Effect of particle size on the photocatalytic activty of Ag_3PO_4

Coleen Angela Velasco[1], Bryan Paulo Banatin[1], James Garth Baron Acedera[1] and Eric Punzalan[1*]

[1] Chemistry Department, De La Salle University, 2401 Taft Ave., Manila 1004

*Corresponding Author: eric.punzalan@dlsu.edu.ph

Abstract: Silver orthophosphate (Ag_3PO_4) is a visible-light-active photocatalyst capable of advanced oxidation processes. This paper explores the effect of particle size on the photocatalytic activity of silver orthophosphate. The photocatalyst was synthesized via ion-exchange precipitation reaction using silver nitrate ($AgNO_3$) and sodium monohydrogen phosphate (Na_2HPO_4). Particle size control was achieved via five different drop rates of the phosphate solution. Synthesized catalysts were washed with distilled water three times and oven dried at 60°C overnight. Elemental composition was determined using Shimadzu EDX-7000 and particle sizes were measured using ImageJ on the SEM images of the catalysts. Analysis confirmed five different particle sizes of the catalyst and statistical analysis using One-way ANOVA and Tukey-Kramer test revealed 6 out of 10 comparisons are significantly different. Photocatalytic activities were tested on Rhodamine B solution (10ppm). Fifty milligrams (50mg) of the catalyst were mixed with 100 mL of dye solution and stirred for 30 minutes before illumination then 5mL aliquots were obtained every six minutes for 1 hour. UV-Vis analysis of the aliquots revealed reaction rates for each synthesized catalyst using pseudo-first order kinetics. Interestingly, catalysts with larger particle sizes showed faster reaction rates.

Key Words: Photocatalysis; silver orthophosphate; particle size; dye degradation; visible light

1. INTRODUCTION

Photocatalysis has been the focus of many studies for the degradation of pollutants in wastewater effluents. Silver orthophosphate (Ag_3PO_4) is a visible-light driven photocatalyst with a highly positive valence band position, low toxicity, high photocatalytic ability, and narrow band gap (Yi et al., 2010) which are ideal for a photocatalyst.

The photocatalytic activity of silver orthophosphate, and other photocatalysts, is due to the formation of the hole, hydoxyl radicals (OH.-) and superoxide radicals (O2.-) (Mohamed & Bahnemann, 2012). These oxidative agents, generated through advanced oxidation processes, degrade the organic pollutants in water.

Studies have shown that smaller particle size both increases the band gap of semiconducting materials and improve the charge separation (Martin

et al, 2015; Samal, Baral & Das, 2018). This calls for investigation on how particle size design can be used for optimization of the synthesis of silver orthophosphate for better photocatalytic activity.

In this study, particle size was controlled via variation in the drop rate of precipitant (phosphate solution) and its effect on the catalytic activity of Ag_3PO_4 was investigated.

2. METHODOLOGY

2.1 Synthesis of the catalyst

The catalysts were synthesized by precipitation reaction following the methods used by Zwara et al (2018). Five batches were made with varying particle sizes. For batch 1, 50 mg of silver nitrate was dissolved with twenty-five mL distilled water and placed inside a 400-mL beaker that is covered with foil. This was then placed inside the reaction vessel for continuous stirring. 50 mg of sodium phosphate was dissolved in twenty-five mL distilled water and was added dropwise to the 400-mL beaker for thirty minutes using a five mL syringe. For Batch 2, the same procedure followed but the reactants were added instantly. For Batch 3 4 and 5, the reactants were dropped for about 45 minutes, 60 minutes, and 90 minutes respectively.

For each batch, the mixture was transferred into six centrifuge tubes and was centrifuged for ten minutes. After centrifugation, supernatant was removed. Distilled water was added to the mixture and it was mixed using a vortex mixer before centrifugation for another 10 mins. This procedure was repeated thrice. The catalysts were dried at 60°C overnight.

2.2 Characterization and particle size measurement

The elemental composition of each synthesized catalyst was determined using Shimadzu EDX-7000 under vacuum within a collimator size of 3mm.

The catalysts were coated with gold using using Jeol JFC-1200 fine coater for SEM sample preparation. SEM images were captured using JSM-5310 scanning microscope. The particle size of each batch of catalyst was determined using ImageJ, an image processing software, by calibrating the SEM image and manually measuring the sizes of the particles and obtaining the average. Statistical analysis using One-way ANOVA and Tukey-Kramer Test was done to determine if the differences in particle sizes of each batch is significant. Tukey-Kramer test was chosen as post-hoc test because of unequal sample sizes.

2.2 Photocatalytic degradation of RhB

The photocatalytic activity of each synthesized catalyst was tested on Rhodamine B (RhB). In a 400mL-beaker, 100 mL of 10 ppm RhB solution was mixed with 50mg of catalyst and the mixture was mixed inside a closed apparatus (Fig. 1) equipped with magnetic stirrer for 30 minutes before turning on the light (Phillips 13 W LED lamp). Five-milliliter aliquots were obtained every 6 minutes for about 1 hr of illumination.
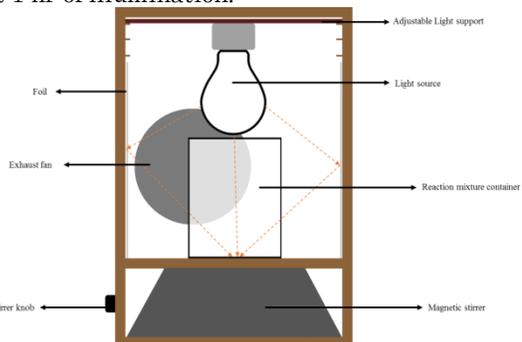
Fig 1. Diagram of the photocatalytic reaction apparatus

The samples were analyzed using UV-Vis at 561nm. Reaction rates were determined using pseudo-first order kinetics (Eq. 1).

$$C = C_0 e^{-kt} \qquad \text{(Eq. 1)}$$

where:

C = Concentration at time t

k = Rate constant

C_0 = Initial concentration

3. RESULTS AND DISCUSSION

3.1 Elemental composition

EDX analysis of the catalyst reveal the following percent elemental composition which is comparable to the expected values.

Table 1. Percent composition of catalysts

Sample	%Ag	%PO$_4$	%impurities
Theoretical	77.311	22.689	--
Batch 1	77.098	22.448	0.455
Batch 2	80.564	19.065	0.371
Batch 3	82.291	17.358	0.352
Batch 4	80.582	18.990	0.426
Batch 5	79.139	20.479	0.382

The analysis was programmed to convert the percent phosphorus into phosphate because EDX is not good for analysis of small elements like oxygen. Common impurities found in the five batches of catalyst include palladium, copper, cadmium and rhodium. Differences of the actual values from the theoretical value can be attributed to the impurities and excess reagents that remained after washing since the values are in percentages which changes relative to each other.

3.2 Particle size

SEM analysis showed that the catalysts have non-uniform rhombic morphology (Fig 2).
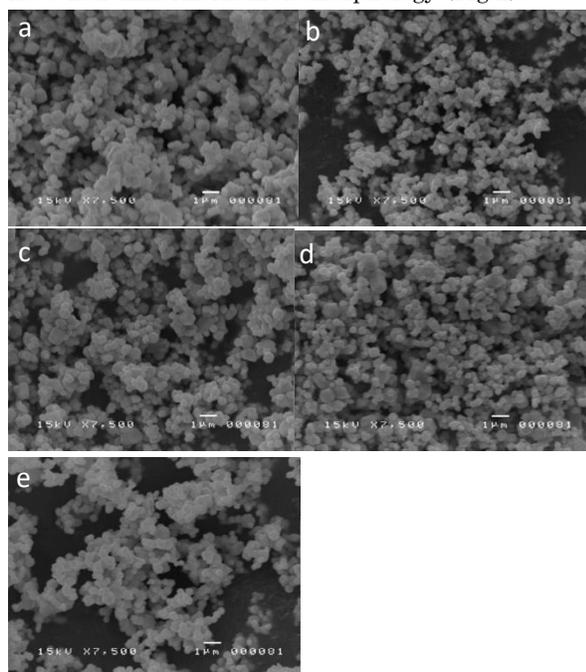
Fig 2. SEM images of (a) Batch 1, (b) Batch 2, (c) Batch 3, (d) Batch 4 and (e) Batch 5 catalysts at x7500 magnification

The average particle sizes of the photocatalysts are shown in Table 2.

Table 2. Average particle sizes of the catalysts

Batch (Sample size)	Average Particle Size (nm)
Batch 1 (n=122)	399 ($\pm$ 124)
Batch 2 (n=100)	414 ($\pm$ 148)
Batch 3 (n=104)	365 ($\pm$ 90)
Batch 4 (n=118)	335 ($\pm$ 103)
Batch 5 (n=104)	324 ($\pm$ 56)

Statistical analysis of the measured particle sizes using One-way ANOVA showed that F-value (14.01770618) is greater than the F-critical (2.388349181) which revealed that there is at least two groups that are significantly different from each other.

Post-hoc analysis using Tukey-Kramer Test was done to determine which groups are significantly different from each other. The two groups are significantly different from each other when the $q_{stat} > q_{critical}$.

Table 3. Results of Tukey-Kramer Test

Comparison			$q_{critical} = 3.858$ q_{stat}	Significance
1	vs	2	1.43863	No
1	vs	3	3.28318	No
1	vs	4	6.444171	Yes
1	vs	5	7.359222	Yes
2	vs	3	4.514259	Yes
2	vs	4	7.549365	Yes
2	vs	5	8.398425	Yes
3	vs	4	2.92846	No
3	vs	5	3.922816	Yes
4	vs	5	1.116158	No

The post-hoc test revealed that the particle sizes of batches 4 and 5 are significantly different from batch 1; batches 3, 4 and 5 are significantly different from batch 2; and particle sizes of batch 5 and 3 are significantly different from each other. The differences in other comparisons are deemed to be statistically insignificant.

By plotting the average particle size against the drop time (assuming that instant equals zero min), a linear trend can be seen (Fig 3) which suggests particle size control via length of dropping was achieved.
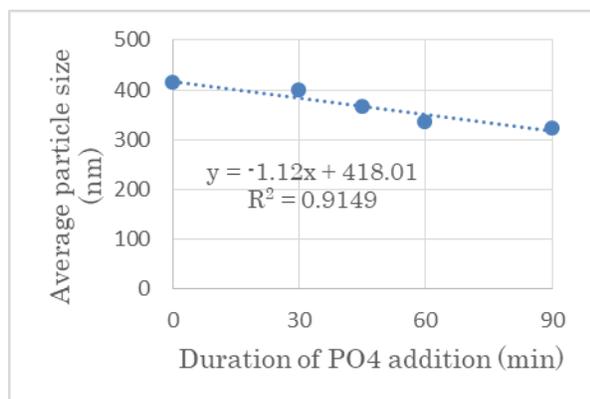
Fig 3. Plot showing the relationship of the duration of precipitant addition with the resulting average particle size.

3.3 Photocatalytic activity

Plot of relative concentration (C/C_0) of Rhodamine B against illumination time (min) is shown in Fig 4. The Rhodamine B dye is almost completely absent after 1hr of illumination.
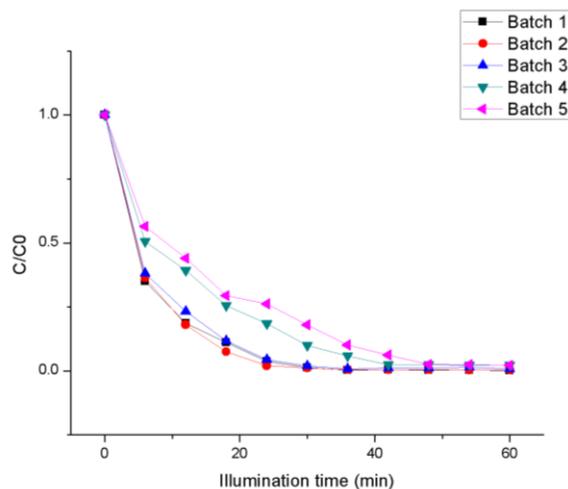
Fig 4. Degradation of Rhodamine B using different sizes of Ag_3PO_4

The rate constants were determined using pseudo-first order kinetics (Eq1) and were tabulated in Table 4.

Table 4. Rate constants of the different batches of catalysts

Batch	Average Particle Size (nm)	Rate Constant (min⁻¹)
1	399 ($\pm$ 124)	0.118
2	414 ($\pm$ 148)	0.101
3	365 ($\pm$ 90)	0.081
4	335 ($\pm$ 103)	0.070
5	324 ($\pm$ 56)	0.067

The effect of particle size on the rate of the degradation reaction is shown in the plot of particle size against rate constant (Fig 5). The plot reveals that the larger particles have higher catalytic activity. This is fascinating to note because the usual assumption for surface catalyzed reactions is that the smaller particles, which have higher surface area, will have higher reaction rates.
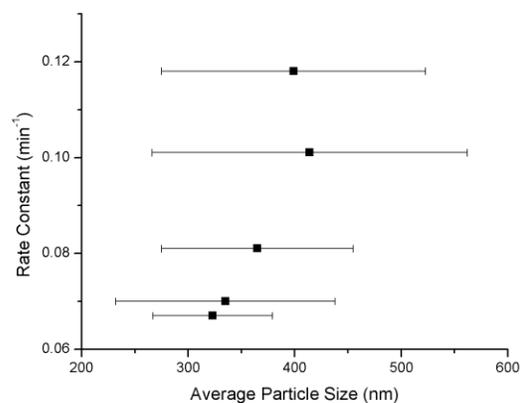
Fig 5. Effect of particle size on the degradation rate constant.

4. CONCLUSIONS

In summary, the method of varying dropping rates of the phosphate solution (precipitant), is effective in controlling the particle size of the silver orthophosphate catalyst. The catalysts with higher average particle size have higher catalytic activity which is contrary to usual assumptions.

It is recommended that the results be verified using a different method of controlling particle size like phosphate concentration or ionic strength of solution. Also, Fig 5 shows a peak pattern rather than a trendline which suggests that there might be an optimum particle size.

5. ACKNOWLEDGMENTS

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