The Preparation of TiO_2 Nanoparticle Photocatalysts by a Flame Method and Their Photocatalytic Reactivity for the Degradation of 2-Propanol

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Bimetal incorporated TiO_2 photocatalysts (FeZn–TiO_2) prepared by a flame method showed higher catalytic activity for the degradation of 2-propanol diluted with water as compared with mono-metal incorporated or unincorporated TiO_2. Using this flame method, the parameters such as a particle size, the crystallinity as well as the anatase and rutile phase ratio, which are important factors to determine the photocatalytic activity of TiO_2, could be controlled without calcination of the catalysts.

In recent years, the preparation of highly efficient semiconductor nanoparticles have attracted much attention due to their high potential for the oxidation of organic pollutants into CO_2 and water.[1–5] It is well known that the photocatalytic properties of such semiconductor nanoparticles depend on various factors such as the particle size, surface area, crystalline phases, and doping elements. Many methods such as sol–gel, impregnation, and pH swing[5] have been employed for the preparation of efficient TiO_2 nanoparticles. However, for all of these conventional methods, it has been necessary to calcine the catalysts at high temperatures (>500 °C) after preparation. In general, during calcination at high temperatures, the anatase phase of the catalysts gradually change to rutile with bigger particle sizes (>200 nm). However, an anatase phase is most desired for the photocatalytic degradation of organic compounds since anatase phase catalysts with very small particle sizes (<50 nm) exhibits high photocatalytic activity for degradation reactions.[6] However, it has also been found that, to an extent, a combination of both phases can enhance the rate of degradation of organic compounds into CO_2 and water.[5]

These findings have opened the way for new approaches in the preparation of catalysts with both anatase and rutile phases, significantly, without further physical treatment. We have successfully used a flame method in which the catalysts were prepared without the need for any prior physical treatment to obtain well-crystalline nanoparticles with anatase and rutile phases. Although the flame method is a common technique, there have not yet been any reports for its use in the preparation of TiO_2 photocatalysts. Moreover, using this method with an inorganic precursor is a useful way to control the particle size and crystalline phases for the large scale production of such applicable TiO_2. In particular, nanoparticles could be synthesized by rapid quenching from the gas state to solid particles. Hence, we have incorporated different transition metals such as Cr, Fe, V, and Zn, as well as bimetal (Fe + Zn) into the TiO_2 prepared by this method and investigated their reactivity for the photodegradation of 2-propanol diluted with water.

TiO_2 nanoparticles were synthesized by a flame method in which the precursor vapors, i.e., titanium(IV) isopropoxide (TTIP) and flammable gases, were burnt together in a combustion reactor at around 900 °C. The precursor was vaporized from the bottle immersed in an oil bath and transported to the burner nozzle with nitrogen as a carrier gas. The amount of the precursor was controlled by the temperature of the oil bath and flow rate of the nitrogen gas. The flow rates of the O_2 (oxidizer) and methane (fuel) could be separately varied. In order to prepare the TiO_2 nanoparticles incorporated with transition metals such as Cr, Fe, V, and Zn (1 at. wt %), we added the precursors of these elements to TTIP in a solution state and vaporized the solution by the flame method.

The diffuse reflectance absorption spectra of the photocatalysts were recorded with a Shimadzu UV-2200A spectrophotometer at 295 K. X-ray diffraction patterns of the photocatalysts were obtained with a Rigaku RDA-γA X-ray diffractometer using Cu Kα radiation with a Nickel filter. The XPS spectra were measured at 295 K with a V. G. Scientific ESCASCOPE photoelectron spectrometer using Mg Kα radiation. The morphology of the TiO_2 were recorded by field emission scanning electron microscopy (FESEM, Philips XL-30 model) and transmission electron microscopy (Philips CM-30). The photocatalyst (50 mg) was suspended in a quartz cell with an aqueous solution of 2-propanol (2.6×10^{-3} mol dm^{-3}, 25 mL). Prior to UV irradiation, the suspension was stirred for 30 min under dark conditions. The sample was then irradiated at 295 K using UV light ($\lambda > 250$ nm) from a 100-W high-pressure Hg lamp with continuous stirring under oxygen atmosphere. The products were analyzed by a gas chromatography.

Figure 1 shows the XRD patterns of the photocatalysts prepared by the flame method in which the catalysts have a good crystalline, small particle sizes and possess both anatase and ru-

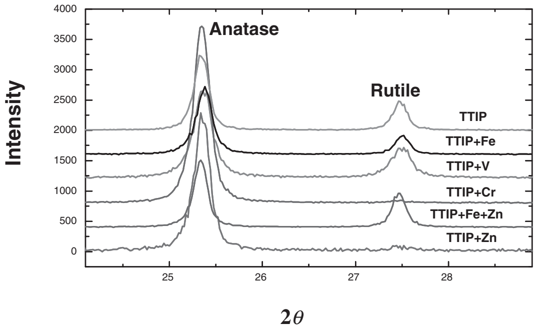

Figure 1. XRD patterns of unmodified (TTIP) and metal incorporated TiO_2 photocatalysts.

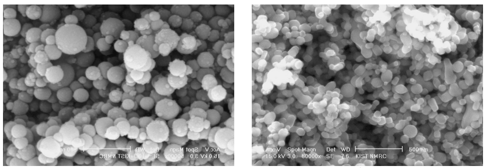
(a) (b)

Figure 2. SEM images of (a) Fe–TiO_2 and (b) FeZn–TiO_2 bimetal incorporated TiO_2 photocatalysts.

tile phases except Cr–TiO_2, without the need for further calcinations at high temperatures. This is a great advantage when compared with conventional or commercially available techniques. However, the photocatalysts incorporated with transition metals did not show any shift in their absorption bands towards higher wavelength regions (DRS figure not presented here).[1] Hence, the incorporated metals may not occupy the band gap position in the TiO_2 particles nor change in their electronic property but were only well dispersed on the TiO_2 particles. XPS measurements of the catalysts did not show any evidence of the presence of the incorporated metal ions on the TiO_2 surface, indicating that they are highly dispersed within the bulk of TiO_2 and not on the top surface. SEM investigations were carried out and two representative images are shown in Figure 2. These SEM images show that the catalysts prepared by the flame method are well crystalline nanoparticles. It is interesting to note that the bimetal incorporated (FeZn–TiO_2) catalysts showed small and well crystalline particles without any further treatment when compared with the mono-metal incorporated or unmodified TiO_2. The second metal may work to improve the crystallinity of the particles along with the dispersion state of the other metal.[7] In order to observe the morphology of the particles, TEM pictures were taken (Figure not shown here) and fine, small particles could be observed. The FeZn–TiO_2 catalysts were shown to be uniform, nanoparticles as compared with the other catalysts, confirming the SEM analysis. The TEM images did not show any incorporated metal clusters on the TiO_2 particles, indicating the homogeneous dispersion of the incorporated metals inside the TiO_2 particles and not on the surface, showing a good correspondence to the XPS spectra results.

The photocatalytic activity of the catalysts was compared by the reaction rates for the complete oxidation of 2-propanol into CO_2 and water under UV light irradiation. Table 1 shows the catalytic activity for the degradation of 2-propanol and characterization of the catalysts. It can clearly be seen that there is a little enhancement in the degradation of 2-propanol with mono-metal incorporated TiO_2 catalysts as compared with unmodified TiO_2, except for the case of V–TiO_2, though we did not know the reason at present. The FeZn–TiO_2 catalyst showed the highest photocatalytic activity for the complete oxidation of 2-propanol, even higher than the standard P-25 TiO_2. This oxidation of 2-propanol into CO_2 and H_2O was much faster than P-25. An increase in the activity by a factor of almost 2 times was observed with the FeZn–TiO_2 than with the unmodified TiO_2. This was due to the formation of small nanoparticles along with a 60:40 anatase to rutile phase ratio.

The anatase/rutile phase ratio is a major factor in the photocatalytic degradation reaction in addition to the particle size and crystallinity.[5,8] The FeZn–TiO_2 possessing an anatase/rutile ratio (60/40) is comparable to P-25 (70/30) which is known as one of the most active photocatalysts. Of the mixed phase TiO_2 with small particle sizes, the morphology of the nanoclusters containing a typically small rutile crystallites interwoven with anatase crystallites has been reported.[6] Such a morphology may allow rapid electron transfer from the rutile to anatase, enabling the efficient photocatalytic activity of the FeZn–TiO_2 catalysts. In addition to that, the presence of the small amounts of the transition metals play an important role in enhancement of transfer of photo-formed electrons from rutile to anatase moiety through the energy barrier of about 0.2 eV, which in turn, suppress the charge recombination of the photo-formed electrons and holes. Hence the charge recombination is circumvented at the maximum extent in the FeZn–TiO_2 catalysts than the unincorporated TiO_2 catalysts, even though unincorporated TiO_2 possessed same particle and surface area of FeZn–TiO_2 (Table 1). It has also been reported that even when catalysts possess mechanically mixed phases of anatase and rutile with bigger particle sizes, they do not exhibit high photocatalytic activity. This may be one reason why the mono-metal incorporated catalysts were found to be less reactive than the FeZn–TiO_2 (Table 1). It could, thus, be concluded that the particle size, crystallinity and phase ratio of the catalysts could all be successfully controlled to develop an efficient TiO_2 catalyst using the flame method with no other physical treatment.

Table 1. Characterization and photocatalytic property of the catalysts prepared by the flame method

Catalyst Name	Anatase :Rutile	Surface area /m^2/g	Particle size /nm	2-Propanol degradation[a] /%
TTIP	75:25	20	39	35
Fe–TTIP	79:21	13	58	40
Zn–TTIP	97:03	16	48	42
Cr–TTIP	100:0	17	46	45
V–TTIP	74:26	17	45	25
FeZn–TTIP	60:40	19	41	75
P-25	70:30	49	22	65

[a] Reaction time: 6 h.

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