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Characterization of Titania (TiO_2) Catalysts Prepared by Sol-Gel Method

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Various TiO_2 catalysts in powder form were prepared by sol-gel method and then characterized for X-ray diffraction and BET surface area. Variation in composition of reactants, choice of hydrolysing catalyst, calcination temperature, and method of drying were among preparative variables evaluated. Addition of Pt, Fe_2O_3, CuO and SiO_2 on the catalysts was also carried out during the initial stage of sol formation. XRD analysis suggests that all catalysts calcined at 450°C were completely in anatase phase. BET surface area of the catalysts revealed that the catalysts prepared using HNO_3, as hydrolysing catalyst, have a surface area larger than the commercial Degussa P25 TiO_2 catalyst, with the highest area of 126 m^2/g. The addition of metals resulted in a lower surface area, while silica provided a considerable increase in surface area, at 257 m^2/g. Analyses of isotherms plot and BJH desorption plots suggest that particle pores were dominated by a bottle-like shape. However, the photocatalytic activity of these catalysts in the degradation of surfactant failed to meet the performance ratings of Degussa P25 TiO_2 catalyst, probably due to less access of surfactant into internal surface of the prepared catalysts. Degradation of the surfactant using different particle sizes suggests that the external surface of TiO_2 catalysts was important under liquid phase degradation.

Keywords: Titanium oxide, Sol-gel method, Porous material, Photocatalyst, Surfactant degradation

INTRODUCTION

The properties of titania (TiO_2) have generated increasing interest in its use as a catalyst in photocatalysis or as support, especially for group VIII metals, where it has a remarkable influence on the surface structure and the catalytic activity of the supported metal. An important limitation to its use obtained by conventional methods is its low surface area. One way of obtaining titania with larger surface areas (>100 m^2/g) has been through the preparation of aerogels using the sol-gel method, which also allows compositional and microstructural tailoring through controlling the precursor chemistry and processing conditions. Sol-gel processing provides for excellent chemical homogeneity and the possibility of deriving unique metastable structures at low reaction temperatures. It involves the formation of a metal-oxo-polymer network from molecular precursors such as metal alkoxides or metal salts (Brinker and Scherer, 1995). For example, the metal alkoxides may be hydrolyzed (Eq. (1)) and polycondensed (Eqs. (2) and (3)) to form a metal alkoxide gel as follows:

$$M-OR + H_2O \longrightarrow M-OH + ROH \quad (1)$$

$$M-OH + M-OR \longrightarrow M-O-M + ROH \quad (2)$$

$$M-OH + M-OH \longrightarrow M-O-M + H_2O \quad (3)$$

where M = metal and R = alkyl group. The relative rates of hydrolysis and polycondensation strongly influence the structure and properties of the resulting metal oxides. Factors affecting the sol-gel process include the reactivity of metal alkoxides, pH of medium, water:alkoxide ratio, reaction temperature, and nature of solvent and additive. By varying these processing parameters, materials with different microstructure and surface chemistry can be obtained.

Typically, sol-gel derived precipitates are amorphous in nature, requiring further heat treatment to induce crystallization. The calcination process frequently gives rise to particle agglomeration and grain growth and may induce phase transformation. Hydrothermal processing represents an alternative to calcination for promoting crystallization under milder temperatures as widely used in the production of advanced ceramic powders (Wand and Ying, 1999).

In the present study, we report the preparation by sol-gel method of TiO_2, for use as photocatalyst. The study was undertaken to evaluate the influences of water:alkoxide ratio, choice of hydrolysing catalyst, calcination temperature, method of drying, and additive on properties of titania. Addition of some metals such as platinum, copper and iron was carried out in the initial stage of sol formation in order to allow better dispersion of dopant in sol matrix. To ensure high porosity of the catalyst, poly(ethylene glycol) [PEG: $HO(-CH_2CH_2-)_nH$] was added (Kajihara *et al.*, 1998). The resulting catalysts were characterized for surface area and crystal phase. Finally, photocatalytic activity of titania catalysts was evaluated in degradation of a surfactant known as SS-70 [polyoxy-ethylene-alkyl-ether: $C_{14}H_{29}O(CH_2CH_2)_7H$], which has hydrophobic and hydrophilic properties. The reaction using the Degussa P25 titania catalyst was also carried out for comparison.

EXPERIMENTAL

Chemicals

Titanium tetraisopropoxide (TTIP) of Wako (Japan) 99.99% purity was used as a titanium precursor. Absolute ethanol (EtOH) of Wako (Japan) 99.9% purity was employed as main solvent. PEG having molecular weight of 2000 (Wako, Japan) was used as polymeric additive. Two different synthesis catalysts were used: HNO_3 and NH_4OH (Wako, Japan). Deionised water was used as hydrolysing reagent. All chemicals were used as received. SS-70 surfactant was kindly provided by Wako (Japan).

Procedure of Sol-Gel Method

The sol-gel method can employ a colloidal inorganic sol precursor often aqueous or organometallic precursors mostly metal alkoxides which are usually in solution with alcohol and water (Fan *et al.*, 2000). In the present work, the second method was selected to prepare TiO_2 catalyst particles. A mixture of TTIP, H_2O, EtOH and synthesis catalyst was prepared with molar ratios as described in Table 1. The titania catalysts were prepared by controlling the hydrolysis process. TTIP was dissolved in half of the prescribed amount of EtOH and kept in a closed reaction flask. Esterification of TTIP occurred to form $Ti(O-C_2H_5O)_4$, a more stable precursor. In this case, the use of small and linear groups such as EtOH improves the stability due to the oligomer nature of the precursor (Guillard *et al.*, 2002). The other half of EtOH was mixed with H_2O and synthesis catalyst either HNO_3 or NH_4OH, and this solution was transferred into a titration burette. As an alkoxide, $Ti(O-C_2H_5O)_4$ is still very reactive to water at ambient temperature. To control hydrolysis of the titania precursor, therefore, the reaction was carried out under ice-cooled condition. The flask containing the titania precursor was placed in an ice bath by certain way that still allowing the solution agitated by a magnetic stirrer. Then, the solution containing H_2O and synthesis catalyst was added drop wise as slow as possible by adjusting the burette stopcock, to the precursor solution with vigorous stirring to avoid local excess water. After the burette was completely drained, a prescribed amount of PEG was added to the resultant solution. The container was sealed and maintained at a temperature of 40°C for 30 min under stirring to dissolve PEG completely. The stirring was continued until a milky solution was observed, indicating the beginning of gelation. Gel was aged for two days to allow release of solvent from the polymeric gel matrix. The aged gel was dried either in an oven (120°C) overnight or in a rotary evaporator (80°C). The dried gel was then calcined in the furnace by raising temperature at a rate of 5°C/min to a final temperature of 450°C and held there for 30 min. In cases where additives were used, these were added into the initial precursor solution, and then stirred for 30 min. The amounts of additives employed as shown in Table 2, were intended to give the molecular loading of 0.4%.

Table 1. Compositions of the sol solution per mol TTIP

H_2O	EtOH	PEG-2000	Catalyst
7.89, 11.05, 14.20, 19.29 or 30.01	65.02	28.41	0.20 (HNO_3 or NH_4OH)

Table 2. Amount of additives used per mol TTIP

Additive	Source	Amount
Pt	H_2PtCl_6	0.8608 g
Fe_2O_3	$Fe(NO_3)_3.9H_2O$	2.3352 g
CuO	$Cu(NO_3)_2.3H_2O$	1.2273 g
SiO_2	$Si(OC_2H_5)_4$	26.65 ml

Catalyst Characterizations

Specific surface areas of the titania samples were measured by adsorption of nitrogen at 77.35K according to the Brunauer-Emmett-Teller (BET) method using a Micromeritics ASAP 2001 System (Shimadzu, Japan). The samples were degassed at 200°C under vacuum of 0.004 mmHg. The measurement results also include pore size, total pore volume, and pore size distribution.

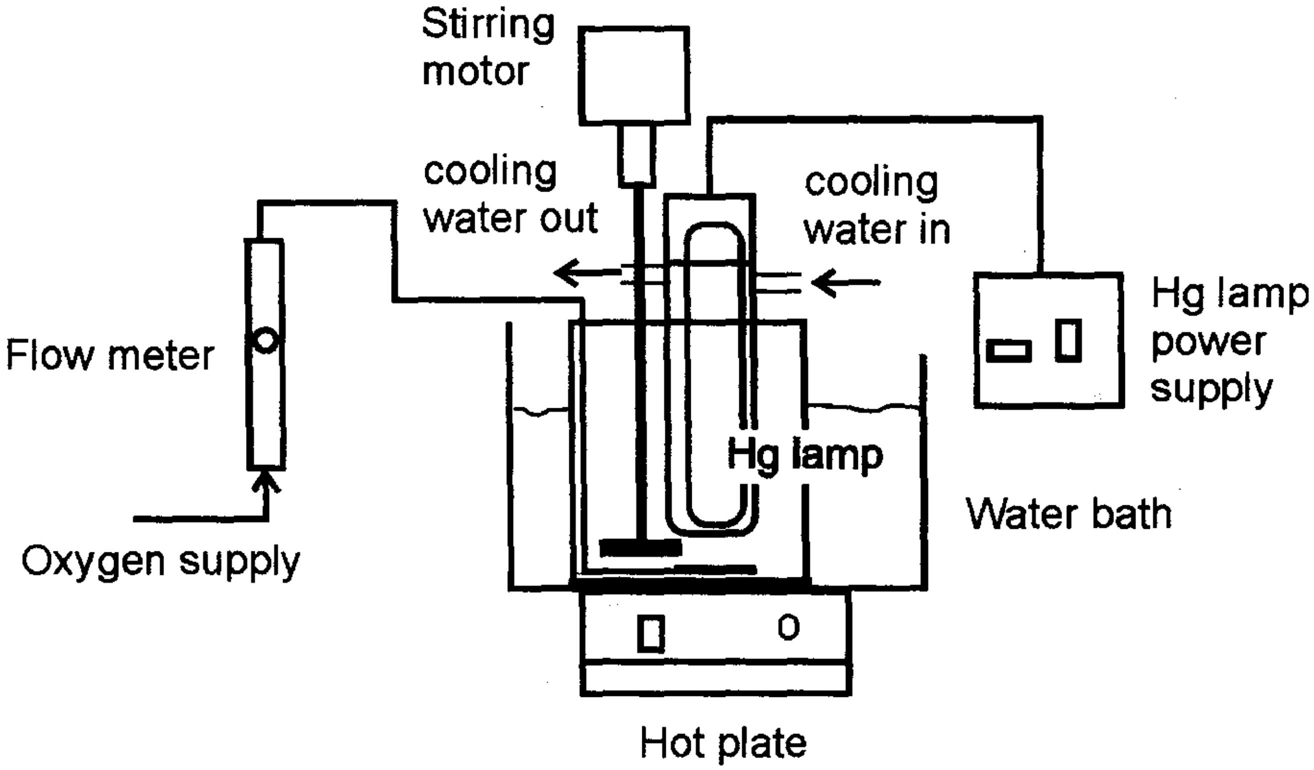

Figure 1. Schematic diagram of photocatalytic reactor unit

Crystal phase of the samples was characterized by powder X-ray diffraction (XRD) with a RINT 2000 Diffractometer (Rigaku, Japan). Samples were loaded on glass slides, and Cu K*a* radiation (*l* = 1.5406 A) was used at 30 kV and 16 mA. The sample scans were collected for 10-90° (2*q*) with an angular increment of 0.2° and a counting time of 2 s.

Photocatalytic Reaction

Photocatalytic activity tests were carried out in a stirred batch photoreactor in which a low-pressure mercury lamp (wavelength 253.7 nm, 20 W, UVL20 PS of Sen Lights Corp., Japan) was immersed as shown in Figure 1. The solution was prepared by dissolving 100 mg SS-70 surfactant into 1 L deionised water. The amount of titania catalyst used was 0.5 g. The pH of the solution was not adjusted. Oxygen was introduced into the solution at a rate of 20 mL/min via a sintered glass distributor. The working solution containing photocatalyst powders was stirred at a speed of 500 rpm. The solution temperature was maintained at 35°C by placing the reactor inside a water bath. Liquid samples were collected periodically using a syringe with a filter made of glass fibre (GF-75, Advantec), and then analysed for surfactant concentration using an HPLC (LC 655, Hitachi) with Inertsil ODS-3 column (GL Science, Japan) and a refractive index detector (Model 504R, GL Science). Total organic carbon was determined using a TOC Analyzer (TOC-5000A, Shimadzu).

RESULTS AND DISCUSSION

XRD Analysis

Figure 2 shows the significant change in crystal form of TiO_2 upon heat treatment. Drying at 120°C resulted in a complete amorphous phase of TiO_2. By raising the treatment temperature, the TiO_2 crystalline was converted to a metastable anatase phase. The latter is typically associated to have a high surface area. Pure anatase was obtained at 450°C. Raising the treatment temperature further to 600°C increased the intensity and narrowed the broadness of the peaks, suggesting crystal growth formation. However, the anatase phase was still predominantly observed. The rutile phase was identified in trace amount reflected by the main diffraction of 2.378 at 37.8°. A complete rutile phase is expected to appear at 900°C (Lee, 2001).

In preparation of metal oxide particle by sol-gel method, the addition of catalysts can accelerate the hydrolysis or condensation reaction rates. It has been reported that hydrolysis rate is increased under acidic conditions, while polycondensation reactions are enhanced by basic catalysts (Brinker and Scherer, 1990). XRD patterns in Figure 3 indicate that different crystallinity or crystal size was obtained by using different synthesis catalysts, *i.e.* HNO_3 and NH_4OH. Smaller crystal size was obtained in acid condition perhaps not only due to the delay in the gelation process, but also because of the role of HNO_3 as an electrolyte that could have

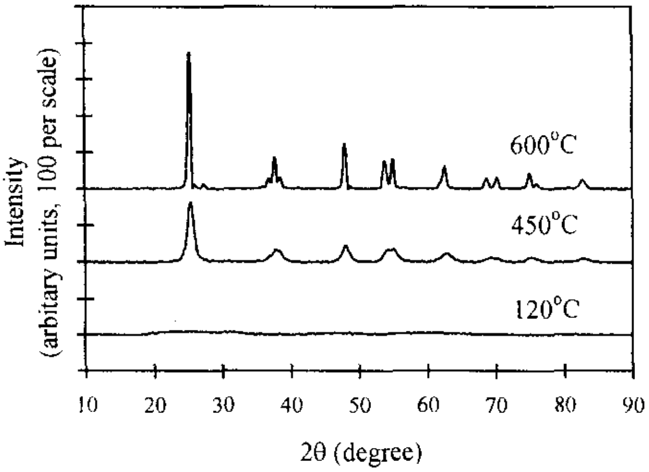

Figure 2. XRD patterns of TiO_2 particles under different temperature treatments

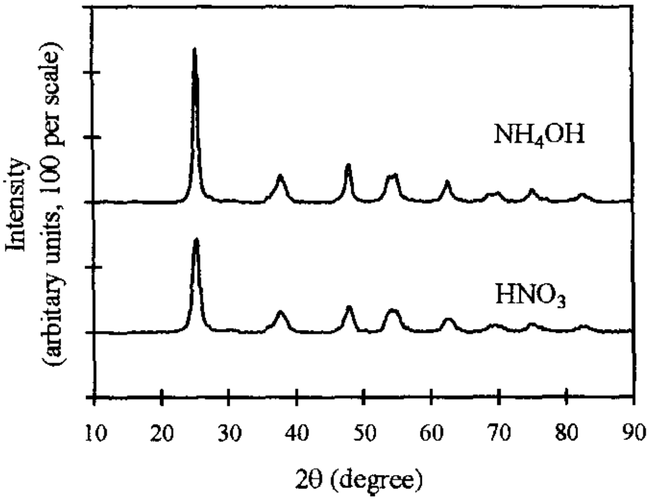

Figure 3. XRD patterns of TiO_2 particles prepared using different synthesis catalysts

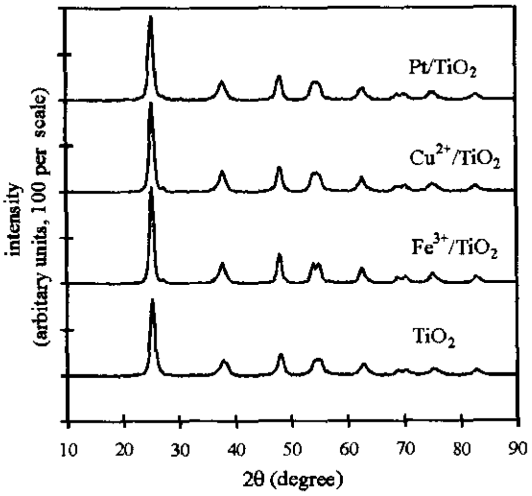

Figure 4. XRD patterns of TiO_2 particles with different additives

prevented particle growth or agglomeration through electrostatic repulsion (Wang and Ying, 1999). Since the isoelectric point of TiO_2 lies at a pH of 5-7, surface charges on the particles in an acidic medium help to keep discrete particles in the dispersed state.

Figure 4 also indicates that the presence of metal additives such as Pt, Fe_2O_3, CuO or SiO_2 promoted higher anatase crystals and no peak of the metals was observed. The latter may suggest that all metal clusters are well dispersed on the TiO_2 surface due to their low concentrations. However, the presence of these metal additives also led to the formation of larger crystalline. Jung *et al.* (2000) reported that the anatase crystal size embedded with SiO_2 increases as the silica content increases up to 10%, beyond which resulting crystal size no longer changes. According to Fotou *et al.* (1994), addition of SiO_2 increases the degree of aggregation, thus, this fact may cause a growth in crystal size.

Water acts as a hydrolysing agent in the reaction with the titania precursor. The amount of water used will control the absolute and relative rates of nucleation and growth of alkoxide clusters. Upon calcinations at 450°C, anatase peaks were noted in the XRD profiles of the various samples. There seems to be no influence of the amount of water added on the crystallinity of TiO_2. This is perhaps due to the presence of PEG 2000 that modifies the reactivity of the titania precursor, leading to inhibition of the condensation reaction. As the condensation rates were slowing down, the influence of hydrolysis rate was surpassed, giving insignificant impact on crystallinity.

Surface Area Analysis

Temperature is known to have significant effect on crystallinity, which then determines surface area and pore properties. Table 3 shows a considerable change of surface area of TiO_2 upon calcinations. Surface area under heat treatment at 120°C was not determined since the crystal was amorphous. At calcination temperature of 600°C, the surface area was greatly reduced to less than 5 m^2/g (the minimum measurement level of the existing analyser), even though the crystals were still dominantly anatase. It seems that above 450°C, the crystallites started to grow rapidly with calcination temperature. As the crystallite size increased, the surface area was reduced. Therefore, 450°C was selected as calcination temperature throughout the catalyst preparation.

BET analysis for samples under the variation of water amount was applied only to catalyst sample of Gel-07 prepared using 30.01 mol water per mol TTIP. The Gel-07 catalyst has white colour particles, while the other samples have shinny black colour. Probably these black samples may still contain burned organics. In the following preparations, therefore, 30.01 mol water per mol TTIP was used. Particles of Gel-07 have surface area of 126.2 m^2/g and pore size of 39.7 Å. The surface area is certainly much larger than one reported for a commercially active P-25 TiO_2 of Degussa, *i.e.* 50 m^2/g (Bessa *et. al*, 2001).

Table 3. Variation of temperature treatment (first drying in rotary evaporator)

Sample No.	Temp (°C)	S_{BET} (m^2/g)	Pore Size (Å)	Pore Vol. (cm^2/g)
Gel-10A	450	83.5	32.1	0.076
Gel-10B	600	<5.0	-	-

The result in Table 4 suggests that drying method prior to calcinations was also an important step. Drying in an oven promoted high surface area of TiO_2 particles. It seems the choice of drying method affected the release path of solvent from polymeric gel matrix that determines the formation of porous gel before calcination. Initial drying in rotary evaporator produced smaller particle sizes, but it fails to preserve the porous structure that could enhance the surface area of sol-gel prepared particles.

The choice between acidic and basic catalysts has led to different mechanisms of process, with the former promoting hydrolysis, while the latter catalyzing condensation. Table 5 shows that the HNO_3 catalysed process yielded significantly higher surface area compared with one catalyzed by a base. Using HNO_3, the process resulted in the formation of gel as expected. However, such phenomenon was not observed when using NH_4OH. When a base catalyst was added to the precursor solution, white precipitates were formed due to fast condensation of oxo-oligomer particles, products of reactions (2) and (3). In the case of HNO_3 catalyst, these oligomers continued to increase in size to form a polymeric cluster of metal oxide gel. XRD analysis suggests that the NH_4OH catalyzed process produced high crystalline anatase, thus, having a small surface area. It indicates that upon solvent removal, TiO_2 crystals from the NH_4OH catalysed process agglomerated when calcined. Therefore, the formation of polymeric gel in a HNO_3 catalyzed reaction minimizes crystal agglomeration and promotes the production of high porous TiO_2 particles during drying and calcinations.

Table 4. Influence of drying method (catalyst: HNO_3)

Sample No.	Drying Method	S_{BET} (m^2/g)	Pore Size (Å)	Pore Vol. (cm^2/g)
Gel-07	Oven 120°C	126.2	39.7	0.134
Gel-16	Rotary Evaporator 80°C + Oven 120°C	81.7	44.5	0.095

A typical plot of nitrogen adsorption-desorption isotherms for TiO_2 catalysts prepared by acid-catalyzed methods is shown in Figure 5. All adsorption isotherms of the catalysts prepared using HNO_3 exhibited capillary condensation at an intermediate relative pressure and a slight rise when closing to the saturation pressure, where secondary capillary condensation in the few large voids between crystalline grains started. This is Type IV isotherms plot, which is commonly obtained from mesoporous particles (Thomas and Lambert, 1980). The pore size of the catalysts was in the range of 32.1-56.4 Å, indicative of mesoporous substances (Igwe, 1995).

Table 5. Variation of synthesis catalyst (first drying in oven)

Sample No.	Catalyst	S_{BET} (m^2/g)	Pore Size (Å)	Pore Vol. (cm^2/g)
Gel-07	HNO_3	126.2	39.7	0.134
Gel-08	NH_4OH	21.5	77.2	0.095

The use of NH_4OH as hydrolysis catalyst led to the formation of particles characterized by macroporous property. Isotherms plot of TiO_2 prepared by base-catalyzed method is shown in Figure 6, a Type II plot, typical for the adsorption of monomolecular layer which often occurs on non-porous or macroporous solids (Thomas and Lambert, 1980). Table 5, however, indicates its pore size of 77.2 Å, a size that is classified under the category of mesopores (Igwe, 1995). Such a contradictory result could be due to the weak interaction of nitrogen-TiO_2, when pore filling also took place, leading to a limited uptake at high relative pressures (Thomas and Lambert, 1980).

Based on the isotherms plots, the trends generally represented the presence of one or a combination of various pore shapes, *i.e.* pore Types 4 to 8, 14, 15, and 17 that firstly identified by de Boer and Broekhoff (1995). But shape details can be predicted by observing pore distribution based on the Barrett-Johner-Halenda (BJH) desorption plot. Basically, all catalyst samples gave a similar trend as shown in Figure

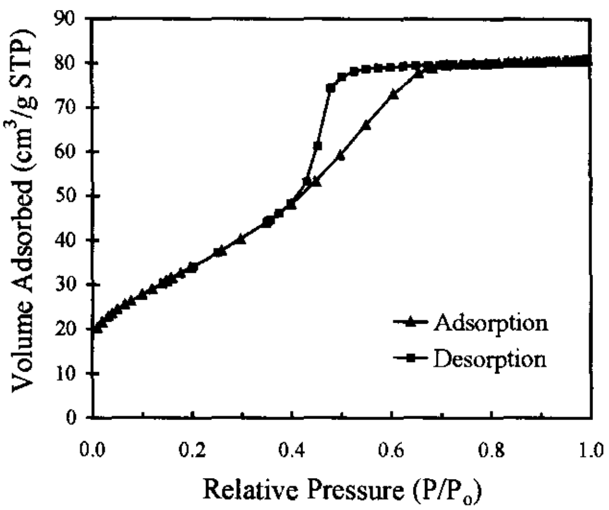

Figure 5. A typical isotherm plot of TiO_2 particles prepared by acid-catalyzed method

7, except for the catalyst prepared by NH_4OH-catalyzed method. It is predicted that the particles have a bottle-like shape pore as represented by Types 4, 6 or 14 in Figure 8.

The use of some metal additives was aimed to modify photoactivity of TiO_2 catalysts. However, it may also determine the growth of a polymeric cluster during the sol-gel process and the formation of surface and pore structures during heat treatment or calcination. Table 5 shows that the addition of Pt, Cu^{2+} and Fe^{3+} reduced the surface area of the catalysts. TiO_2 doped with silica exhibits a significant improvement in specific surface area of the catalyst; the area expanding to 257.3 m^2/g. This could be due to the considerably large porosity. This fact is in accordance with the findings by Jung and Park (2000), who found that the addition of amorphous silica into titania matrix helps to suppress the reduction of surface area at high calcination temperatures. High pore volume has been suggested as the reason behind such a high specific surface area.

Table 5. Influence of Additives

Sample No.	Additive	S_{BET} (m^2/g)	Pore Size (Å)	Pore Vol. (cm^3/g)
Gel-07	-	126.2	39.7	0.134
Gel-19	Pt	94.2	50.3	0.123
Gel-17	Fe^{3+}	74.3	46.2	0.090
Gel-18	Cu^{2+}	83.1	46.2	0.101
Gel-20	Si^{4+}	257.3	31.3	0.227

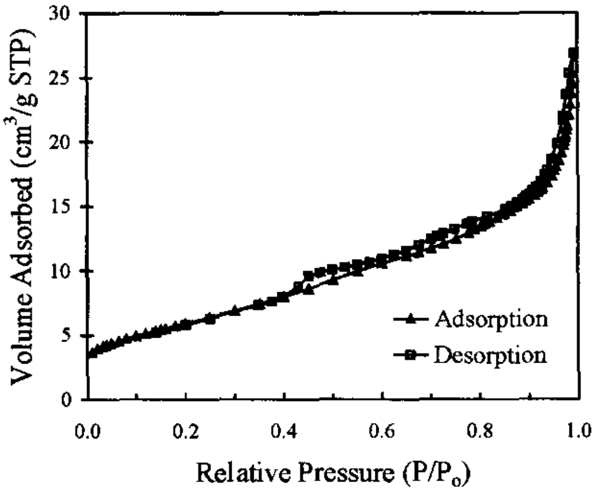

Figure 6. A typical isotherm plot of TiO_2 particles prepared by base-catalyzed method

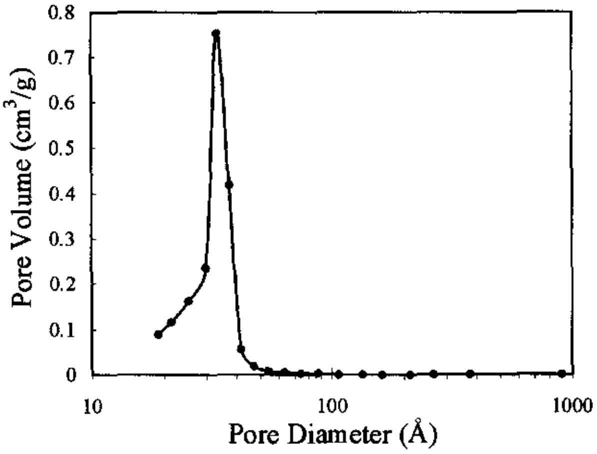

Figure 7. A typical BJH desorption plot of TiO_2 catalyst prepared by acid-catalyzed method

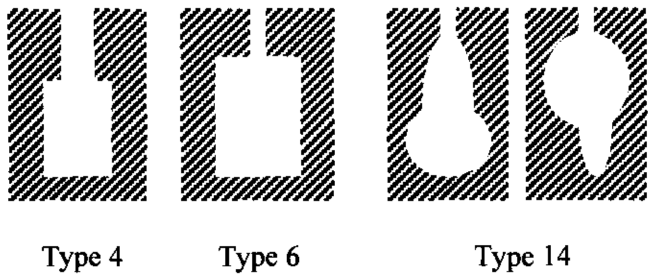

Figure 8. Predicted pore shapes of TiO_2 particles

Photocatalytic Oxidation of a Surfactant

Photoactivity of the powder catalysts was evaluated in degradation of SS-20 surfactant. The titania Gel-7 catalyst was selected to be tested since it has the highest surface area among the prepared catalysts, except when compared to the Gel-20 catalyst containing silica. As reference, the degradation using a commercial Degussa P25 TiO_2 catalyst was carried out with the result shown in Figure 9. Complete surfactant removal was achieved in 90 min, but total mineralization required longer time, as at 240 min (see Figure 10) 29% of initial TOC has remained. TOC concentration initially decreased up to TOC removal of 50% and then increased slightly before decreasing again at nearly linear rate. According to Suzuki *et al.* (2000), such trend is due to strong adsorption of surfactant and is followed by desorption of some intermediates resulting from surfactant breakdown, which are hydrophobic and less adsorbable. Figures 9 and 10 show that using the as prepared Gel-7 catalyst, surfactant degradation and TOC removal only reached 46% and 6%, respectively, after 240 min which were certainly much lower than Degussa P25 achievement. It was observed that the particle size of Gel-7 catalyst (0.5-1 mm) was much larger than Degussa P25 particles, giving the latter much higher contact surface between catalyst and reactants. The Degussa P25 catalyst has particle size of 30 nm. Although the as prepared catalyst has larger surface area, its mean pore size is possibly too small to allow easy access of liquid phase reactant. And also, some those large particles settled down on the bottom of reaction flask, resulting in less catalyst utilization.

In order to study the effect of particle size, the titania Gel-7 particles were gently crushed and then sieved to obtain the sizes of +100 mesh and +200 mesh. The results using smaller sizes of Gel-7 particles are given in Figures 9 and 10 for surfactant degradation and TOC removal, respectively. It appears that even the activity of Gel-7 catalyst was improved by reducing its particle size their performance did not meet the Degussa P25 catalytic activity. It seems that higher BET surface area of the original Gel-7 did not cause better activity, but in fact, its external surface has affected the reaction performance. Similar effect was also observed by Xu *et al.* (1999) in photocatalytic degradation of methylene blue. However, the large particle size will be easy to settle down, thus overcoming separation problem. If Gel-7 particle size can be made smaller, it might meet the Degussa P25 performance but with consideration on practical settling rate of catalyst particles. So far, +200 mesh particles quickly settled down as soon as the reaction was terminated.

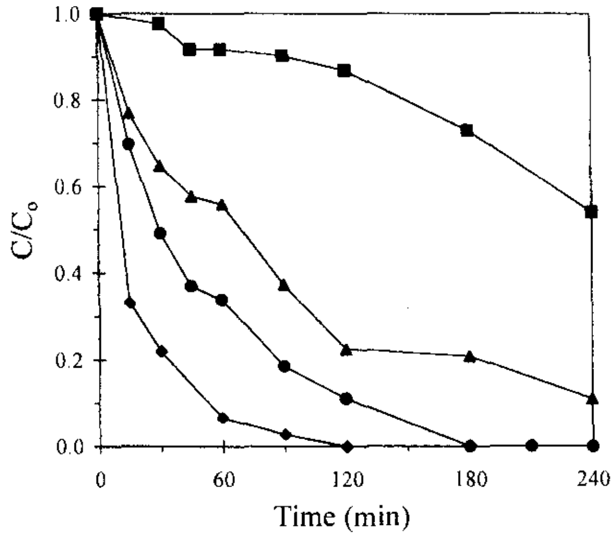

Figure 9. Remaining surfactant fraction (see Figure 10 for legends)

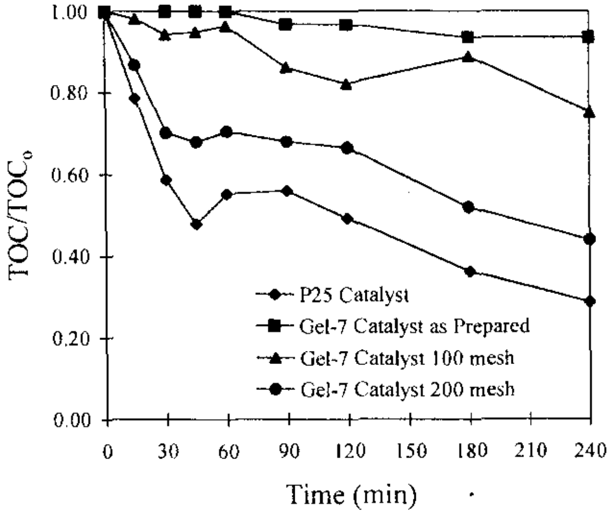

Figure 10. Remaining TOC fraction in surfactant degradation

A Fe doped TiO_2 catalyst (+200 mesh) was also used for photocatalytic oxidation of surfactant. However, this attempt to improve TiO_2 activity has failed, even reducing its activity further. After 240 min, the reaction only achieved surfactant conversion of 89%. Other modified TiO_2 catalysts were not employed for this reaction.

CONCLUSIONS

Preparation of titania catalysts by the sol-gel method was carried out under variation of water amount, synthesis catalyst, calcinations temperature, method of drying and metal additive. The resultant photocatalysts were characterized for crystal phase and surface properties. Basically, anatase form of titania crystal was obtained at calcination temperature of 450°C. The use of HNO_3, as a synthesis catalyst, yielded titania catalysts that have significantly higher surface area compared to commercial Degussa P25 TiO_2 catalysts. Analysis of isotherm and BJH desorption plots suggest that the catalysts were dominated by bottle-like shape mesopores. Photocatalytic performance of the prepared titania was evaluated by comparing it with the activity of Degussa P25 catalysts. Unfortunately, their activities could not meet one shown by the Degussa P25 catalyst, probably due to less accessibility of surfactant into the pore structure of titania prepared by sol-gel method. When the particles size of the prepared catalyst was reduced, the activity increased suggesting the importance of external surface area in a liquid phase photocatalytic process.

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