particle size has been reported earlier[35]. The wavelength of $Co:TiO_2$ has been decreased due to the formation of a cobalt oxygen bond.

SEM (Scanning electron microscopy)

The morphology of the samples was investigated by scanning electron microscopy and it resumes the most interesting outcomes. Figure 2(a) and (b) clearly show that both the prepared samples were obtained agglomerate in nanometric dimension. The doping of cobalt is indicating that the particle size reduces due the penetration of cobalt in the lattice of titanium dioxide.
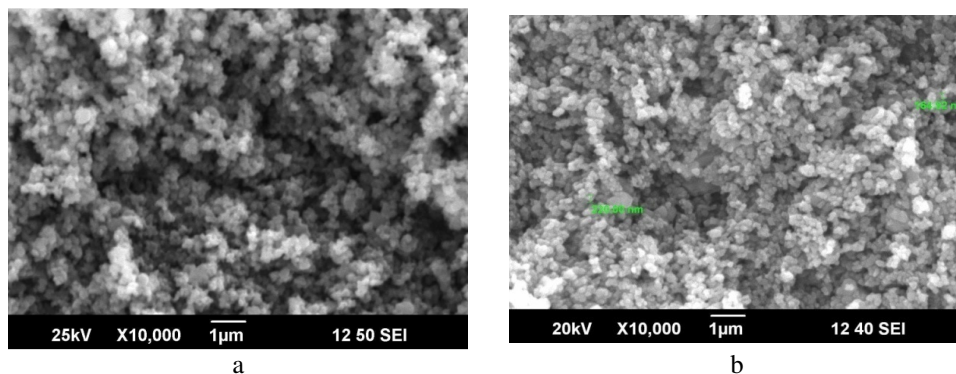
Figure 2. Observed SEM image of (a) TiO_2 (b) $Co:TiO_2$

Surface area analysis (B.E.T)

The specific surface area, pore volume and average pore size of the TiO_2 and Co:TiO2 as-prepared photocatalyst were characterized by using the N_2 adsorption technique BET. Table 2 summarizes their physical properties. The TiO_2 modified by cobalt are fragmentized to some extent during thermal treatment, leading to a marked increase of the BET surface areas and the average pore radius size and decreasing of the pore volume[36].

Table 2. Phase surface areas, pore volume, average particle sizes of TiO_2 and $Co:TiO_2$

| Sample	Surface area, m^2/g	Pore volume, cm^3/g	Pore radius, nm
TiO_2	6.4	0.018	11
$Co:TiO_2$	13.2	0.031	6

Photo-degradation of acetic acid

In this study, photo-catalytic degradation of acetic acid was investigated. The samples of TiO_2 and $Co:TiO_2$ were used as photocatalyst in the photo-degradation of acetic acid. 200 mg/10 mL of the photo-catalyst was dispersed in acetic acid solution of 10.6×10^{-3} M, 5.3×10^{-3} M, and 2.65×10^{-3} M concentration and the reaction mixture were illuminated with UV-Visible light, while keeping under agitation. The results presented in this Section comprise the residual concentrations (10.6×10^{-3}, 5.3×10^{-3} and 2.65×10^{-3} M) of acetic acid in the reaction mixture, measured by titrimetrically against NaOH at different time intervals. The measured values of residual concentration of acids in the reaction mixture at different times of illumination (or reaction time) have been shown in Figures 3-5. It is clear from the results shown that both TiO_2 and $Co:TiO_2$ are proving as an effective photo-catalyst for the degradation of acetic acid. However $Co:TiO_2$ seems to be a more effective photo-catalyst as compared to TiO_2, for the degradation of acetic acid[13].
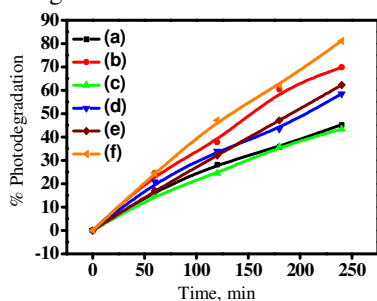
Figure 3. Photodegradation at different concentration (a) 10.6×10^{-3} M with TiO_2 (b) 10.6×10^{-3} M with $Co:TiO_2$ (c) 5.3×10^{-3} M with TiO_2 (d) 5.3×10^{-3} M with $Co:TiO_2$ (e) 2.65×10^{-3} M with TiO_2 (f) 2.65×10^{-3} M with $Co:TiO_2$
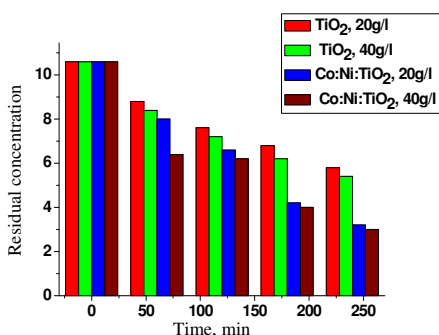
Figure 4. Effect of photocatalyst amount on photodegradation
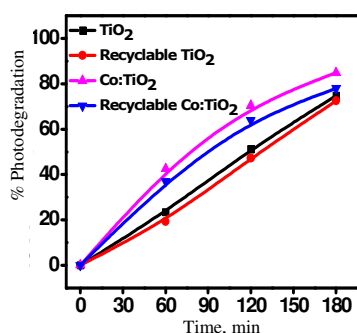
Figure 5. Effect of recyclable photocatalyst on photodegradation

Effect of concentration

Effect of acid concentration was investigated at a constant temperature and the amount of photocatalyst 200 mg/10 mL of acetic acid solution, the effect of varying amounts of the acid was studied on its rate of its degradation (10.6×10^{-3}, 5.3×10^{-3} and 2.65×10^{-3} M) as given in Figures 3. With increasing concentration of acetic acid the rate of degradation was found to decrease. This is because as the number of acetic acid moleColes increase, the amount of light (quantum of photons) penetrating the acetic acid solution to reach the catalyst surface is

reduced owing to the hindrance in the path of light. Thereby the formation of the reactive hydroxyl and superoxide radicals is also simultaneously reduced. Thus, there should be an optimum value maintained for the catalyst and the acetic acid concentration, wherein maximum efficiency of degradation can be achieved.

Effect of photocatalyst

It is clear from the results shown in Figures 4 & 5 that both TiO_2 and $Co:TiO_2$ are proving as an effective photo-catalyst for the degradation of acetic acid. However $Co:TiO_2$ seems to be more effective as photo-catalyst for the degradation of acetic acid. The prominent degradation of acetic acid was found in the presence of $Co:TiO_2$ in comparison to TiO_2. This is due to the large surface area of $Co:TiO_2$ as compared to TiO_2.

Effect of photocatalyst amount

It is clear from the results shown in Figure 4 & 5, that both TiO_2 and $Co:TiO_2$ are proving as an effective photo-catalyst for the degradation of acetic acid. But when the amount of photocatalyst increases the photodegradation of acid also increase. It is observed that Co-TiO_2 is the more effective photocatalyst than TiO_2.

Recyclability of photocatalyst

The photocatalyst and acetic acid mixture was agitated, illuminated with visible light and after desired time, the mixture was centrifuge to remove the photocatalyst. The obtained photocatalyst was washed three times with distilled water and kept in oven for 24 h at 60 ^oC and reused for the degradation of acetic acid. The photodegradation of acetic acid by the recyclized Photocatalyst are showing in Figure 5. The result shows that the recyclized photocatalyst efficiency is decreased probably due to the loss of some active sites and decrease of collection efficiency of photon.

Kinetic study

The pseudo-first-order rate constant (k, min^{-1}) for the photodegradation reaction of acetic acid was determined through the following relation where, k can be calculated from the plot of ln(Co/Ct) against time (t), Co and Ct denote the initial concentration and reaction concentration, respectively.

$$ln\ Co/Ct = k_1 t \qquad\qquad (2)$$

In addition, the linear feature of plots of ln(Co/Ct) *versus* time (Figure 6) indicates that this photocatalytic degradation reactions follow the pseudo-first-order rate law. The rate constant of the photocatalysis at 30 ^oC is 0.005260 to 0.01103 min^{-1}.
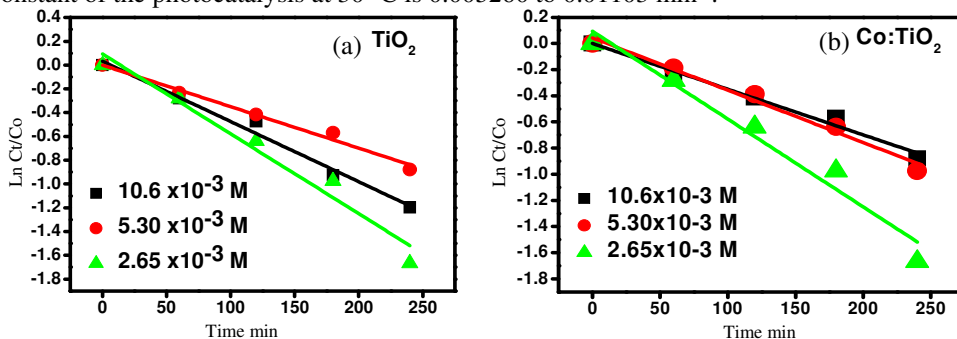
Figure 6. Change in concentration of acetic acid *vs.* time for (a) TiO_2 and (b) $Co:TiO_2$ at 40 ^oC temperature

Conclusion

The particle size was found 35 and 80 nm in case of cobalt titania and pure titania respectively. The morphology of the Titania and Cobalt Titania was investigated by scanning electron microscopy and it resumes that Titania and Cobalt Titania are obtained agglomerate in nanometric dimension. The doping of cobalt is indicating that the particle size reduces due the penetration of cobalt in the lattice of titanium dioxide. The prepared sample of titania and cobalt titania were subjected to photocatalytic degradation of acetic acid was done. The degradation of acetic acid found efficiently. The prominent degradation was found in case of $Co:TiO_2$ in comparison to TiO_2.

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