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Effect of Calcination Temperature On Structure of Silica Doped On Zirconia for Photodegradation of 2-Chlorophenol

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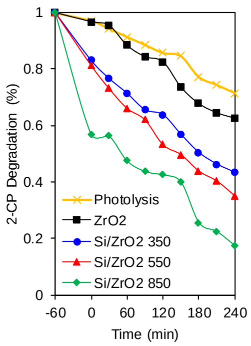
GRAPHICAL ABSTRACT



ABSTRACT

Simple microwave assisted method was employed to prepare silica (SiO_2) doped zirconia (ZrO_2) that synthesized under different calcination temperature which are 350, 550 and 850 °C and denoted as Si/ZrO_2-350, Si/ZrO_2-550 and Si/ZrO_2-850, respectively for photodegradation of 2-chlorophenol (2-CP). The synthesized catalysts were characterized by X-ray diffraction, Fourier transform infrared and ultraviolet-visible diffuse reflectance spectroscopy. The results showed that higher calcination temperature and the presence of Si induced the tetragonal phase of ZrO_2 as well as narrowed the band gap energy, which affected the photocatalytic activity. The catalyst was subsequently tested for the photocatalytic activity on 2-CP degradation under various parameters such as pH, catalyst dosage and initial concentration of 2-CP under visible light irradiation. Si/ZrO_2-850 showed the highest photodegradation of 2-CP due to presence of tetragonal phase on ZrO_2 that resulting stabilize the structure. The photocatalytic performance of the catalysts towards degradation of 10 mgL^{-1} of 2-CP at pH 3 and 0.125 g L^{-1} catalyst under visible light after 240 minutes as following order: Si/ZrO_2-850 (88%) > Si/ZrO_2-550 (65%) > Si/ZrO_2- 350 (57%) > ZrO_2-850 (37%). The photodegradation followed the pseudofirst order Langmuir-Hinshelwood kinetic model. This study demonstrated that the Si/ZrO_2 has a potential to be used in photocatalytic degradation of various organic pollutant.

Keywords: Calcination temperature; Microwave; Silica-zirconia; 2-chlorophenol

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1. INTRODUCTION

2-chlorophenol (2-CP) is a common organic compound found in wastewater as it is introduced mainly by chemical and pharmaceutical industry. It has been widely used as an antiseptic, as manufacture of insecticide profenofos and as an organic synthesis dye. Numerous industries have utilized 2-CP as intermediated chemical [1]. However, this intermediate is very risky in the situation of skin exposure (irritant), swallowing, inhalation and in the condition of eye contact (irritant). Excessive over-exposure will contribute to the death [2]. The resilience of the C-Cl bond in halo hydrocarbons is responsible for its toxicity and consistency in the biological system [3]. Hence, degradation of 2-CP into harmless product should be discovered rapidly before many people can get infected.

Nowadays, advanced oxidation processes (AOPs) have gained much attention as a promising method that can effectively degrade the organic pollutant in the wastewater [4,5]. This approach is characterized as oxidation processes involving the in-situ production of powerful oxidizing agents such as hydroxyl radicals (•OH) at appropriate concentrations to effectively decontaminate wastewater [6,7]. AOPs concept has been enlarge nowadays such as oxidative processes with sulfate radicals [8]. The effectiveness of AOPs will be decided by the production of reactive free radicals predominantly •OH.

Photocatalysis is one of the methods that employed from the AOPs. Zirconia (ZrO_2), one of the most suitable semiconductor photocatalysts, was widely used to degrade of organic pollutants [9]. However, the photocatalytic efciency of ZrO_2 is constrained by three key drawbacks [10, 11]. First, the small spectral response interval limits the UV region absorption range, which only accounts for less than 5% of the entire solar range. Then, the high electron–hole recombination rate results in low quantum yield. In addition, tetragonal phase (*t*-ZrO_2) stabilization typically involves higher temperatures (> 1000 °C) and/or suitable dopants with different valency, size, and electronegativity characteristics. Therefore, several efforts have been done to stabilize its phase and improve the photocatalytic efficiency of ZrO_2 as well as application potential of ZrO_2 [12]. Besides, altering the catalyst's physicochemical properties also enhanced the photocatalytic activity, mainly via calcination temperature [13]. Thus, in this study, synthesis of ZrO_2 by doping with SiO_2 will be focused on varying the calcination temperature that could increase the effectiveness of photodegradation of 2-CP. The ZrO_2 and SiO_2/ZrO_2 was synthesized by using microwave-assisted method and calcined under different calcination temperature (350, 550 and 850°C). The physicochemical properties of Si/ZrO_2 was analyzed by using X-ray diffraction, Fourier transform infrared and ultraviolet-visible diffuse reflectance spectroscopy. Photocatalytic activity of the photocatalysts was conducted under various parameters such effect of pH (3-11), catalyst dosage (0.125-0.625 g L^{-1}) and initial 2-CP concentration (10-100 mg L^{-1}).

2. EXPERIMENTS

2.1 Materials

2-CP, cetyltrimethylammonium bromide (CTAB), 2-propanol (Pr-OH), zirconium (IV) propoxide (ZrP), (3-aminopropyl)triethoxysilane (APTES) and ammonium hydroxide solution (NH_4OH) were purchased from Sigma Aldrich. Other than that, the all reagents were prepared using deionized water.

2.2 Catalyst Preparation

The Si/ZrO_2 was synthesized by using microwaveassisted method. Firstly, 4.8 g of CTAB surfactant was dissolved in the solution which is contained with 720 mL distilled water, 29 mL of 8 M NH_4OH and 120 mL propanol. The mixture then was stirred continuously for 30 min at 50 °C. 5.7 mL of ZrP was added into the mixture followed by 1.053 mL of APTES and stirred for 2 hours. The white solution was heated by using the microwave under a frequency of 2.45 GHz and heating power of 450W for 2 hours. The final product was dried overnight in oven before calcined at 850 °C for 3 hours and denoted as Si/ZrO_2-850. Similar procedure was applied for various calcination temperature of 350˚C, 550˚C and 850˚C and denoted as Si/ZrO_2-350, Si/ZrO_2-550 and Si/ZrO_2-850, respectively.

2.3 Characterization

The catalysts crystallinity were verified by D8 ADVANCE Bruker X-ray diffractometer. Meanwhile, Meanwhile, the chemical properties of the catalysts were detected by the KBr method via Perkin Elmer Spectrum GX FT-IR. The optical properties of the catalyst were measured by using Agilent Technologies Cary 60 UV-Vis spectrometer.

2.4 Catalytic testing

The photodegradation of 2-CP was carried out in a batch reactor, which fixed with cooling system, employing 400 W metal halide lamps. Before 0.375 g L^{-1} catalyst in 100 mL 2-CP solution (10 mg L^{-1}) being exposed to light radiation, the catalyst was stirred at pH = 5 in the dark for 1 h to achieve the equilibrium of adsorption/desorption. Each series of experiment was performed three times to ensure the consistency.

3. RESULTS AND DISCUSSION

Figure 1 shows a wide angle of XRD diffractogram of the commercial ZrO_2 and synthesized of Si/ZrO_2 under different calcination temperatures (350 °C, 550 ºC and 850 °C). The Si/ZrO_2-350 only showed the existence of the monoclinic phase (*m*-ZrO_2) with XRD peak at 2θ= 22° and 28.1º (ICDD No-01-083-0944) [14]. The Si/ZrO_2 synthesized catalysts is well indexed to *t*-ZrO_2 (ICDD No-01-079-1765) with the prominent XRD at 29.9° (101), 34.8° (110), 50.1° (112) and 60.0° (211) [15] when the calcination temperature increases up to 550 ºC. Interestingly, increased up to 850 ºC, the catalyst possessed the higher *t*-ZrO_2 phase without any phase impurities evidently confirmed by presence of additional peaks at 2θ= 34.8º (200), 50.1º (220) and 59.9º (311). In fact, the tetragonal crystalline form of ZrO_2 is most commonly used in catalysis and related activities and is therefore a technologically significant product. Both *t*-ZrO_2 and *m*-ZrO_2 were observed for commercial ZrO_2. This result shows that the presence of Si and higher calcination temperature could stabilize the *t*-ZrO_2.

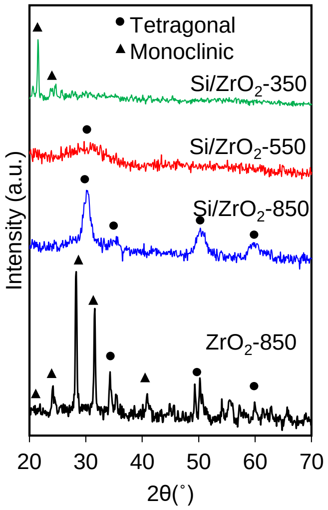

Figure 1: XRD patterns of all catalysts

For chemical properties studies, all the catalysts were then characterized by FTIR and the spectra in the region of 4000-400 cm^{-1} are shown in Figure 2. The Si/ZrO2 catalysts showed five main bands, which attributed to hydroxyl stretching (–OH, 3456 cm^{-1}), –OH vibration of the surface-adsorbed water (1620 cm^{-1}), Zr–OH bond (1384 cm^{-1}), Si–O–Si asymmetric stretching (1070 cm^{-1}), and t-ZrO_2 (464 cm^{-1}) [16,17]. The band at 740 cm^{-1} was observed only for Si/ZrO_2-350 and Si/ZrO_2-550, which correspond to the *m*-ZrO_2. Similarly, these phase also was observed for ZrO_2-850. As seen, the band at 1384 cm^{-1} was disappeared for Si/ZrO_2-550 and Si/ZrO_2-850, suggesting that the higher of calcination temperature could dispersed the Si well on the surface of ZrO_2 and the Si species may interact with ZrO_2 [16, 18]. Among all Si/ZrO_2 catalyst, Si/ZrO_2-850 showed the higher intensity of the band at 464 cm^{-1}, indicated that this catalyst possessed higher *t*-ZrO_2 which in line with XRD analysis.

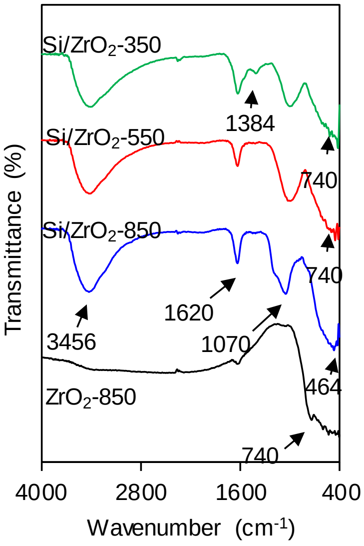

Figure 2: FTIR spectra of all catalysts

Band gap of the photocatalysts play an important key role in photocatalytic applications. The catalysts were then subjected to UV-Vis DRS to analyse band gap energy. Figure 3 illustrates the wavelength measurement to calculate bandgap energy. The bandgap of the samples was calculated using the equation of $E = 1240/\lambda$, where E is the band gap energy in eV and λ is the wavelength in nanometres [19]. The summary of the band gap for all catalysts are stated in Table 1. Si/ZrO_2-850 showed the lowest band gap energy (2.64 eV) compared to commercial ZrO_2 (4.35 eV). The reduction of bandgap after Si doped on ZrO_2 at higher temperature is might be due to the more formation of surface defect [3]. While, among all synthesized Si/ZrO_2, Si/ZrO_2-850 showed the lowest band gap energy and this result led to the potential use of it in visible light responsive photocatalytic reaction.

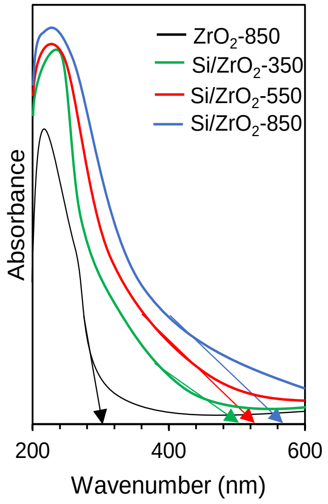

Figure 3: UV-Vis DRS for all catalysts

Table 1 Band gap of the catalysts

Catalyst	Band Gap (eV)
ZrO_2-850	4.35
Si/ZrO_2-350	2.33
Si/ZrO_2-550	2.29
Si/ZrO_2-850	2.21

The photocatalytic performance of the synthesized catalysts was evaluated on photodegradation of 2- CP and the results are shown in Figure 4 under visible light irradiation for 240 minutes. The photolysis of 2-CP shows only 30% of 2-CP is degraded, indicating the pollutant's higher stability. The 2-CP degradation was activated by electronically excited 2-CP via direct light absorption, resulting in cleavage of the C–CI bond. Si/ZrO_2-850 (83%) catalyst was exhibited the highest photocatalytic performance compared to the Si/ZrO_2-550 (65%), Si/ZrO_2-350 (57%) and ZrO_2-850 (37%). This is due to higher of tetragonal phase of zirconia and narrowing of its band gap which can led to decrease in electron-hole recombination rate [20,21].

In fact, the optimum pH was found to be 3 after varying the pH from 3 to 11 (Figure 5A). This result may be explained by the amphoteric behavior of the catalyst when the photoreaction takes place on its surface, which is dependent on the basis of the zero-pointcharge (pH_{ZPC}). The inset figure shows that the pH_{ZPC} was found to be at pH 6. Indeed, the catalyst surface would be positively charged below this pH value and electrostatically attracted to the negatively charged of 2-CP, and vice versa [16,18]. Thus, the optimum reaction conditions are in acidic conditions.

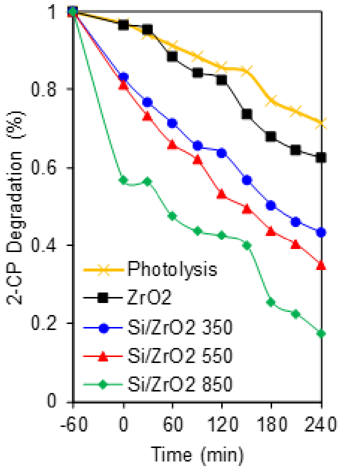

Figure 4: Photodegradation of 2-CP using different type of catalyst ([2-CP] = 10 mgL^{-1}, W= 0.375 g L^{-1}, pH=3).

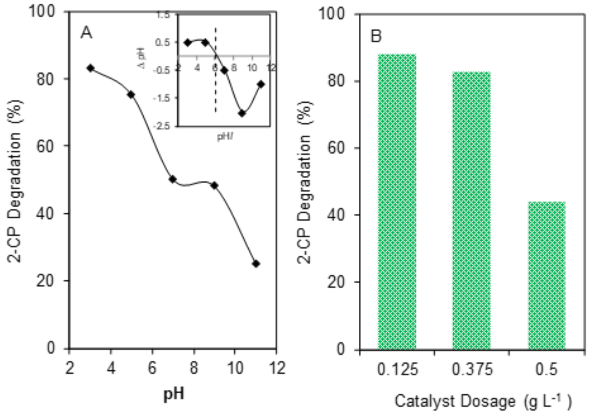

Figure 5: Effect of (A) pH and (B) catalyst dosage towards photodegradation of 2-CP using Si/ZrO_2-850

While the optimum catalyst dosage was 0.375 g L^{-1} to give 83% degradation of 2-CP, due to after the optimum catalyst loading is accomplished (Figure 5B). This is because the higher the catalyst dose, the higher the number of active sites that could absorb more photons and 2-CP. However, excess catalytic dosage may create greater turbidity, which would reduce its penetration because of light dispersed and inhibit the photocatalytic mechanism [18,22]. Nevertheless, the number of active sites and the formation of reactive oxygen species (ROS) will increase correspondingly when the amount of catalyst dosage increased [23]. Adequate loading of the catalyst enhances the efficiency of generation of electron/hole pairs to boost the degradation of pollutants [2,3].

The initial concentration of 2-CP is one of the driving parameters in photodegradation of 2-CP. The effect of the initial concentration on 2-CP degradation was studied by preparing different number of 2-CP solutions (10-100 mgL^{-1}). Figure 6A shows that the photocatalytic activity was decreased with increasing the initial concentration of 2-CP over constant catalyst dosage. This reaction was favourable at low concentration which is 10 mg L^{-1}. In fact, the penetration of light to the surface of the catalyst has been hampered, most likely due to the deposition of contaminants covering the surface of the catalyst [4,18].

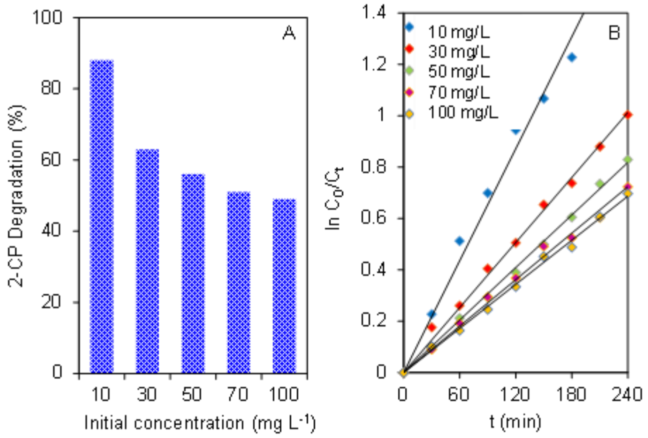

Figure 6: (A) Photodegradation of 2-CP with different initial concentrations of 2-CP and (B) Photodegradation kinetics of 2-CP using Si/ZrO_2-850 at different initial concentrations (W=0.125 g L^{-1}, pH= 3).

In general, the kinetics of most organic compounds undergoing photocatalytic reactions are defined in a pseudo first-order model, which is rationalised in terms of the Langmuir-Hinshelwood model modified to accommodate reactions that have occurred at the solid-liquid interface [24]. At low initial 2-CP concentration, the simplest equation for the rates of photodegradation of 2-CP is given by the equation 1 and 2 [24].

$$\ln C_t = -kt + \ln C_0 \tag{1}$$

where k is the pseudo first-order rate while C_o and C_t are the concentrations of 2-CP initially and at time t, respectively. The integration of (Equation 1) yields the (Equation 2),

$$\ln\left(\frac{C_o}{C_t}\right) = k_r\,K\,t = k_{app}\,t \tag{2}$$

The linearity of the ln (C_0/C_t) plot vs. the irradiation time shown in Figure 6B confirmed that the reaction process implemented the pseudo-first order kinetics model. Line slope was the apparent first-order rate constant (k_{app}) and the value obtained (Table 2) showed an important and beneficial

Table 2 Percentage degradation at different initial concentration of PCT and pseudo-first-order apparent constant values for PCT degradation using 5% Fe_3O_4/WTC [W= 0.4 g/L, t=2 h, pH=5, T= 30°C].

Initial concentration of 2-CP, C_o (mg L^{-1})	Degradation (%)	Reaction rate, k_{app} (x 10^{-2} mg L^{-1} min^{-1})	Initial rate, r_o (x 10^{-1} mg L^{-1} min^{-1})
10	83	7.30	7.3
30	63	4.20	12.6
50	56	3.40	17.0
70	51	0.30	21.0
100	49	0.29	29.0

effect of the Si/ZrO_2-850 on the photodegradation of the 2-CP. The k_{app} values decreased with an increasing initial concentration, suggesting that the system is favourable at a low concentration [25]. At a lower concentration, the reaction rate is able to manage the mechanism, since the active sites on the catalyst's surface were only partly occupied by adsorbed 2-CP molecules. As a result, at higher concentrations, hydroxyl radicals become a restricting reactant and thus lower the reaction rate**.**

The line with an intercept of $1/k_r$ and $1/k_r K_{LH}$ was obtained from the Langmuir Hinshelwood (L-H) kinetic formula (Equation 3) [6],

$$\frac{1}{r_o} = \left[\frac{1}{k_r K_{LH}}\right]\left[\frac{1}{C_o}\right] + \frac{1}{k_r} \qquad (3)$$

where k_r is the reaction rate constant (mg L^{-1} min^{-1}), K_{LH} is the adsorption coefficient of the reactant (L mg^{-1}) and C_o is the initial concentration of 2-CP (mg L^{-1}). The calculated values of k_r and K_{LH} were 0.012 mg L^{-1} min^{-1} and 0.003 L mg^{-1}, respectively. These results illustrated that since k_r, > K_{LH}, suggesting that 2-CP adsorption on the surface of Si/ZrO_2- 850 was controlling step in the photodegradation [6].

4. CONCLUSION

In this study, silica loaded on zirconia (Si/ZrO_2) was successfully synthesized by microwave-assisted method under various calcination temperature, which were then characterized by XRD, FTIR and UV-Vis/DRS. The results showed that higher calcination temperature and the presence of Si induced the tetragonal phase of ZrO_2 as well as narrowed the band gap energy, which affected the photocatalytic activity. The photocatalytic performance of the catalysts towards degradation of 10 mg L^{-1} of 2-CP at pH 3 and 0.125 g L^{-1} catalyst for 240 minutes under visible light was in the following order: Si/ZrO_2-850 (88%) > Si/ZrO_2-550 (65%), Si/ZrO_2-350 (57%) > ZrO_2-850 (37%). Si/ZrO_2-850 shows the highest photocatalytic performance due to narrow band gap, high crystallinity and more tetragonal phase.

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