

Synthesis of Nanoparticles of Mixed Oxides Containing Titanium Cerium Silver and Silicon: Phase Transformation

Akkarat Wongkaew, Waree Jansome, Supachai Khemchan,
Netnapa Sawaengmit and Sarawadee Mitpapan
Department of Chemical Engineering, Burapha University, Chonburi, Thailand, 20131

Abstract: Problem statement: Titanium dioxide is a well known material using with self-cleaning application. This is due to its properties after exposed to UV light: Superhydrophilicity and photocatalysis. The addition of other oxides could prolong these properties without continuing exposed to UV. However, titanium dioxide phase is essential. In order to obtain these properties, titanium dioxide needs to be in anatase phase. **Approach:** In this Research, phase transformation temperatures of mixed oxide of titanium dioxide and other oxides were determined. Samples of different mixed oxides were prepared by sol gel method. The first sample contained 30%TiO₂ and 70%SiO₂. The second sample contained 30%TiO₂, 15%CeO₂ and 55%SiO₂. The last sample contained 30%TiO₂, 15%CeO₂ and 55%SiO₂. Each sample was separately calcined at various temperatures from 350-850°C stepping by 50°C and followed by grinding and sieving to obtain in the form of powders. Then, each powder was characterized for its microstructure and phases of titanium dioxide, crystallite size by X-Ray diffraction. **Results:** The results from XRD showed that for a 30%TiO₂/SiO₂, an increase in calcined temperatures from 350-850°C (increasing by 50°C) increased average crystallite sizes of titanium dioxide (from 5.1-11.8 nm). Also, titanium dioxide phase found in the samples was only anatase. For a 30%TiO₂/15%CeO₂/SiO₂, an increase in calcined temperatures was not affect to the structure of the samples and XRD patterns seemed to be in an amorphous structure. Finally, for a 30%TiO₂/15%AgO/SiO₂, titanium dioxide was found in an anatase phase at 350°C until 650°C. Then, at calcined temperatures greater than 700°C, rutile phase started appearing in the structure while anatase phase peaks slowly declined with an increasing in calcined temperatures. This result showed that using these mixed oxides to coat over glass slides or mirrors for self-cleaning purposes, the films should be treated at certain temperatures to obtain an anatase phase. **Conclusion:** Phase transformation of titanium dioxide depends on calcined temperatures. The addition of other oxides such as silica, cerium or silver can effectively suppress the anatase-rutile phase transformation and resulted in an increase of anatase-rutile phase transformation temperatures.

Key words: Anatase phase, calcination temperatures, titanium dioxide, phase transformation temperature

INTRODUCTION

Titanium dioxide is of great interest owing to its applications related to photo-splitting of water, photocatalyst, photovoltaic devices and so on (Besor *et al.*, 2009; Meen *et al.*, 2009). Moreover, its thin film can induce hydrophilic surface with a water contact angle of 0-5° under UV light irradiation. This is so called "superhydrophilicity". This property of TiO₂ thin film makes it possible to be utilized for many applications such as anti-fogging or self-cleaning mirrors (Liu *et al.*, 2008). Phases of titanium dioxide

affected to superhydrophilic property of the films. The anatase phase in TiO₂ thin films resulted in superhydrophilic property (Kontos *et al.*, 2007). Therefore, phases of titanium dioxide are of importance to their applications. The other oxides cooperated with titanium dioxide enhanced photocatalytic and superhydrophilic properties (Houmard *et al.*, 2007). However, the addition of other oxides affected the anatase-rutile phase transformation temperatures (Kumar *et al.*, 1999). In this research, the effect of calcined temperatures to titanium dioxide phase transformation and crystalline sizes of titanium dioxide

Corresponding Author: Akkarat Wongkaew, Department of Chemical Engineering, Burapha University, Chonburi, Thailand, 20131

mixed with others was studied. The amount of titanium dioxide was kept constant at 30% wt and the rest is other oxides.

MATERIALS AND METHODS

Sample preparation: Mixed oxide of titanium dioxide with other oxides was prepared by sol gel method. Titanium isopropoxide obtained from Sigma Aldrich was a titanium precursor. For a 30%TiO₂/SiO₂ preparation, it began with dissolving the desire amount of Tetraethylorthosilicate (TEOS) into ethanol. The solution was stirring for 30 min. and then a stoichiometric amount of water was added into the solution to obtain hydrolysis reaction. The solution was continuing stirring. The known amount of nitric acid was added to peptize the solution. Then, the desire amount of titanium isopropoxide was added into the solution. The solution was kept stirring for 30 min. The obtained solution was aged for overnight and is called "sol". The sol was heated until it became gel. The obtained gel was aged overnight. After aging, the gel was dried at 110°C followed by calcined at different temperatures from 350-850°C (increased by 50°C). The final oxide was ground and sieved to 100 mesh.

For a 30%TiO₂/15%CeO₂/SiO₂ and a 30%TiO₂/15%AgO/SiO₂ preparation, the same procedure was used. It was started with dissolving the desire amount of Tetraethylorthosilicate (TEOS) into ethanol. The solution was stirring for 30 min. and then a stoichiometric amount of water was added into the solution to obtain hydrolysis reaction. The solution was continuing stirring. The known amount of nitric acid was added to peptize the solution. The known amount of cerium nitrate or silver nitrate was added into the solution. The obtained solution was stirring for 30 min. and then the known amount of titanium isopropoxide was added and the solution was kept stirring for another 30 min. to obtain the uniformity. The process of drying and calcining was followed the procedure of a 30TiO₂/SiO₂ preparation.

Sample characterization: Average crystalline sizes of each oxide were determined by Scherrer's equation using the X-ray line broadening from X-ray diffraction, Bruker AXS model D 8 Discover equipped with a CuK α radiation with a nickel filter. Diffraction intensity was measured in the 2 theta ranges between 20 and 85°, with a step of 0.02° for 8 sec point⁻¹.

RESULTS AND DISCUSSION

As been known, phase transformation of titanium dioxide depends on the calcination temperatures.

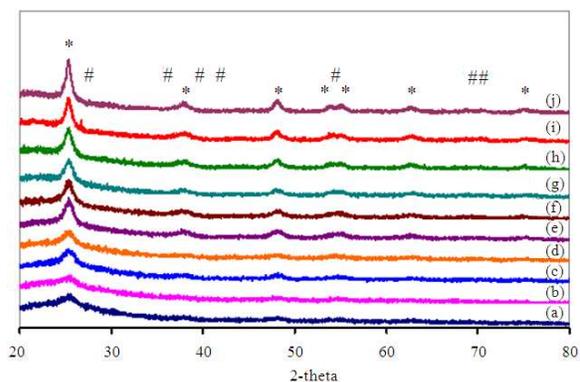


Fig. 1: XRD patterns of a 30%TiO₂/SiO₂ calcined at different temperatures: (a) 350°C; (b) 400°C; (c) 450°C; (d) 500°C; (e) 600°C; (f) 650°C; (g) 700°C; (h) 750°C; (i) 800°C; (j) 850°C and *: Represents standard peak position of TiO₂ anatase phase, #: Represents standard peak position of TiO₂ rutile phase

For pure titanium dioxide, it was found that an increase in calcined temperatures led to changes of anatase to rutile. Qingju *et al.* (2002) observed the anatase occurred at the most when the sample was calcined at temperature of 450°C and further increasing in calcined temperature rutile phase appeared. At calcined temperature of 800°C, titanium dioxide was completely in the form of rutile. In this research, the study of titanium dioxide phase transformation in the mixed oxide of titanium and other was investigated. The results were showed as following:

Phase and average crystallite size of a 30%TiO₂/SiO₂: Samples containing 30%TiO₂ and 70%SiO₂ were prepared by sol gel. The obtained solid powders were calcined at different temperatures from 350-850°C with increments of 50°C. All samples were analyzed for their phase and average crystallite sizes by X-Ray Diffraction method (XRD). The results were shown in Fig. 1.

XRD measurements were performed in order to verify the occurrence of TiO₂ phases at differences in calcined temperatures. Fig. 1 shows the XRD diffraction patterns obtained with 2 θ = 20-80°. * represents peak positions of TiO₂ anatase phase at 25.4, 38.1, 48.1, 54.8, 62.5 and 75.1°. # represents standard peak position of TiO₂ rutile phase at 27.4, 36.1, 41.2, 56.6, 69.1 and 69.9°. These data were obtained from the references of spinel code 00-021-1272 and 01-076-0317, respectively, attached with the XRD instrument. Figure 1a is an XRD pattern of the sample calcined at 350°C. As can be seen, the XRD pattern was quite smooth except at 25.4°

appearing as a small hill. An increasing of calcined temperatures increased intensity of peaks at this position and the peaks were getting sharp as been seen in Fig.1a-c. Further increasing in calcined temperatures to 500°C increased a number of peak positions matching with peak positions of TiO₂ anatase phase. The peak positions were found at 25.4, 38.1, 48.1, 54.8 62.5 and 53.9°. These peak positions appeared in the samples calcined at 500-850°C and the intensities of each peaks increased with increasing of calcined temperatures. These results indicated that at low calcined temperatures, it was an amorphous structure appearing in the sample. An increase in calcined temperatures increased crystallinity of titanium dioxide and anatase phase was appeared in the samples calcined at temperature 450-850°C. Interestingly, no rutile phase was observed in the all samples. Kumar *et al.* (1999) prepared a 90%TiO₂/SiO₂ by cohydrolysis method and the samples were calcined at 800 and 1000°C. They found that TiO₂ was in only anatase phase for both calcined temperatures while a sample contained 95% TiO₂ and 5% SiO₂, TiO₂ was in anatase phase at calcined temperature of 800°C and TiO₂ was found in rutile phase at calcined temperature of 1000°C. The addition of silica in the samples resulted in an increase of anatase-rutile phase transformation temperature.

From XRD results, average crystallite sizes of TiO₂ were calculated using Scherer equation. The results were showed in Table 1.

As in Table 1, average crystallite sizes of titanium dioxide increased with an increase of calcined temperatures. The XRD pattern of a sample calcined at 350°C was a bump and this could be described as

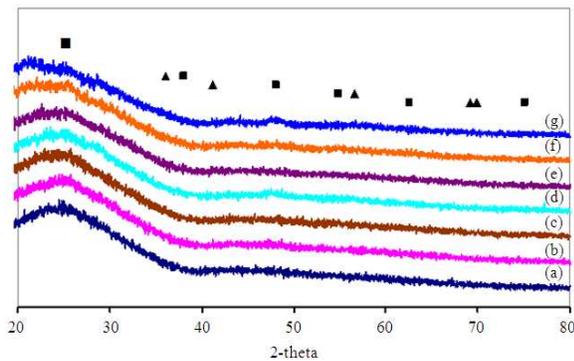


Fig. 2: XRD patterns of a 30%TiO₂/15%CeO₂/SiO₂ calcined at different temperatures: (a) 350°C; (b) 400°C; (c) 450°C; (d) 500°C; (e) 550°C; (f) 600°C; (g) 700°C and ■: Represents standard peak position of TiO₂ anatase phase, ▲: Represents standard peak position of TiO₂ rutile phase

either an amorphous structure of the oxide or a crystallite structure and the particles were well dispersed in the samples. An increase of calcined temperatures from 350-850°C increased an average crystallite size of titanium dioxide from less than 3-11.1 nm. The sample calcined at 850°C has the largest crystallite size of 11.1 nm. This was due to the agglomeration of TiO₂ at high temperatures (Tian *et al.*, 2009).

Phase and average crystallite size of a 30%TiO₂/15%CeO₂/SiO₂: The samples contained 30% TiO₂, 15% CeO₂ and 55% SiO₂ were calcined at different temperatures. The results from XRD showed in Fig. 2.

XRD measurements were performed in order to verify the occurrence of TiO₂ phases at differences in calcite temperatures. Figure 2 shows the XRD diffraction patterns obtained with 2θ = 20-80. ■ represents peak positions of TiO₂ anatase phase at 25.4, 38.1, 48.1, 54.8, 62.5 and 75.1°. ▲ represents standard peak position of TiO₂ rutile phase at 27.4, 36.1, 41.2, 56.6, 69.1 and 69.9°. These data were obtained from the references of

Table 1: Average crystallite sizes of the 30%TiO₂/SiO₂ samples calcined at different temperatures

Calcined temperature (°C)	Average size (nm)
350	<3.0
400	4.9
450	5.4
500	5.8
600	6.7
650	8.2
700	8.6
750	8.8
800	10.2
850	11.1

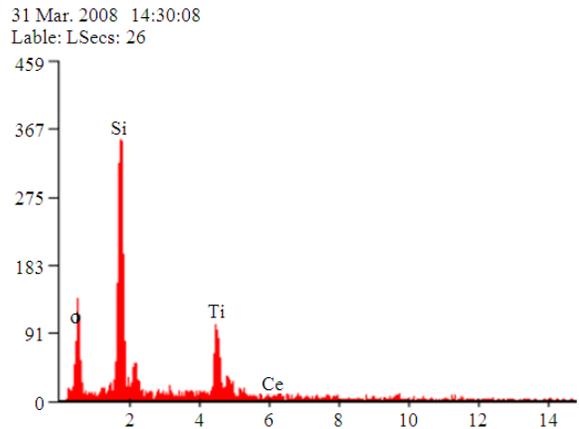


Fig. 3: EDX results for a 30%TiO₂/15%CeO₂/SiO₂ sample calcined at 450°C

Table 2: Chemical compositions obtained from EDX comparing with those of preparation

Element	Preparation (%)	EDX (%)	Error (%)
Ti	17.9	19.6	8.9
Si	25.7	27.5	7.0
Ce	12.2	11.8	2.9
O	44.1	41.0	6.9

Table 3: Average crystallite sizes of substances in samples contained 30% TiO₂, 15% Ag and 55% SiO₂. Each sample was calcined at different temperatures

Calcined temperature (°C)	Crystallite size (nm)		
	TiO ₂		Ag
	Anatase	Rutile	
350	8.1	-	-
400	6.2	-	16.8
450	8.1	-	20.5
500	8.9	-	21.7
550	11.2	-	19.3
600	10.6	-	24.6
650	10.7	-	30.7
700	24.1	32.6	32.0
750	35.4	37.6	33.5
800	36.4	48.9	36.9
850	36.3	46.7	36.3

spinel code 00-021-1272 and 01-076-0317, respectively, attached with the XRD instrument. As can be observed from the XRD patterns of all samples, there were no peak positions appeared except the bumps at $2\theta = 25^\circ$. It means that either all particles are well dispersed in the samples or there was an amorphous structure existing in the samples. However, an increase in calcined temperatures was not affected to the structure at all. Further investigation was conducted with EDX to determine the chemical composition in the sample. The results showed in Fig. 3.

As can be seen in Fig. 3, the results indicated the presence of titanium, cerium, silicon and oxygen in the sample. The composition of each atom was reported in Table 2.

From Table 2, the sample contained 30% TiO₂, 15% CeO₂ and 55% SiO₂ calcined at 450° was analyzed for their chemical composition using EDX. The results indicated that there were 19.6% Ti, 27.5% Si, 11.8% Ce and 41.0% O in the sample. Comparing these data with those of calculating from the precursors during the preparation, it was found that there were 17.9% Ti, 25.7% Si, 12.2% Ce and 44.1% O and these brought about to errors less than 10% for each element. The differences in results from preparation and those from EDX may cause from the loss of chemicals during preparation. Consequently, the results from EDX confirmed that all chemicals were present in the samples even though no peak positions of TiO₂ and CeO₂ were observed from XRD.

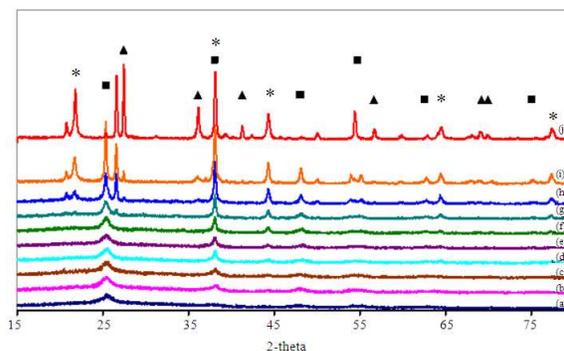


Fig. 4: XRD patterns of a 30%TiO₂/15%AgO/SiO₂ calcined at different temperatures: (a) 350°C; (b) 400°C; (c) 450°C; (d) 500°C; (e) 600°C; (f) 650°C; (g) 700°C; (h) 750°C; (i) 800°C; (j) 850°C and *: Represents standard peak position of Ag, ■: Represents standard peak position of TiO₂ anatase phase, ▲: Represents standard peak position of TiO₂ rutile phase

Phase and average crystallite size of a 30%TiO₂/15%AgO/SiO₂: The samples contained 30% TiO₂, 15% AgO and 55% SiO₂ were calcined at different temperatures. The results from XRD showed in Fig. 4.

XRD measurements were performed in order to verify the occurrence of TiO₂ phases at differences in calcined temperatures. Figure 4 shows the XRD diffraction patterns obtained with $2\theta = 15-80^\circ$. * represents peak positions of Ag at 21.8, 38.1, 44.3, 64.5 and 77.4°. ■ represents peak positions of TiO₂ anatase phase at 25.4, 38.1, 48.1°, 54.8° 62.5° and 75.1°. ▲ represents standard peak position of TiO₂ rutile phase at 27.4, 36.1, 41.2, 56.6, 69.1 and 69.9°. These data were obtained from the references of spinel code 01-089-3722, 00-021-1272 and 01-076-0317, respectively, attached with the XRD instrument. In Fig. 2a, XRD pattern of the sample calcined at 350°C indicated an amorphous structure of the oxide. An increase in calcined temperatures increased the peak intensity and appearing of peaks at different angles. Most likely, these peaks were peak positions of TiO₂ anatase phase. Up until the calcined temperature of 500°C, peak positions of Ag appeared in the XRD patterns. Each peak intensity increased with an increase of calcined temperatures until calcined temperatures of 700°C, rutile phase appeared. Further increasing in calcined temperatures increased peak intensities of all compounds. These results indicated that the anatase-rutile phase transformation depended on calcined temperatures. Moreover, for a sample of titanium dioxide cooperated with other oxides, the phase

transformation temperatures were higher than that of pure compound (Guan, 2005).

From XRD results, average crystallite sizes of TiO₂ were calculated using Scherer equation. The results were showed in Table 2.

As can be seen from Table 2, average crystallite sizes increased with an increase of calcined temperatures for all compounds. The sample calcined at 800°C has the biggest crystallite sizes for anatase, rutile and silver. For the samples containing anatase and rutile phases, average crystallite size of anatase was smaller than that of rutile at any calcined temperatures. Ag appeared in the sample calcined at temperatures greater than 400°C. Interestingly, the preparation method was sol gel. Theoretically, the final product from this method is oxide. This was due to the condensation reaction (Brinker *et al.*, 1990). However, in this experiment, the amount of water added during the hydrolysis reaction was less than the stoichiometric amount. That could be the reason for obtaining Ag instead of Ag₂O.

CONCLUSION

- Phase transformation of titanium dioxide depends on calcined temperatures
- The addition of other oxides such as silica, cerium or silver can effectively suppress the anatase-rutile phase transformation and resulted in an increase of anatase-rutile phase transformation temperatures
- Anatase phase was only species found in 30% TiO₂/SiO₂ samples calcined at temperatures up to 850°C
- The addition of cerium oxide in mixed oxide of titanium and silica led to well dispersion of all oxides in the samples
- Average crystallite sizes increased with an increase in calcined temperatures
- The addition of silver in mixed oxide of titanium and silica lowered the anatase-rutile phase transformation temperatures to 700°C

ACKNOWLEDGEMENT

This research has been granted by the Faculty of Engineering, Burapha University under the contract # 35/2550.

REFERENCES

Besor, A.S., A.V. Vorontsov and V.N. Parmon, 2009. Fast adsorptive and photocatalytic purification of air from acetone and dimethyl methyl phosphonate by TiO₂ aerosol. *Applied Catal. B: Environ.*, 89: 602-612. DOI: 10.1016/J.APCATB.2009.01.024

Brinker, J.C., W. George and S. Scherrer, 1990. *Sol-gel science: The physics and chemistry of sol-gel processing*. Boston, Acad, ISBN: 0-12-134970-5, 1990.

Guan, K., 2005. Relationship between photocatalytic activity, hydrophilicity and self-cleaning effect of TiO₂/SiO₂ composite film. *Surface Coat. Technol.*, 191: 155-160. DOI: 10.1016/j.surfcoat.2004.02.022

Houmar, M., D. Riassetto, F. Roussel, A. Bourgeois and G. Berthome, 2007. Morphology and natural wettability properties of sol-gel derived TiO₂-SiO₂ composite thin films. *Applied Surface Sci.*, 254: 1405-1414. DOI: 10.1016/j.apsusc.2007.06.072

Kontos, A.I., A.G. Kontos, D.S. Tsoukleris, G.D. Vlachos and P. Falaras, 2007. Superhydrophilicity and photocatalytic property of nanocrystalline Titania sol-gel films. *Thin Solid Films*, 515: 7370-7375. DOI: 10.1016/J.TSF.2007.02.082

Kumar, S.R., C.S. Asha, K. Vasudevan, R. Suja and P. Mukundan, 1999. Phase transformation in sol-gel titania containing silica. *Mater. Lett.*, 38: 161-166. DOI: 10.1016/S0167-577X(98)00152-9

Liu, Z., X. Zhang, T. Murakami and A. Fujishima, 2008. Sol-gel SiO₂/TiO₂ bilayer films with self-cleaning and antireflection properties. *Solar Energy Mater. Solar Cells*, 92: 1434-1438. DOI: 10.1016/J.SOLMAT.2008.06.005

Meen, T.H., W. Water, W.R. Chen, S.M. Chao and L.W. Ji, 2009. Applications of TiO₂ nano-particles on the electrode of dye-sensitized solar cells. *J. Phys. Chem. Solids*, 70: 472-476. DOI: 10.1016/J.JPCS.2008.12.002

Qingju, L., W. Xinghui, W. Baoling and L. Qiang, 2002. Preparation and super-hydrophilic properties of TiO₂/SnO₂ composite thin film. *Mater. Res. Bull.*, 37: 2255-2262. DOI:10.1016/S0025-5408(02)00972-8

Tian, G., K. Pan, H. Fu, L. Jing and W. Zhou, 2009. Enhanced photocatalytic activity of S-doped TiO₂-ZrO₂ nanoparticles under visible-light irradiation. *J. Hazard. Mater.*, 166: 939-944. DOI:10.1016/j.jhazmat.2008.11.090