

# Preparation of unique TiO<sub>2</sub> nano-particle photocatalysts by a multi-gelation method for control of the physicochemical parameters and reactivity

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A novel multi-gelation method to prepare TiO<sub>2</sub> nano-particle photocatalysts showed good performance in controlling the important parameters determining the photocatalytic reactivity, i.e., the particle size, surface area, crystallinity, pore-volume, pore-diameter as well as the anatase and rutile phase composition of the catalysts. In particular, this method at higher pH swing times could prevent the phase transition from anatase to rutile, leading to higher photocatalytic activity. By adopting variations in the pH swing, the TiO<sub>2</sub> nano-particle photocatalysts showed significantly higher photocatalytic reactivity for the complete oxidation of 2-propanol diluted with water into CO<sub>2</sub> and H<sub>2</sub>O. It can be considered a viable alternative method for the preparation of high performance TiO<sub>2</sub> nano-particle photocatalysts for widespread commercial applications

**KEY WORDS:** TiO<sub>2</sub> photocatalysts; multi-gelation method; photocatalytic degradation of 2-propanol.

## 1. Introduction

Over the last two decades, a variety of semiconductor photocatalysts have been developed to improve the efficiency and selectivity for the photocatalytic degradation of toxic organic pollutants [1–11]. Among the various photocatalysts, TiO<sub>2</sub> has attracted a great deal of attention due to its high photocatalytic activity, thermal stability and non-corrosive properties, in addition to its non-toxic and environmentally harmonious nature. It is well known that TiO<sub>2</sub> has three modification phases: anatase, rutile and brookite. Of these, the anatase TiO<sub>2</sub> is more active than the other two forms for the degradation of organic compounds [12] since anatase crystalline catalysts are constructed of very small-sized particles (< 50 nm) with high concentrations of surface OH groups, exhibiting high photocatalytic activity for degradation reactions [13].

Furthermore, it has been found that the interfaces between anatase and rutile can enhance the rate of the degradation of organic compounds into CO<sub>2</sub> and water, being believed that such interfaces play an important role as a major factor in the high photocatalytic activity of the standard P-25 TiO<sub>2</sub> (anatase/rutile = 70/30). However, the details are not clear yet since the photocatalytic activity of TiO<sub>2</sub> easily differs depending on the preparation and treatment conditions. Many researchers have studied the retardation of phase transformation from anatase to rutile by doping TiO<sub>2</sub> with metal ions or

supported with alumina, silica, zirconia, alumina–silica [14–19].

Recently, we have studied the preparation of TiO<sub>2</sub> nano-particle photocatalysts by a multi-gelation method and found that the method is able to prevent phase transformation from anatase to rutile even at high calcination temperatures when we applied variations with pH values during preparation. In the present work, we will report the details of this unique multi-gelation method to prepare the highly active TiO<sub>2</sub> nano-particle photocatalysts. Special attention has been focused on the unique nature of the multi-gelation method to lead a high performance in controlling the particle size, surface area, pore-volume, pore-diameter, crystallinity of the particles as well as the retardation of phase transformation with this multi-gelation method.

## 2. Experimental

### 2.1. Catalysts preparation

The principles behind the multi-gelation method of synthesizing the TiO<sub>2</sub> particles are illustrated in figure 1. The TiCl<sub>4</sub> solution was prepared by mixing equal weights of TiCl<sub>4</sub> (obtained from Wako chemicals, Japan) with crushed ice made from distilled water. The TiO<sub>2</sub> photocatalysts were prepared by the alternate addition of the TiCl<sub>4</sub> solution (20 mL) and aqueous ammonia solution (30 mL) into hot water (500 mL), already heated and maintained at 80°C under vigorous stirring. A white precipitate of hydrous TiO<sub>2</sub> particles was formed. This entire process was referred to as “one

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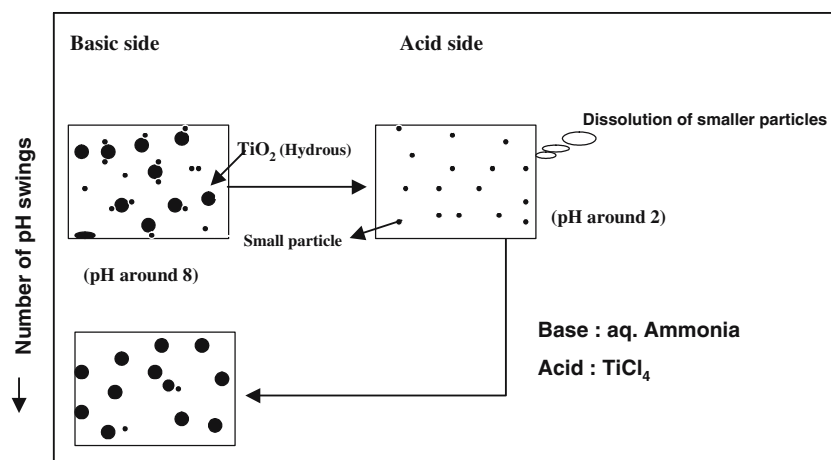


Figure 1. Outline of the multi-gelation method.

pH swing”. After a 5 min interval, the alternate addition of the same quantity of both TiCl<sub>4</sub> (20 mL) and aqueous ammonia (30 mL) were again added to the same hydrous TiO<sub>2</sub> particles system. This was referred to as “two pH swings”. In this way, photocatalysts with different pH swing numbers were prepared under the same experimental conditions. Finally, a white precipitate of the hydrous TiO<sub>2</sub> was filtered and dried at 120°C for 15 h. The dried TiO<sub>2</sub> was then calcined at various temperatures (400–600°C) with an electric furnace under a flow of air and then ground to fine powders using a pestle and mortar.

## 2.2. Catalyst characterization

The diffuse reflectance absorption spectra of the photocatalysts were recorded with a Shimadzu UV-2200A spectrophotometer at 24°C. X-ray diffraction patterns of the photocatalysts were obtained with a Rigaku RDA-? A X-ray diffractometer using Cu K $\alpha$  radiation with a Nickel filter. The morphology and size distribution of the TiO<sub>2</sub> were recorded by field emission scanning electron microscopy (FESEM, Philips XL –30 model). Before analyses, the samples were placed onto the surface of the carbon membrane and dried under ambient conditions. The photoluminescence spectra were measured at –196°C using a Shimadzu RF-5000 spectrophotofluorometer. The N<sub>2</sub> BET surface area of the TiO<sub>2</sub> catalysts was also determined.

## 2.3. Photocatalytic activity measurements

The photocatalytic activity was compared by the reaction rates for the oxidative degradation of 2-propanol, in which 2-propanol was seen to be completely oxidized into CO<sub>2</sub> and water on the TiO<sub>2</sub> photocatalysts under UV light irradiation in the presence of water and oxygen. The photocatalyst (50 mg) was suspended in a quartz cell with an aqueous solution of 2-propanol ( $2.6 \times 10^{-3}$  mol dm<sup>-3</sup>, 25 mL). Prior to UV light irradi-

ation, the suspension was stirred for 30 min under oxygen atmosphere in dark conditions. The sample was then irradiated at 24°C using UV light ( $\lambda > 250$  nm) from a 100 W high-pressure Hg lamp with continuous stirring under oxygen atmosphere in the system. At periodic intervals, 2 mL aliquots were taken from the system, centrifuged, and then filtered through a Millipore filter to remove the TiO<sub>2</sub> particles. The products were then analyzed by a gas chromatography.

## 3. Results and discussion

### 3.1. Characterization studies of the photocatalysts

The XRD patterns of the catalysts prepared by different numbers of pH swings and calcined at 550 and 600°C are shown in figures 2 and 3. Table 1 summarizes the physicochemical characterizations of the photocatalysts prepared by variations in the pH swing and calcined at 400, 550 and 600°C. All of the catalysts exhibited XRD patterns assigned to the well-crystalline anatase and rutile phases. It was clearly seen that the anatase and rutile ratio changed by an increase in the number of pH swings. For example, in the case of the catalysts calcined at 550°C, the anatase/rutile phase ratio was found to be 14/86 for 1 time pH swing (figure 4), whereas, the anatase/rutile ratio was 53/47, 70/30 and 94/06 for the catalysts prepared by 15, 20 and 30 times pH swings, respectively. An increase in the number of pH swings was seen to steadily increase the percentage of the anatase phase until finally reaching almost 100% at 30 times pH swings, as shown in figure 4. The number of swings enhanced the crystallization of the anatase phase and simultaneously reduced the rutile phase. One of the advantages of the multi-gelation method is that a higher proportion of the anatase phase can be established at the same calcination temperature using higher pH swings, since anatase is the most desired phase for the photocatalytic degradation of organic pollutants.

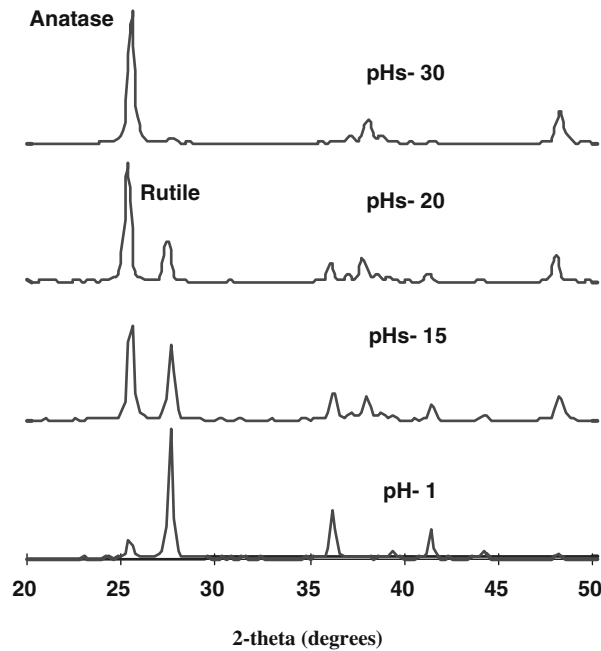


Figure 2. XRD patterns of TiO<sub>2</sub> photocatalysts prepared by variations in the number of pH swings and calcined at 550°C.

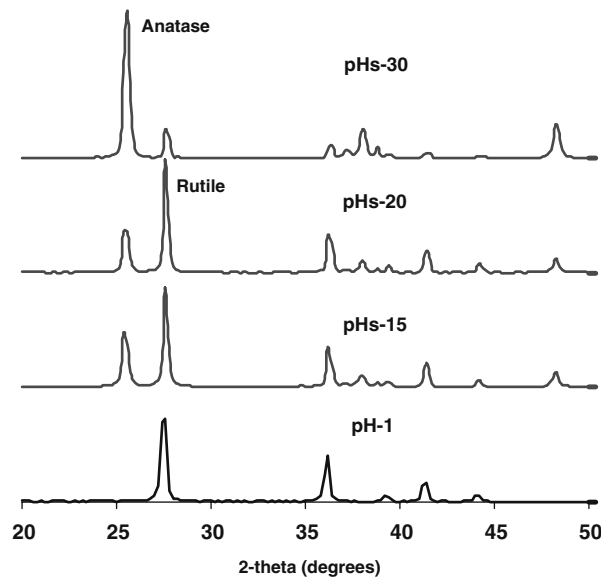


Figure 3. XRD patterns of TiO<sub>2</sub> photocatalysts prepared by variations in the number of pH swings and calcined at 600°C.

Usually, when the calcination temperature is increased to more than 550°C, the anatase phase is seen to gradually change into a rutile phase with larger particle sizes unfavorable for photocatalytic degradation reactions. However, with this method, even catalysts calcined at 600°C were able to retain a 80/20 anatase/rutile ratio by undergoing 30 times pH swings, as shown in figure 3. Here, the XRD patterns of the catalysts prepared at different pH swing numbers show that the major portion of the anatase phase changes to rutile, except for the catalysts prepared by 30 times pH swings. These results clearly illustrate that catalysts prepared at

higher pH swing times can avoid phase transition from anatase to rutile.

Table 1 shows that the anatase particle size gradually increased from 17 to 22 nm when the number of pH swings was increased from 7 to 30 times for the catalysts calcined at 550°C, showing that with the pH swing method, the average crystalline size of the anatase particles increases. And although the particle size of TiO<sub>2</sub> gradually increased with the increase in the number of pH swings, the surface area was also observed to gradually increase with the number of pH swings, as shown in figure 5.

Table 1

Physicochemical properties of TiO<sub>2</sub> photocatalysts prepared by the multi-gelation method

Number of pH swings	Calcination temperature (°C/40 h)	Particle size (nm)	Anatase: Rutile	
7	400	10	80:20	
7	550	17	45:55	
7	600	19	06:94	
15	400	10	91:09	
15	550	19	53:47	
15	600	21	30:70	
20	400	13	93:07	
20	550	21	70:30	
20	600	20	35:65	
30	400	12	100:0	
30	550	22	94:06	
30	600	23	80:20	
P-25	—	22	70:30	

Generally, the surface area gradually decreases when the size of the TiO<sub>2</sub> particles increases [11,14,20,23]. However, with this method, an increase in the number of pH swings led to a steady increase in the surface area of the particles, as shown in figure 5. These results can be attributed to the increase in the pore size as well as the pore volume of the particles which, in turn, increased the surface area of the particles, as shown in figures 6 and 7.

The effect of the different pH swing numbers on the average pore size and pore volume of the TiO<sub>2</sub> particles calcined at 550°C are shown and both the size and volume were gradually enhanced with the number of pH swings up to 25 times, then decreased. Interestingly, the pH swing is not only able to control the anatase/rutile phase ratio but also important parameters such as the particle size, surface area, pore diameter and pore volume of the catalysts. However, it is interesting to note that the pore volume and pore size decreased after 25

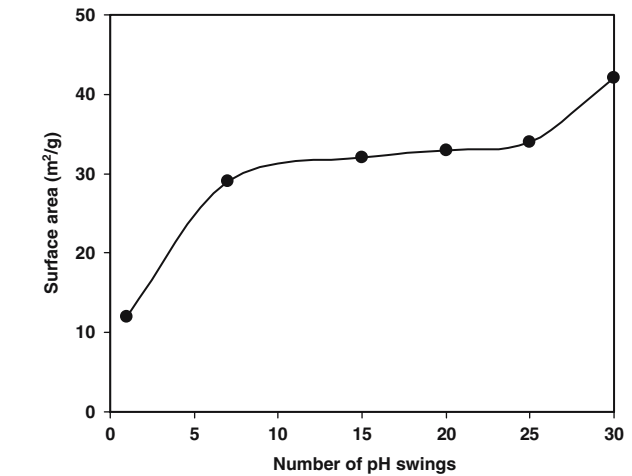


Figure 5. Specific surface area of photocatalysts calcined at 550°C versus the number of pH swings.

times pH swings even while the surface area steadily increased even after 25 times pH swings, as shown in figure 5. The catalysts prepared at 30 pH swings showed an anatase phase of 94% at 550°C calcination, whereas, the catalysts prepared by 7 to 25 pH swings possessed a rutile phase of more than 25% in their structure (table 1). Since rutile particles are aggregated and larger (200 nm), they may be responsible for the higher pore size and volume of the TiO<sub>2</sub> particles until 25 pH swings. However, for the catalysts prepared at 30 times pH swings, only an anatase phase is formed, explaining the decrease in the pore size and volume. No difference in the surface area could be observed due to the presence of an anatase phase since the anatase particle size is smaller than rutile which, in turn, increases the surface area of the particles.

Yu *et al.* have reported that the effect of F-doping on TiO<sub>2</sub> powders showed the pore size of TiO<sub>2</sub> particles to increase due to an enhancement of anatase crystalliza-

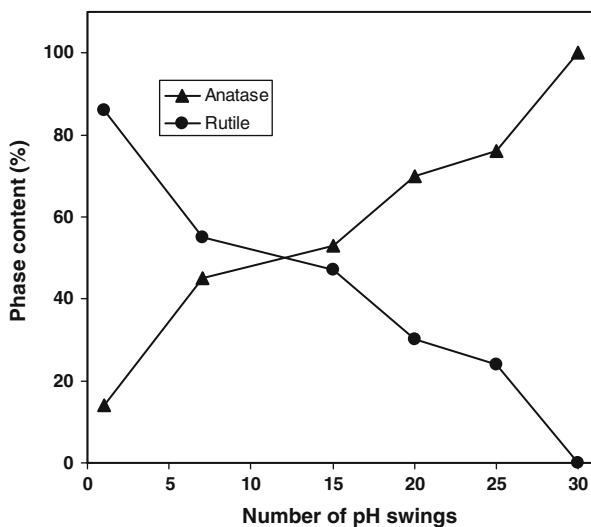


Figure 4. Effect of the number of pH swings on the anatase and rutile phase content of TiO<sub>2</sub> particles calcined at 550°C.

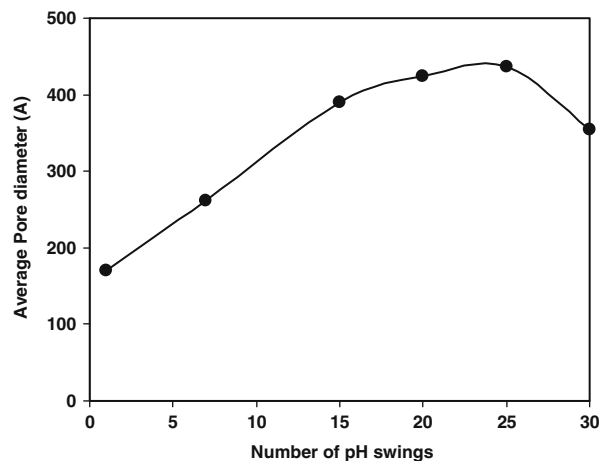


Figure 6. Pore-diameter of photocatalysts calcined at 550°C versus the number of pH swings.

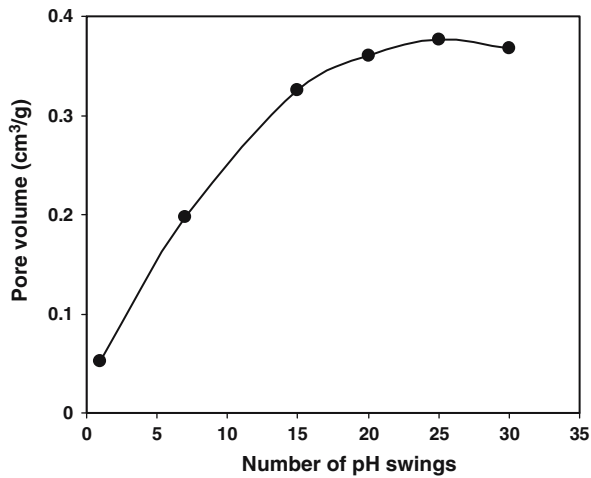


Figure 7. Pore-volume of photocatalysts calcined at 550°C versus the number of pH swings.

tion which was similar to our results [14]. However, at high proportions of rutile in the particles, a reduction in the pore size due to the rutile phase was explained. Although it is known that rutile particles are bigger in size with more aggregation, our experimental studies showed that, even in the absence of a rutile phase at 30 times pH swings, the pore size and volume of the TiO<sub>2</sub> particles decreased (figures 6 and 7) and this did not affect the surface area of the particles, as shown in the figure 5. It is interesting to note that anatase phase only is not responsible for the higher pore size and volume of particles prepared by this method.

The morphology of the particles was analyzed by SEM images which showed fine and small particles, as can be seen in figure 8. The catalysts prepared by the multi-gelation method are shown to be well-crystalline nano-particles. It was clear that the secondary particles formed are smaller in size for the catalysts prepared at 7 times pH swings than at 30 times, confirming the results obtained by XRD analysis.

Li *et al.* have reported that the photoluminescence of the TiO<sub>2</sub> photocatalysts at around 550 nm is related to the absorption at the UV region of the TiO<sub>2</sub> particles

which indicates the formation of more charged carriers serving as active sites for the degradation of organic compounds [20]. They have distinguished two different TiO<sub>2</sub> photocatalysts by their photoluminescence intensities. However, when we analyzed the photoluminescence spectra of the TiO<sub>2</sub> prepared by the multi-gelation method, photoluminescence at around 520 nm by excitation at around 280 nm at -196°C was observed. In particular, the catalysts prepared using 20, 25 and 30 times pH swings showed almost the same lifetimes. These results indicate that these photocatalysts may form the same charged carriers which serve as active sites for the oxidation of 2-propanol, irrespective of the difference in particle size and surface area of the TiO<sub>2</sub> photocatalysts.

### 3.2. Photocatalytic oxidation of 2-propanol diluted with water

The percentage of the degradation of 2-propanol with different photocatalysts prepared by the pH swing method is shown in figure 9, and the catalysts prepared at 400°C showed less photocatalytic activity during the reaction due to its amorphous nature. However, the catalysts prepared at 500°C were more active due to the formation of an anatase phase with a well-crystalline structure since anatase exhibits lower rates of recombination of the photo-formed electrons and holes due to its higher rate of hole trapping [21] and a higher surface adsorptive capacity [22]. Moreover, an increase in the pH swing times increased the photocatalytic activity, irrespective of the calcination temperatures. However, 20 times pH swings was found to be the optimum number and the photocatalytic activity for the degradation of 2-propanol decreased with a further increase in the number of pH swings after 20 (figure 9a). The catalysts prepared at 550°C with 20 times pH swings were shown to be more highly active for this degradation reaction (figure 9a), not only for their well-crystalline structure but also due to the varied composition ratio of anatase to rutile (table 1). Although the anatase phase is considered to be more active, a combination of rutile and anatase is favorable in enhancing the rate of the degradation of organic

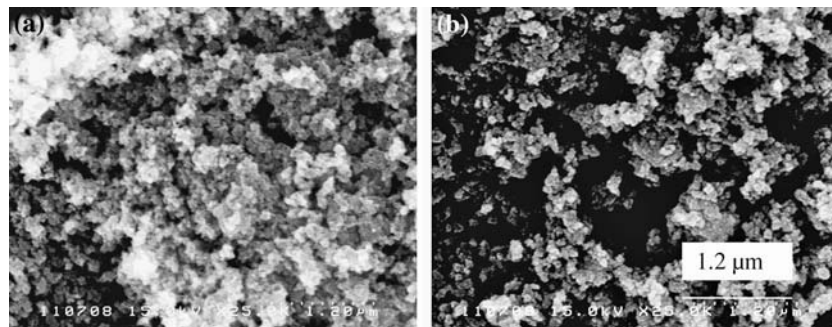


Figure 8. SEM images of TiO<sub>2</sub> photocatalysts prepared by: (a) 7 times pH swings; and (b) 30 times pH swings calcined at 550°C.

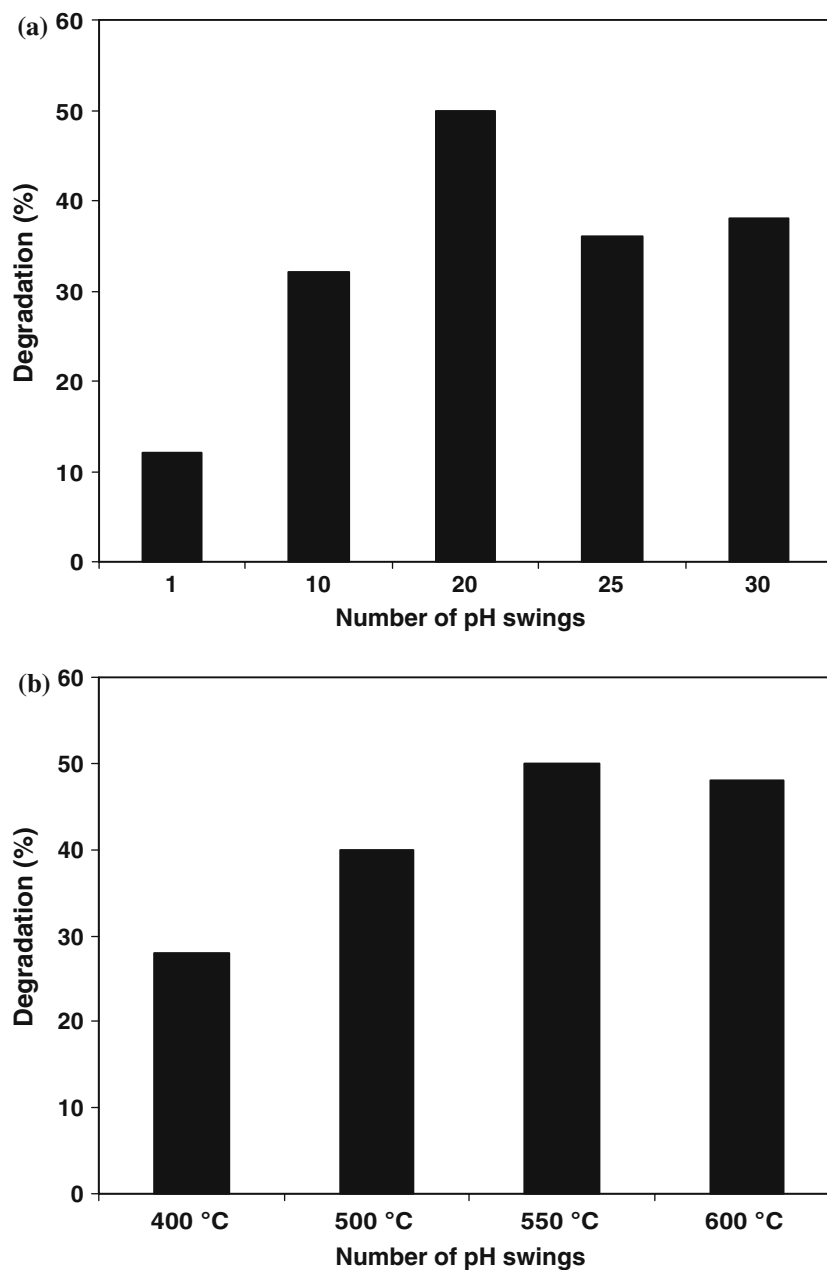


Figure 9. The effect of the pH swings numbers (top) and of the calcination temperatures (bottom) on the efficiency of the TiO<sub>2</sub> photocatalysts for the oxidative degradation of 2-propanol into CO<sub>2</sub> and H<sub>2</sub>O (UV irradiation for 4 h at 24°C).

pollutants [7,21,23]. The TiO<sub>2</sub> catalysts prepared by 20 times pH swings at 550°C possessed a good anatase/rutile ratio (70/30) comparable to the standard P-25 TiO<sub>2</sub> (70/30), the most active photocatalyst in present use.

Ohno *et al.* have reported that P-25 TiO<sub>2</sub> showed very high activity for the degradation of 2-propanol diluted with water in the presence of oxygen [24]. However, the photocatalytic activity drastically decreased when its anatase phase was completely removed by the HF solution [24]. They have proposed a mechanism where the electrons generated in the rutile phase by photoabsorption are transferred to the anatase

phase across an energy barrier of about 0.2 eV and then transferred to the oxygen. This is attributed to the higher absorption of light by the rutile phase even when the anatase phase is present in the catalysts, i.e., the rutile phase extends the photoactive range into the visible light region, thus harvesting more light since rutile has a smaller band gap of 3.0 eV with an excitation wavelength that extends to the visible region at 410 nm. Thus, the catalysts prepared at 20 times pH swings showed good performance for the degradation of 2-propanol.

Similarly, the oxidation of 2-propanol was carried out with catalysts prepared by 20 times pH swings at 600°C

calcination temperature, however, less photocatalytic activity was seen (figure 9b). This is due to the presence of a more rutile than anatase phase (table 1) which is unfavorable for photocatalytic degradation reactions and leads to a decrease in the surface area. However, the catalysts prepared at 25 and 30 times pH swings did not show any higher activity for this reaction. This is due to the more anatase phase of catalysts prepared by 25 times pH swings, whereas, with 30 times pH swings, the catalysts possessed a complete anatase phase with a smaller pore-size and pore-volume compared to the catalysts prepared at 20 times pH swings (figures 6 and 7). These results clearly suggest that not only the particle size and surface area of the TiO<sub>2</sub> are major factors for the efficient degradation of organic compounds but the pore-volume and pore-diameter are also equally important factors affecting the photocatalytic behavior of the catalysts.

#### 4. Conclusions

Variations in the pH swing to prepare TiO<sub>2</sub> photocatalysts was found to control the phase transition, particularly from anatase to rutile, which was favorable for higher activity, a great advantage of the multi-gelation method presented here. In addition, this method showed good performance in controlling not only the phase transition but also the surface area, pore-diameter, pore-volume and particle size. These results clearly showed that adopting variations in the pH swing plays an important role in controlling the phase transition and led to higher photocatalytic activity for such reactions as the degradation of 2-propanol.

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#### References

- [1] M. Anpo, Bull. Chem. Soc. Jpn. 77 (2004) 1427 and other references cited therein.
- [2] M. Anpo and M. Takeuchi, J. Catal. 216 (2003) 505.
- [3] M. Anpo and H. Yamashita, Catal. Surv. Asia 8 (2004) 35.
- [4] J.L. Zhang, Y. Hu, M. Matsuoka, H. Yamashita, M. Minagawa, H. Hidaka and M. Anpo, J. Phys. Chem. B 105 (2001) 8395.
- [5] M. Anpo, Res. Chem. Intermed. 11 (1989) 67.
- [6] M. Anpo, T. Shima, S. Kodama and Y. Kubokawa, J. Phys. Chem. 91 (1987) 4305.
- [7] M. Yan, F. Chen, J. Zhang and M. Anpo, J. Phys. Chem. B 109 (2005) 8673.
- [8] J.M. Herrmann, C. Guillard, J. Disdier, C. Lehaut, S. Malato and J. Blanco, Appl. Catal. B 35 (2002) 281.
- [9] C.Y. Wang, J. Rabani, D.W. Bahnemann and J.K. Dohrmann, J. Photochem. Photobiol. A 148 (2002) 169.
- [10] S. Bakardjieva, J. Subrt, V. Stengl, M.J. Dianez and M.J. Sayagues, Appl. Catal. B 58 (2005) 193.
- [11] B. Neppolian, H.S. Jie, J.P. Ahn, J.K. Park and M. Anpo, Chem. Lett. 33 (2004) 1562.
- [12] M.A. Fox and M.T. Gulay, Chem. Rev. 93 (1993) 341.
- [13] H. Yamashita, Y. Ichihashi, M. Harada, G. Stewart, M.A. Fox and M. Anpo, J. Catal. 158 (1996) 97.
- [14] J.G. Yu, J.C. Yu, B. Cheng, S.K. Hark and K. Iu, J. Solid State Chem. 174 (2003) 372.
- [15] K.N.P. Kumar, K. Keizer and A.J. Burggraaf, J. Mater. Chem. 3 (1993) 917.
- [16] J. Yang, Y.X. Huang and J.M.F. Ferreria, J. Mater. Sci. Lett. 16 (1997) 1933.
- [17] J. Kim, K.C. Song, S. Foncillas and S.E. Pratsinis, J. Eur. Ceram. Soc. 21 (2001) 2863.
- [18] M. Anpo, T. Kawamura, S. Kodama, K. Maruya and T. Onishi, J. Phys. Chem. 92 (1988) 438.
- [19] M. Anpo, H. Nakaya, S. Kodama, Y. Kubokawa, K. Domen and T. Onishi, J. Phys. Chem. 90 (1986) 1633.
- [20] H. Li, J. Zhu, G. Li and Y. Wan, Chem. Lett. 33 (2004) 574.
- [21] D.C. Hurum, A.G. Agrios, K.A. Gray, T. Rajh and M.C. Thurnauer, J. Phys. Chem. B 107 (2003) 4545.
- [22] U. Stafford, K.A. Gray, P.V. Kamat and V. Varma, Chem. Phys. Lett. 205 (1993) 55.
- [23] T. Ohno, K. Tokieda, S. Higashida and M. Matsumura, Appl. Catal. A 244 (2003) 383.
- [24] T. Ohno, K. Sarukawa and M. Matsumura, J. Phys. Chem. B 105 (2001) 2417.