

Preparation of TiO₂ Photocatalysts by Multi-gelation and Their Photocatalytic Reactivity for the Degradation of 2-Propanol

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TiO₂ photocatalysts, prepared by a multi-gelation method, showed higher photocatalytic activity for the degradation of 2-propanol diluted in water. This multi-gelation method showed a good performance in controlling the parameters viz. particle size, surface area, crystallinity as well as anatase and rutile phase composition, which are responsible for the higher activity of these photocatalysts.

A variety of semiconductor photocatalysts have been developed in recent years to improve the selectivity and efficiency for the photocatalytic degradation of organic pollutants.^{1–7} Among the various photocatalysts, TiO₂ has attracted a great deal of attention because of its high photocatalytic activity, thermal stability, and non-corrosive properties. It is well known that TiO₂ has three modification phases: anatase, rutile, and brookite, in which anatase TiO₂ is more active than the other two forms for the degradation of organic compounds.⁸ It has been widely reported that the photocatalytic activity of TiO₂ differs depending on the preparation and treatment conditions. In our recent studies, we have prepared TiO₂ photocatalysts by a multi-gelation method^{9,10} in which variations in the pH values are applied. Photocatalysts prepared by this method have a well-defined crystalline structure, uniform particle size, high surface area and more anatase phase in comparison with other commercially available catalysts. Since TiCl₄ and ammonium solutions are added to the vessel alternately and hydrous titanium oxide particles are formed periodically with the dissolution of the smaller particles, the multi-gelation method showed high performance in controlling the particle size, surface area and crystallinity of the particles.

The TiCl₄ solution was prepared by mixing equal weight of TiCl₄ (obtained from Wako chemicals, Japan) with crushed ice made from distilled water. The TiO₂ catalysts used were prepared by continuous heating and stirring of the TiCl₄ solution (500 mL) with an aqueous ammonia solution (14 wt %, 710 mL) under different pH swings at 353 K. A white precipitate of TiO₂ was formed, filtered and dried at 393 K for 15 h. The dried TiO₂ was calcined at various temperatures with an electric furnace under a flow of air. The UV-vis absorption spectra and X-ray diffraction (XRD) patterns of the catalysts were then recorded and analyzed. The N₂ BET surface area of the TiO₂ catalysts was also determined. The photocatalyst (50 mg) was transferred to 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 1 h 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 in the system. The products were analyzed

by a gas chromatograph.

The oxidative degradation of 2-propanol proceeded as a photocatalytic reaction on TiO₂ prepared by the multi-gelation method and produced acetone as the intermediate product as well as CO₂ and water as the final products under UV light irradiation. The catalysts prepared at 673 K (Cat-1 and Cat-2) showed less photocatalytic activity during the reaction with 2-propanol due to its amorphous nature (Figure 1). However, the catalysts prepared at 773 K (Cat-3 and Cat-4) were more active due to the formation of an anatase phase with a well-crystalline structure. Since the anatase phase exhibits lower rates of recombination of the photo-formed electrons and holes due to its higher rate of hole trapping¹¹ and a higher surface adsorptive capacity,¹² it is generally considered to be a photocatalytically active phase of TiO₂ for the degradation of organic compounds.⁸ However, the catalysts prepared at 823 K (Cat-5 and Cat-6) were shown to be more highly active (Figure 1) not only for their well-crystalline structure but also due to the varied composition ratio of anatase and rutile as with P-25 (Degussa) (Table 1). Although the anatase phase is considered to be more active, a combination of rutile and anatase is favourable in enhancing the rate of the degradation of organic pollutants.^{11,13}

It is interesting to note that the pH swing has a strong influence on the degradation of 2-propanol, which is observed with Cat-6 prepared after 7 times pH values swing (Figure 1). This is due to the dissolution of smaller particles by the alternate addition of TiCl₄ solution as an acidic reagent and ammonium hydroxide as a basic reagent. Similarly, the oxidation of 2-propanol was carried out with catalysts prepared at 873 K calcination tem-

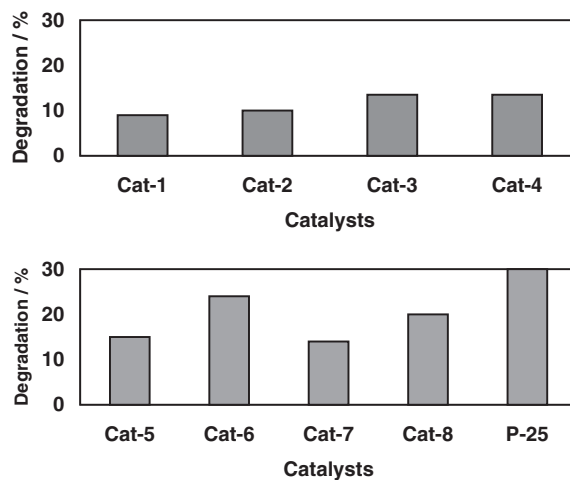


Figure 1. Oxidative degradation of 2-propanol with the different photocatalysts after 1 hr irradiation.

Table 1. Characterization of the TiO₂ photocatalysts prepared by the multi-gelation method

Catalyst Name	Cal. temp. /K	Number of pH swings	Surface area /m ² /g	Particle size /nm	Anatase : Rutile
Cat-1	673	3	106	09.8	-
Cat-2	673	7	107	17.5	-
Cat-3	773	3	59	11.7	87:13
Cat-4	773	7	73	18.5	92:08
Cat-5	823	3	38	12.8	62:38
Cat-6	823	7	59	19.0	80:20
Cat-7	873	3	16	20.8	25:75
Cat-8	873	7	29	23.9	50:50

Cal. temp.: calcination temperature

perature (Cat-7 and Cat-8), however, less photocatalytic activity was seen (Figure 1). This is due to the presence of a more rutile phase than anatase which is unfavorable for photocatalytic degradation reactions and leads to a decrease in the surface area.

It is clearly seen from the Table 1 that there is a marked difference in the ratio of the formation of anatase and rutile phases. The anatase phase ratio of Cat-6 (7 times pH swings) was found to be higher than Cat-5 (3 times pH swings) though the calcination temperature is the same for both (823 K). Similarly, a remarkable difference in the ratio of the two phases was observed for Cat-7 (3 times pH swings) and Cat-8 (7 times pH swings) prepared at 873 K. These results also illustrate that the catalyst prepared at higher pH swing times is able to prevent the phase transition from anatase to rutile. Increase in the pH swing times increases the photocatalytic activity irrespective of the calcination temperatures. The photocatalytic degradation of 2-propanol over Cat-6 and Cat-8 are significantly higher than for Cat-5 and Cat-7 (Figure 1). The higher photocatalytic activity of Cat-6 and Cat-8 is ascribed to the existence of a larger anatase phase than rutile. Hence, it could be confirmed that the pH swing is able to control the phase transition, particularly from anatase to rutile, which in turn favors the higher photocatalytic activity, a great advantage with the multi-gelation method. In addition, this method showed a good performance in controlling not only the phase transition but also the surface area and particle size.

It is clear from these results that the control of the pH swing plays an important role in the phase transition leading to higher photocatalytic activity.

From our experimental observations, it was confirmed that TiO₂ catalysts prepared by this unique multi-gelation method, i.e., adopting variations in the pH swing, significantly showed higher photocatalytic activity for the degradation of 2-propanol. Further research is underway to improve the nature and photocatalytic properties of the prepared TiO₂ photocatalysts.

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