Photoinduced oxidation of benzhydrol over lanthana modified sol-gel titania

N. B. Shali · S. Sugunan

Abstract Lanthana modified sol-gel titania is prepared through particulate sol-gel route and the physico-chemical characterizations of the prepared systems were done using X-Ray diffration, EDX, BET surface area-pore volume measurements and TG-DTG analysis. Benzophenone was observed to be the sole product in the TiO_2 photocatalyzed oxidation of benzhydrol in oxygen purged acetonitrile. The influence of various parameters, like irradiation time, amount of catalyst, concentration of the catalyst and other factors on the photocatalytic oxidation has been investigated. The proposed mechanism envisages the involvement of a superoxide radical anion.

Keywords Lanthana modified titania · Sol-gel route · Photocatalytic oxidation · Benzhydrol

1 Introduction

Environmental pollution and destruction on a global scale, as well as the lack of sufficient clean and natural energy sources have drawn much attention and concern to the vital need for ecologically clean and chemical technology, materials and processes-one of the most urgent challenges facing chemical scientists. Since the discovery of the photosensitization effect of the TiO_2 electrode on the electrolysis of water into H_2 and O_2 by Honda and Fujishima in 1972 [1], photocatalysis by TiO_2 semiconductors has been widely studied with the aim of efficiently converting light energy into reliable and ef-

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fective chemical energy [2–14]. Organic synthesis is another active research field of TiO_2 photocatalysis [15–21]. The direct removal of oxygen from an organic substrate without affecting other parts of the molecule will be a good synthetic strategy. Photocatalytic oxidation of several organic molecules by optically excited semiconductor oxides is thermodynamically allowed in the presence of oxygen at room temperature. The oxidation of secondary alcohols on irradiated titania in general yields the corresponding ketones [22]. Vijaikumar et al. carried out successfully the oxidation of benzhydrol and reduction of benzil on irradiated titania surface [23].

It is well known that titania has three crystalline forms of anatase, rutile and brookite. Among these crystalline forms, rutile phase is the most thermodynamically stable, whereas anatase and brookite are metastable and transformed to rutile on heating. In many applications, anatase TiO_2 powders consisting of particles with a large surface area are used as the photocatalysts. These powders are advantageous to absorb compounds included in the reaction system at low concentrations. TiO_2 is a commonly used photocatalyst because of its stability in UV light and water. Its non-toxic nature, chemical stability, ready availability and its ability to be used repeatedly without substantial loss of catalytic activity have come to the utilization in the environmental business.

Irradiation of TiO_2 using low energy UV radiation ($\lambda > 350$ nm) promotes an electron from the valence band (VB) to the conduction band (CB), making it available for the transfer, while the positive equivalent, the hole (h^+) in the valence band is ready to accept an electron from the substrate. Since the position of the VB and CB of TiO_2 is $+2.2$ V and -1.20 V versus SCE, respectively in acetonitrile [24], a variety of redox reactions may be expected on the surface of an irradiated TiO_2. It may be noted that the oxidation potential of TiO_2 is considerably higher than those of

more conventional oxidizing agents such as chlorine (1.36 V versus SHE) and ozone (2.03 V versus SCE).

Sol-gel process is used for the preparation of the catalytic powder. The incorporation of the active metal in the sol during the gelation stage allows the metal to have a direct interaction with the support, therefore the material possess special properties. The gel precipitation process allows the production of mixed oxides of high homogeneity. By the sol-gel method, single phases can be achieved at low temperatures and nanocrystalline particles can be easily obtained [25]. Titania samples prepared and treated by different methods exhibit a great variety in photocatalytic efficiency eventhough they have the same crystal form [26, 27].

Here we report an attempt to prepare lanthana incorporated sol-gel titania system and its photocatalytic efficiency towards the oxidation of benzhydrol, a secondary alcohol, is studied in detail.

2 Experimental

2.1 Preparation of lanthana incorporated sol-gel titania catalyst

The catalytic systems reported in the present study have been prepared through sol-gel route from metatitanic acid precursor. Titanyl sulphate is obtained by dissolving the precursor in concentrated sulphuric acid. Ammonia is added to this until complete precipitation of titanium hydroxide occurs. The sulphate freed precipitate is suspended in hot water and 10% HNO_3 was added dropwise until a stable sol is obtained at a pH of around 1.5. Appropriate amount of lanthanum nitrate is added to the sol before gelation. The dried composite gel was calcined at 500°C to get the catalyst powder.

2.2 Catalyst characterization

XRD patterns of the samples were recorded for 2θ between 10 and 70° on a Rigaku D-max C X-ray diffractometer using Ni filtered Cu Kα radiation source ($\lambda = 1.5406$ Å). The BET surface area and pore volume measurements were carried out by nitrogen adsorption at 77 K using a Micromeritics Gemini-2360 surface area analyzer. The precalcined samples

were outgassed for 4 h at 400°C in nitrogen atmosphere prior to the sorption measurement. Thermogravimetric analysis between room temperature and 800°C were carried out in nitrogen atmosphere with a ramp of 20° min^{-1} using a TGAQ V2.34 thermal analyzer (TA instrument make). EDX spectra of the samples were recorded in an EDX-JEM-35 instrument (JEOL Co. link system AN-1000 Si-Li detector).

2.3 Catalytic reactions

In a typical experiment, benzhydrol (10 ml of 1 mM) in acetonitrile was taken in a 20 ml glass tube and 0.01 g of TiO_2 (0.1%) was added to it. After being purged with oxygen for 15 min, it was irradiated in an annular photoreactor with lamps arranged concentrically. The reaction mixture was collected at regular intervals of time, centrifuged to remove the catalytic powder and analyzed using a gas chromatograph by taking out a small aliquot out.

3 Results and discussion

3.1 Physico chemical characterisation

The elemental composition of the prepared catalyst systems is shown in Table 1. The EDX results clearly indicate that the expected catalyst profile can be successfully achieved by the present preparation method since the amount of the metal in the samples were very close to the expected value. XRD profiles of the prepared systems are shown in Fig. 1. After calcination at 500°C, the anatase appears as a crystalline phase manifested by its 101 peak ($2\theta = 25.5°$). The anatase phase is stable in both 2 and 6 wt% lanthana incorporated systems. There is no peak corresponding to lanthana indicating efficient dispersion of the incorporated metal. The average crystallite size was determined using the Scherrer equation. The intensity of the peaks decreases upon metal incorporation. The XRD spectrum corresponding to the TiLa10 is less intense, indicative of its reduction in crystallinity. The peak corresponding to the rutile phase is also slightly more pronounced at this high metal loading. Thermogravimetric analysis of the samples heated under a flow of nitrogen can be seen in Figure 2. The initial weight loss in the temperature range of 90–150°C is attributed to the removal of surface

Table 1 Surface parameters of the prepared systems

Catalyst	Elemental composition from EDX (%)		BET Surface area (m^2 g^{-1})	Pore volume ($\times 10^{-6}$ m^3 g^{-1})	Crystallite size ($\times 10^{-9}$) m
	TiO_2	La			
Ti	100	0	79	0.1	8.6
TiLa2	97	3	118	0.2	8.9
TiLa6	90	10	110	0.3	8.5
TiLa10	86	14	106	0.2	7.1

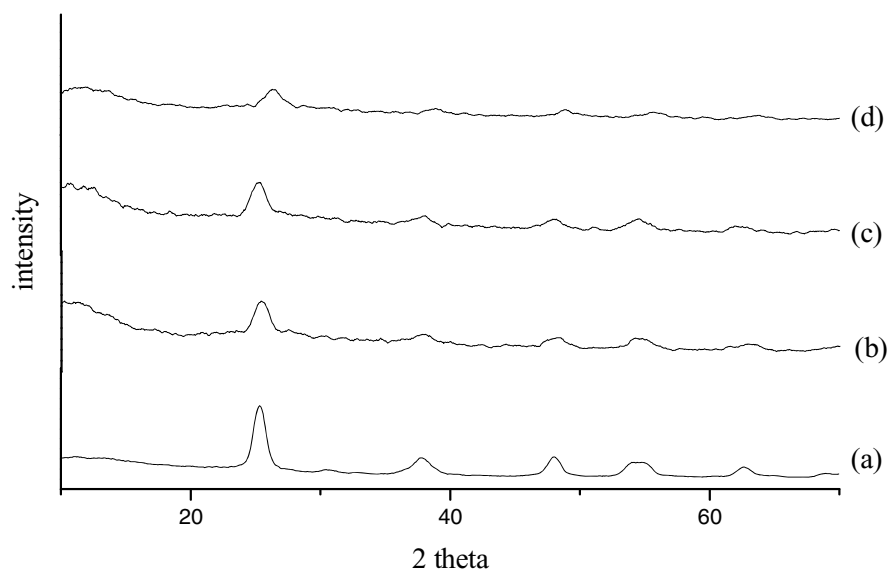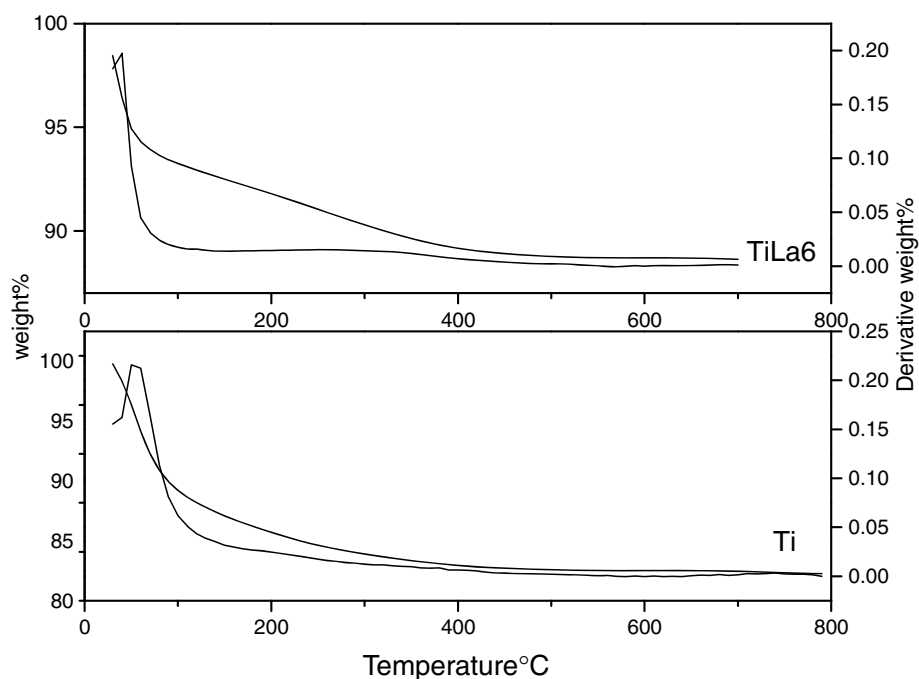**Fig. 1** XRD profiles of (a) Pure Titania, (b) TiLa2, (c) TiLa6, (d) TiLa10

**Fig. 2** TG/DTG profiles of Pure Ti and TiLa6

adsorbed water. Lanthana incorporated systems exhibited a high thermal stability.

3.2 Photocatalytic activity measurements

An appropriate reaction time is the main assurance for a perfect reaction. The oxidation of benzhydrol was carried out using acetonitrile as solvent, which is stable under photocatalytic conditions. When the photooxidation was investigated in methanol and ethanol, benzophenone was not formed and the solvents have been oxidized. When an oxygen purged solution of benzhydrol in acetonitrile was irradiated with

light for several minutes in the absence of a photocatalyst, benzophenone was not formed. The photooxidation reaction is carried out in the dark using an oxygen purged solution of the photocatalyst in acetonitrile and the product analysis revealed the absence of benzophenone. Similarly when the photocatalytic oxidation of benzhydrol was carried out in the presence of purged nitrogen (instead of purged oxygen), the substrate was not oxidized. A graphical representation of the above results is illustrated in Fig. 3. From these observations, it is clear that the photocatalyst, oxygen and light are essential for the sustained photocatalytic oxidation of benzhydrol to benzophenone. The presence of oxygen is also

Fig. 3 Influence of reaction time on the %conversion of benzhydrol (a) Oxygen purged solution of benzhydrol in acetonitrile (1 mM) with titania in the absence of light (b) Photolysis of an oxygen purged solution of benzhydrol in acetonitrile (1 mM) in the absence of titania catalyst (c) Photolysis of a nitrogen purged solution of benzhydrol in acetonitrile (1 mM) with light in the presence of titania catalyst (d) Irradiation of a solution of benzhydrol in acetonitrile (1 mM) with titania catalyst and oxygen
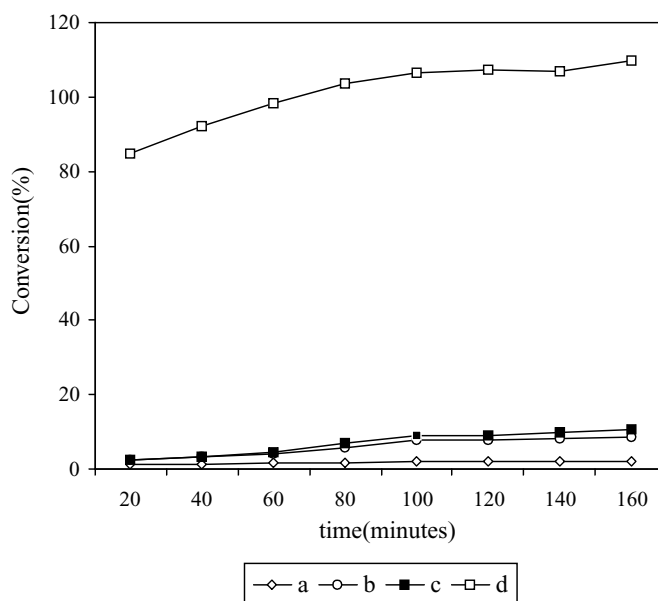
beneficial, as it prevents carrier recombination by trapping the photogenerated electrons [28] and forming a superoxide anion radical. When an oxygenated solution of benzhydrol in the presence of the photocatalyst was irradiated with light, oxidation of the reactant resulted in the formation of benzophenone. The amount of benzophenone increases upon increase of irradiation time. Irradiation is carried out for 160 min and it is seen that the yield of benzophenone has reached an almost steady value after 80 min.

The influence of the amount of catalyst is studied by varying the amount of the catalyst from 0.0025 g to 0.0125 g keeping all other factors constant. An increase in the amount of benzophenone was observed with increasing amount of the catalyst for the same volume of a fixed concentration of the solution. The variation of product formation with the amount of the catalyst is shown in Table 2, which indicates that saturation is attained with a catalyst weight of 0.01 g.

The effect of concentration of benzhydrol on the photocatalytic oxidation was studied by taking solutions of different initial concentrations of benzhydrol and keeping all other factors identical (Fig. 4). It can be seen from the figure that the concentration has a significant effect on the photoreaction. An optimum concentration of 0.8 mmol benzhydrol is chosen for all the experiments after that the benzohydrol falls off. Similarly light intensity also influences the reaction strongly. With an increase in light intensity, the number of photons striking the semiconductor per unit area of the cata-
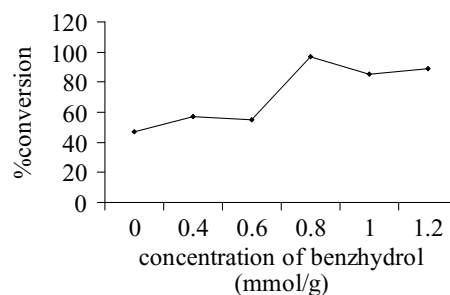

Fig. 4 Influence of concentration of benzhydrol (Catalyst weight– 0.01 g, Irradiation time–80 min)

lyst increases. This has resulted in an increase in the amount of too many increase formation of the product, as the yields of benzophenone with 2, 4, 6 and 8 lamps are 21.6, 57.1, 96.5 and 96.9%. The optimum light intensity was obtained when 6 lamps are used in the study.

Under the optimized conditions, the reaction is carried out over all the prepared systems and benzophenone is observed as the only product obtained in the reaction. The percentage conversion is almost the same in pure titania, TiLa2 and TiLa6 in which case anatase is the only crystalline phase. But in TiLa10 where rutile is the predominant phase, a reduction in photocatalytic activity is noticed (Table 3). These observations clearly indicate that the photooxidation process occurs predominantly over the anatase phase of titania.

Table 2 Variation in benzhydrol conversion with the amount of the catalyst (1 mM benzhydrol, reaction time-80 min, light intensity-6 lamps)

Amount of the catalyst(g)	0	.0025	0.0050	0.0075	0.0100	0.0125
%Conversion of benzhydrol	1.2	9.4	14.4	46.2	96.5	95.6

Table 3 Comparison of catalytic systems

Systems	% Conversion of benzhydrol	% Selectivity to benzophenone
Ti	93	100
TiLa2	91	100
TiLa6	94	100
TiLa10	59	100

3.3 Mechanism of photooxidation of benzhydrol

During the heterogeneous photooxidation of benzhydrol sensitized by the photocatalyst in acetonitrile, an inert solvent under oxidative conditions involves a single electron transfer from the adsorbed substrate to the photogenerated hole in the valence band, while the electron in the conduction band is captured by the oxygen forming a superoxide anion radical. The same reaction is carried out in the presence of benzophenone and gives the same conversion as in the absence of benzophenone. This result clearly indicates that, though benzophenone is a sensitizer for generation of singlet oxygen, it doesn't have a significant role in this reaction. The formation of hydrogen peroxide in several titania photocatalyzed reactions has been proposed. The oxidation of benzhydrol with 0.2 mM hydrogen peroxide has not oxidized benzhydrol under our experimental conditions. Therefore we believe that the hole and the superoxide radical anion are mainly responsible for the photooxidation of benzhydrol.

4 Conclusions

Lanthana incorporated sol-gel titania catalysts are promising catalysts for the photooxidation of benzhydrol. Lanthana imparts anatase phase stability to the system when incorporated in lower percentage. The photooxidation process takes place entirely on the anatase phase of titania and the presence of the rutile phase in TiLa10 shows a reduction in the photooxidation of benzhydrol. All the systems gave benzophenone as the sole product.

References

1. Honda K, Fujishima A (1972) Nature 238:37
2. Inoue T, Fujishima A, Honishi S, Honda K (1979) Nature 277: 637
3. Kawai T, Sakata T (1980) Chem Phys Lett 72:87
4. Kawai T, Sakata T (1980) Nature 286:31
5. Schrauzer GN, Bard AJ (1977) J Am Chem Soc 99:7189
6. Kraeutler B, Bard AJ (1978) J Am Chem Soc 100:2239
7. Heller A, Shalom AA, Bonner WA, Miller B (1982) J Am Chem Soc 104:1688
8. Fox MA (1983) Acc Chem Res 16:314
9. Fox MA, Dulay MT (1993) Chem Rev 93:341
10. Sato S, White JM (1980) J Am Chem Soc 102:7206
11. Courbon H, Herrmann JM, Pichat P (1981) J Catal 72:129
12. Anpo M, Yamashita H (1996) In: Anpo M (ed) Surface photochemistry. Wiley, London
13. Anpo M, Yamashita H (1997) In: Schiavello M (ed) Heterogeneous catalysis. Wiley, London
14. Anpo M (1997) In: Ertel G, Knozinger H, Weitkamp J (eds) Handbook of heterogeneous catalysis. Wiley-VCH, Weinheim (references therein)
15. Yanagida S, Ishimaru Y, Miyake Y, Shiragami T, Pac C, Hashimoto K, Sakata T (1989) J Phys Chem 93:2576
16. Ohtani B, Kawaguchi J, Kozawa M, Nishimoto S, Inui T (1995) J Chem Soc Faraday Trans 91:1103
17. Cermenati L, Richter C, Albini A (1998) Chem Commun 1998:805
18. Ohno T, Kigoshi T, Nakabeya K, Matsummura M (1998) Chem Lett 1998:877
19. Ohno T, Nakabeya K, Matsummura M (1998) J Catal 176:76
20. Jia J, Ohno T, Matsummura M, Masaki Y (1999) Chem Lett 1999: 963
21. Jia J, Ohno T, Matsummura M, Masaki Y (2000) Chem Lett 2000:908
22. Pichat P, Mozzanega MN, Courbon HJ (1987) J Chem Soc Faraday Trans 83:697
23. Vijaikumar S, Somasundaram N, Srinivasan C (2002) Appl Catal A Gen 223:129
24. Hoffmann MR, Martin ST, Choi W, Bahnemann DW (1995) Chem Rev 95:69
25. Jung GB, Huang TJ, Huang MH, Chang CL (2001) J Mat Sci 36:5839
26. Rivera AP, Tanaka K, Hisanaga T (1993) Appl Catal B Environmental 3:37
27. Sclafani A, Palmisano L, Schiavello M (1990) J Phys Chem 94: 829
28. Hoffmann MR, Martin ST, Choi W, Bahnemann DW (1995) Chem Rev 95:69