Synthesis, structure and photocatalytic activity of nano TiO$_2$ and nano Ti$_{1-x}$M$_x$O$_{2-\delta}$ (M = Cu, Fe, Pt, Pd, V, W, Ce, Zr)

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Abstract. We have synthesized 5–7 nm size, highly crystalline TiO$_2$ which absorbs radiation in the visible region of solar spectrum. The material shows higher photocatalytic activity both in UV and visible region of the solar radiation compared to commercial Degussa P25 TiO$_2$. Transition metal ion substitution for Ti^{4+} creates mid-gap states which act as recombination centers for electron–hole induced by photons thus reducing photocatalytic activity. However, Pt, Pd and Cu ion substituted TiO$_2$ are excellent CO oxidation and NO reduction catalysts at temperatures less than 100°C.

Keywords. Titania; nanomaterial; photocatalysis; three-way catalysis.

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1. Introduction

Water pollution due to the release of chemicals from industrial sectors has been a major concern in recent times. The major constituents of the pollutants are heavy metals, pesticides, dyes, aliphatic and aromatic detergents, degreasing agents, volatile organics, and chlorophenols. Many conventional methods have been proposed to treat these effluents; each method has its shortcomings. In the last decade photocatalytic degradation using semiconductors have been shown to be effective for the destruction of these pollutants. Although several semiconductors such as ZnO, Fe$_2$O$_3$ and CdS have been used, TiO$_2$ has been the photocatalyst of choice due to its photostability, non-toxicity, red-ox efficiency and availability. Since the photocatalytic activity of TiO$_2$ is influenced by the crystal size, crystal structure, crystallinity, and surface hydroxylation, the synthesis of phase pure nanocrystalline anatase TiO$_2$ is challenging [1–5]. In this paper, we present recent advances we have made on the new method of synthesis of nano TiO$_2$, its structure, and photocatalytic activity of dyes as well as gas phase catalytic activities.

2. Experimental

Nano TiO$_2$ is synthesized by the combustion of aqueous solution of titanyl nitrate TiO(NO$_3$)$_2$ and glycine, an organic fuel. Titanyl nitrate is prepared by dissolving titanyl hydroxide in 1 : 1 nitric acid. Stoichiometric amounts of titanyl nitrate and glycine are taken in a 300 cc borosilicate dish and introduced into a furnace at 300°C. The solution boils and burns with a mild flame giving nano TiO$_2$ [6]. Transition metals in the form of nitrates are taken and mixed with the solution for synthesizing metal-substituted titania. The material is used in the as-synthesized form for catalytic studies without any further processing.

3. Results and discussion

The combustion-synthesized materials have been extensively characterized by X-ray diffraction, Raman and TEM studies earlier [6]. Combustion-synthesized TiO$_2$ are indeed nanocrystalline materials in anatase phase. TiO$_2$ has also been made using other fuels such as oxalyl dihydrazide (ODH) and hexamethylene tetramine. The material made with glycine gave unique properties. The sizes are in the narrow range of 5 to 7 nm. BET measurements show that these are high surface area (240 m^2/g) materials. TiO$_2$ shows a red-shift in its optical absorption spectrum, and it has two optical absorption thresholds at 570 and 467 nm that correspond to the band-gap energy of 2.18 and 2.65 eV respectively. TiO$_2$ absorbs appreciably at wavelengths less than 600 nm. Contrary to this, Degussa P25 has a band-gap energy of 3.1 eV and sizes are in the range of 100–150 nm. The decrease in the band-gap energy is found to be due to carbide ion substitution for oxide ion in TiO$_2$ giving TiO$_{2-2x}$C$_x$ V$_O^{2-}$ where V$_O^{2-}$ represent oxide ion vacancies ($x = 0.04$) [6]. Yet another result that is distinct in this material is the large amount of surface hydroxyl species. TGA shows about 15% weight loss. Temperature programmed desorption confirms that weight loss is due to adsorbed water. FTIR and NMR studies support this observation [6]. Increase in the band gap (blue-shift) is not observed for combustion-synthesized 5–7 nm TiO$_2$ particles. Quantum size effect is seen, only when the sizes are below 4 nm.

Combustion-synthesized titania was used for the photocatalytic degradation of various dyes such as heteropolyaromatic dye (methylene blue), anthraquinonic dye (alizarin S) and azoic dyes (methyl red, congo red and orange G) under UV exposure. The effects of catalyst loading, initial concentrations of the dyes, pH on the rate of dye degradation were investigated. The photoactivity of the combustion-synthesized TiO$_2$ was higher than Degussa P25, the commercial TiO$_2$. The initial rate of degradation of methylene blue was 0.427 and 0.271 μmol l^{-1} s^{-1} with combustion-synthesized and Degussa P25 TiO$_2$ respectively [7–9]. The experimental data followed Langmuir–Hinshelwood (L–H) rate form and the kinetic parameters were evaluated.

Solar photocatalytic degradation of various dyes such as remazol bril blue R, methylene blue and orange G was carried out over combustion-synthesized titania and the activity was compared with that of commercial Degussa P25 under identical conditions. The initial degradation rates with combustion-synthesized nano TiO$_2$ was 20 times higher for RBBR, four times higher for MB and 1.6 times higher for

OG, compared to Degussa P25 TiO$_2$. Since the band gap of combustion-synthesized TiO$_2$ corresponds to maximum irradiance of the solar spectrum (450–480 nm), it can absorb relatively higher photon flux compared to Degussa P25. The photon flux ratio for combustion-synthesized TiO$_2$ is 2.32 times higher than Degussa P25 TiO$_2$. Thus superior activity of combustion-synthesized TiO$_2$ is due to the crystallinity, nanosize, lower band gap and large amount of surface hydroxyl groups [6]. The deactivation studies of the catalysts were also investigated. Degussa P25 undergoes deactivation due to the blocking of active sites by dye molecule as confirmed by the higher value of adsorption coefficient K_0 ($K_0 = 0.45 \times 10^4$ and 1.625×10^4 l/mol for combustion TiO$_2$ and Degussa P25, respectively). Though the activity progressively decreased with each cycle in the case of combustion-synthesized TiO$_2$, the decrease in activity was much lower than the decrease in activity for Degussa P25.

Photocatalytic degradation of various organics such as phenol, p-nitrophenol and salicylic acid over combustion-synthesized nano TiO$_2$ under UV and solar exposure has been carried out. Under identical conditions of UV exposure, the initial degradation rate of phenol with combustion-synthesized TiO$_2$ is two times higher than the initial degradation rate of phenol with Degussa P25, the commercial TiO$_2$. The intermediates such as catechol (CC) and hydroquinone (HQ) were not detected during the degradation of phenol with combustion-synthesized TiO$_2$, while both the intermediates were detected when phenol was degraded using Degussa P25. The rate of secondary photolysis of CC and HQ occur extremely faster than the rate at which they are formed from phenol which further implies that the primary hydroxylation step is the rate limiting step for the combustion-synthesized TiO$_2$ aided photodegradation of phenol [10]. Photocatalytic degradation of phenol as a function of time is shown in figure 1. The degradation rates of salicylic acid and p-nitrophenol were also investigated and the initial degradation rates with combustion-synthesized TiO$_2$ were 4.4 times higher for p-nitrophenol and 2.26 times higher for salicylic acid, compared to degradation rates with Degussa P25 TiO$_2$.
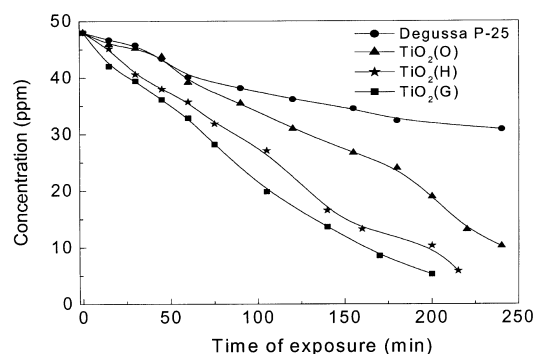

Figure 1. Degradation profiles of phenol with initial concentration of 0.5 mM (48 ppm) and catalyst loading of 1 kg/m^3 with combustion-synthesized TiO$_2$(G) (with glycine), TiO$_2$(H) (with hexamethylene tetramine), TiO$_2$(O) (with oxalyl dihydrazene) (ref. [6]) and Degussa P25 TiO$_2$ under solar exposure.
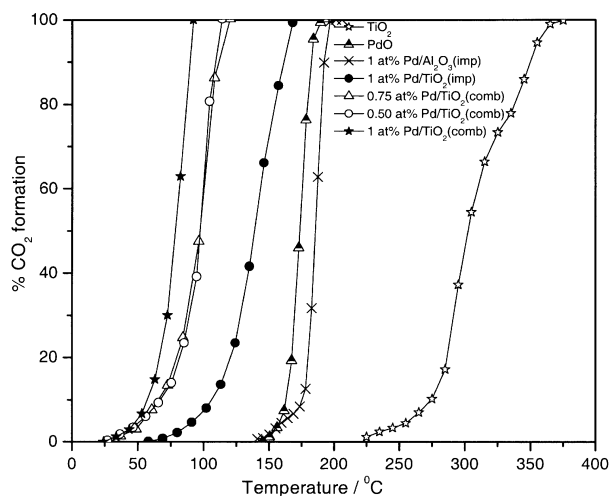
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Figure 2. CO conversion over TiO_2, PdO, Pd/TiO_2 catalysts. Notice high conversion of CO at low temperature over Pd ion substituted TiO_2.

In an attempt to understand the effect of transition metal ion substitution for Ti in TiO_2 on photocatalytic activity, W, V, Ce, Zr, Fe and Cu metal ions substituted nanocrystalline TiO_2 were prepared. The structural studies such as XRD, Raman, BET, EPR, and XPS indicate that the solid solution formation is limited to a narrow range of concentrations of the dopant ions. The photocatalytic degradation of *p*-nitrophenol under UV and solar exposure was investigated with metal ion doped TiO_2. The degradation rates were lower than the degradation rates with undoped TiO_2. The decrease in the degradation rates of dyes over metal ion substituted TiO_2 was correlated with the photoluminescence of metal-substituted TiO_2 [11].

We have made Pt and Pd ion substituted ceria nanomaterials by combustion method and they show high catalytic activity for CO oxidation and NO reduction as well as hydrocarbon oxidation. Pt-substituted ceria indeed shows high conversion of benzene to cyclohexane at atmospheric hydrogen pressure [12]. We have recently shown that Cu ion substituted ceria nanocrystallites are excellent three-way catalysts and also good oxide ion conductors [13]. Oxidation of carbon monoxide over $Ti_{1-x}M_xO_2$ (M = Pt, Pd, Cu) catalysts has been studied here. Complete oxidation of CO was observed below 100°C when catalyzed by 2 atom% Pd/TiO_2. Typical CO conversion over Pd ion substituted TiO_2 is shown in figure 2. Complete conversion occur below 100°C. Similarly, CO oxidation with NO occurs at temperatures lower than 100°C. The Pd-substituted titania catalysts are far superior to Pt- and Pd-substituted ceria catalysts.

Acknowledgements

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