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Understanding the effect of the calcination process on the structure of mesoporous silica zirconia photocatalysts for Bisphenol A degradation

N.S. Hassan[1,2]*, A.A. Jalil[1,2]

[1] *Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia*
[2] *Centre of Hydrogen Energy, Institute of Future Energy, 81310 UTM Johor Bahru, Johor, Malaysia*

**Corresponding Author: nurulsahida@utm.my*

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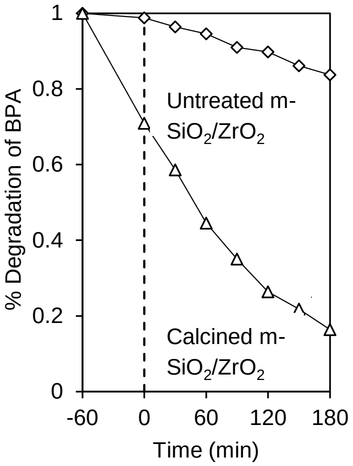

ABSTRACT

The mesoporous silica zirconia (m- SiO_2/ZrO_2) was successfully synthesized in this study using a microwave method, and the effect of the calcination process was studied. In this study, half of the sample was left untreated (labeled "untreated sample"), while the other half was calcined at 850 °C for 3 hours in an air atmosphere in a muffle furnace to remove the surfactant. X-ray diffraction, Fourier transform infrared spectroscopy, ultraviolet-visible differential reflectance spectroscopy, nitrogen adsorption-desorption spectroscopy, and electron spin resonance spectroscopy were utilized in order to analyze the catalysts that were produced. The findings from the characterization showed that the calcination procedure caused the creation of oxygen vacancies and increased the surface area, both of which affected the photocatalytic activity. The photocatalytic activity of the calcined m-SiO_2/ZrO_2 (80%) catalyst was superior to that of the untreated m-SiO_2/ZrO_2 (19%) catalyst. This result demonstrated that the calcined m-SiO_2/ZrO_2 gave the highest degradation percentage of 10 mgL^{-1} of BPA at pH 7 and 0.375 g L^{-1} catalyst under visible light within 180 minutes. Zirconia's greater surface area and its natural occurrence in the tetragonal phase are both to blame for this phenomenon. In addition, there is the possibility that a greater proportion of oxygen vacancy will result in a smaller band gap and a lower electron-hole recombination rate. After five cycles, the photocatalytic activity exhibited by calcined m-SiO_2/ZrO_2 remained unchanged.

Keywords: Calcination process, Microwave, Silica-zirconia, Bisphenol A

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1. INTRODUCTION

Bisphenol A (BPA) is a chemical that is commonly used in the production of plastic products, such as epoxy and polycarbonate resins, as well as in the lining of food and beverage containers [1]. However, BPA has been found to have xenoestrogenic activity, which means that it can mimic the effects of estrogen in the body, leading to potential health risks such as reproductive and developmental problems, obesity, and some cancers [2]. As a result, there has been increased concern about the potential risks of BPA exposure to the environment and human health, and various methods have been explored to remove or reduce its presence in water and other substances [3]. These methods include adsorption, where BPA is physically removed from the water by attaching to a surface, filtration, which uses physical barriers to trap BPA, and chemical oxidation, which uses chemical reactions to break down and remove BPA [4]. Overall, the use of these methods can help reduce BPA exposure and mitigate its potential risks to human health and the environment. However, it's important to note that preventing exposure in the first place is the best way to avoid potential risks associated with BPA [5]. This can be achieved by reducing the use of BPA-containing products and choosing safer alternatives.

Advanced oxidation processes (AOPs) have been gaining popularity as a promising method for effectively degrading organic pollutants in wastewater [6]. AOPs are characterized as oxidation processes that involve the in-situ production of powerful oxidizing agents such as hydroxyl radicals (·OH) at appropriate concentrations to effectively decontaminate wastewater [7]. AOPs can produce hydroxyl radicals by different methods, such as photochemical processes using UV radiation, photocatalytic processes, and chemical processes using hydrogen peroxide, ozone, or other oxidants. Recently, AOPs have been expanded to include oxidative processes with sulfate radicals, which are also powerful oxidizing agents that can effectively degrade organic pollutants. Overall, AOPs offer a promising approach for the effective degradation of organic pollutants in wastewater [8]. However, the use of AOPs must be carefully optimized and tailored to the specific contaminants and wastewater characteristics to achieve maximum efficiency and minimize any potential negative impacts on the environment.

Photocatalysis is a type of AOP that uses semiconductors to produce reactive oxygen species, such as hydroxyl radicals, to degrade organic pollutants in wastewater. Zirconia (ZrO_2) is one of the most suitable semiconductor photocatalysts that have been used for this purpose [9].However, there are some limitations to the photocatalytic efficiency of ZrO_2. One of the main limitations is its small spectral response interval, which limits its ability to absorb UV radiation, which only accounts for less than 5% of the entire solar range. Another limitation is the high electron-hole recombination rate, which results in low quantum yield, limiting the efficiency of the photocatalytic process. Additionally, the tetragonal phase (t-ZrO_2) stabilization typically involves high temperatures (> 1000 °C) and/or suitable dopants with different valency, size, and electronegativity characteristics, which can limit its application potential [10, 11].

To address these limitations, several efforts have been made to stabilize the tetragonal phase of ZrO_2 and improve its photocatalytic efficiency, including altering the catalyst's physicochemical properties through calcination temperature [12, 13]. Previously, we have sythezised Si/ZrO_2 catalyst with different calcination temperature which are 350, 550 and 850 °C and tested for photodegradation of 2-chlorophenol (2-CP). We have found that the t-ZrO_2 was stabilized at temperature up 850 °C. Only a few studies explored the differences between untreated and calcined catalysts. Therefore, this study will contribute to the literature with the help of providing more details about the calcination effect on mesoporous silica zirconia (m-SiO_2/ZrO_2). In this study, m-SiO_2/ZrO_2 was synthesized by using the microwave-assisted method and tested for degradation of BPA. The catalyst was characterized by X-ray diffraction (XRD), N_2 adsorption-desorption, Fourier-transformed infrared spectroscopy (FT-IR), ultraviolet-visible diffuse reflectance spectroscopy (UV/DRS), and electron-spin resonance (ESR). The influence of the calcination process on the properties is discussed in detail in the discussion section.

2. EXPERIMENTS

2.1 Materials

The following chemicals were obtained from Sigma Aldrich: bisphenol A (BPA), cetyltrimethylammonium bromide (CTAB), 2-propanol (Pr-OH), zirconium (IV) isopropoxide (ZrP), 3-aminopropyl)triethoxysilane (APTES), and ammonium hydroxide solution (NH_4OH). Everything else, including the reagents, was made with deionized water.

2.2 Preparation of catalyst

The m-SiO_2/ZrO_2 was synthesized by using the microwave-assisted method. Firstly, 4.8 g of CTAB surfactant was dissolved in the solution which contained 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 the oven. The material obtained was divided into two parts. While half of the sample was not subjected to the calcination procedure (labeled as untreated sample), the other half was calcined at 850 °C for 3 hours in an air atmosphere in a muffle furnace to eliminate the CTAB from the sample.

2.3 Characterization

The catalyst's crystallinity was verified by the D8 ADVANCE Bruker X-ray diffractometer. Meanwhile, the chemical properties of the catalysts were detected by the KBr method via Perkin Elmer Spectrum GX FT-IR and JESFA100 ESR spectrometer, respectively. Textural properties were determined by the Quantachrome Autosorb-1 analyzer. The optical properties of the catalyst were measured by using Agilent Technologies Cary 60 UV-Vis spectrometer.

2.4 Catalytic testing

The photodegradation of BPA was carried out in a batch reactor, which was fixed with a cooling system, employing 400 W metal halide lamps. Before 0.375 g L^{-1} catalyst in 100 mL BPA solution (10 mg L^{-1}) was exposed to light radiation, the catalyst was stirred at pH = 7 in the dark for 1 h to achieve the equilibrium of adsorption/desorption. Each series of experiments was performed three times to ensure consistency.

3. RESULTS AND DISCUSSION

3.1 Catalyst characterization

Figure 1 shows a wide angle of the XRD diffractogram of the untreated and calcined m-SiO_2/ZrO_2. ZrO_2 can exist in three different crystal structures or phases: monoclinic (*m*), tetragonal (*t*), and cubic. The crystal structure of ZrO_2 depends on factors such as temperature and pressure. It's interesting to note the difference in the crystal structures of the two ZrO_2 catalysts, and how the calcination process affected their crystal structure and XRD patterns. The presence of the prominent XRD peaks at 17.9°, 24.3°, and 28.2° in the untreated catalyst is consistent with the monoclinic phase of ZrO_2, while the major peaks at 29.9°, 34.8°, 50.1°, and 60.0° in the calcined catalyst are characteristic of the tetragonal phase of ZrO_2 [10].

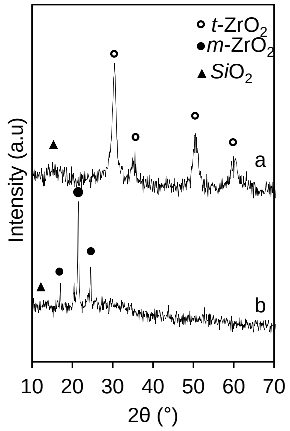

Figure 1 XRD patterns of (a) calcined m-SiO_2/ZrO_2, (b) untreated m-SiO_2/ZrO_2 catalysts

The absence of the diffraction peak for the monoclinic phase in the calcined catalyst suggests that the calcination process may have transformed the monoclinic phase into the tetragonal phase [9, 11]. It's also interesting to note the potential advantages of the tetragonal phase for liquid-phase reactions, such as the increased number of active sites for photocatalytic activity. The more symmetrical lattice structure of the tetragonal phase may allow for more efficient adsorption and reaction of the reactants on the catalyst surface [13]. This result is in line with the higher surface area of the calcined catalyst (135.7 m^2/g) that possessed the tetragonal phase structure (Table 1). The untreated m-SiO_2/ZrO_2 only exhibit 50.1 m^2/g of surface area.

For chemical properties studies, all the catalysts were then characterized by FTIR and the spectra in the region of 1600-400 cm^{-1} are shown in Figure 2. The band at 3401 cm^{-1} was assigned as hydroxyl stretching, which this band decreased slightly after the calcination process. In addition, the bands at 2920, 2846 and 2356 cm^{-1} were only observed in untreated m-SiO_2/ZrO_2, which corresponded to the C-H stretching of the methyl group in the organic surfactant molecules [14]. After calcined the catalyst, those bands vanished, confirming that CTAB was eliminated or removed at a higher calcination temperature. The band at 1610 cm^{-1} was found to be made up of surface-adsorbed hydroxyl groups [9]. This species significantly improves photocatalytic systems by interacting with photogenerated holes to improve charge transfer and prevent recombination of electron-hole pairs. The band at 1465 cm^{-1} was attributed to the ammonium ions [15]. FT-IR spectra of both materials showed the typical characteristic peaks of silica at ~1060-760 cm^{-1}, agreeing with the vibrations of the Si–O–Si bond [10]. Meanwhile, the metal-OH and metal-O were detected at 1380 and 501 cm^{-1}. Interestingly, the band at 464 cm^{-1} in calcined catalyst could be attributed to the tetragonal ZrO_2, which is in line with XRD analysis.

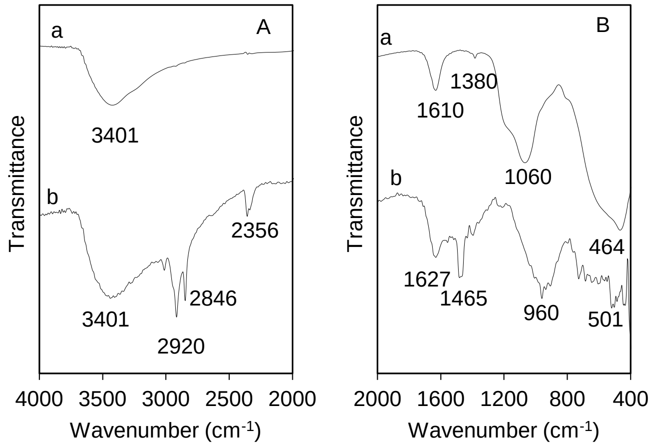

Figure 2 FTIR spectra of (a) calcined m-SiO_2/ZrO_2, (b) untreated m-SiO_2/ZrO_2 in the range of (A) 4000-2000 cm^{-1} and (B) 2000-400 cm^{-1}

Table 1 Properties of the catalysts

Catalyst	Wavelength (nm)	Band Gap (eV)	Surface Area (m^2/g)
Untreated m-SiO_2/ZrO_2	345	3.60	50.1
Calcined m-SiO_2/ZrO_2	420	2.95	135.7

The band gap of the photocatalysts plays an important key role in photocatalytic applications. The catalysts were then subjected to UV-Vis DRS to analyze band gap energy. Figure 3 illustrates the wavelength measurement to calculate bandgap energy. The band gap 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 [16]. The summary of the band gap for all catalysts is stated in Table 1.

The calcined m-SiO_2/ZrO_2 showed the lowest band gap energy (2.95 eV) compared to untreated m-SiO_2/ZrO_2 (3.60 eV). This may be due to the higher amount of oxygen vacancies in the calcined m-SiO_2/ZrO_2 as a consequence of the drastic condensation during the synthesis and calcination process. In contrast, the formation of oxygen vacancies in the untreated m-SiO_2/ZrO_2 only occurred during the synthesis. This result was confirmed by the ESR analysis with the higher intensity of g-value at 2.011 in calcined m-SiO_2/ZrO_2 representing the oxygen vacancies [3]. These characteristics hold significant promise for visible-light-driven photocatalytic processes.

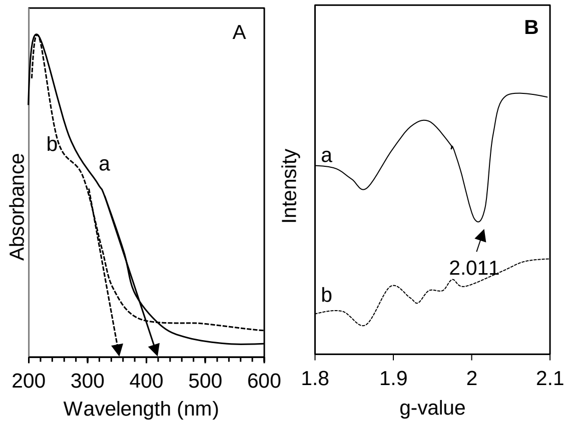

Figure 3 (A) UV-Vis DRS spectra and (B) ESR spectra for (a) calcined m-SiO_2/ZrO_2, (b) untreated m-SiO_2/ZrO_2 catalyst

3.1 Catalytic performance

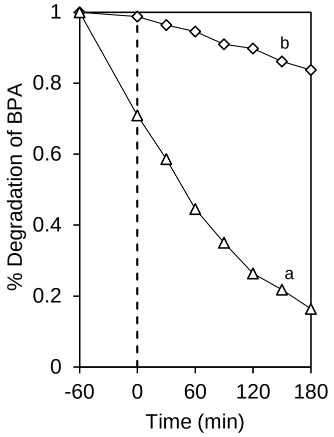

Figure 4 Photodegradation of BPA using a different type of catalyst which (a) calcined m-SiO_2/ZrO_2 and (b) untreated m-SiO_2/ZrO_2 ([BPA] = 10 mgL^{-1}, W= 0.375 g L^{-1}, pH=7).

Photodegradation of BPA was used to test how well the synthesized catalysts worked as photocatalysts. The results are shown in Figure 4, which was exposed to visible light for 180 minutes. The calcined m-SiO_2/ZrO_2 (80%) catalyst exhibited the highest photocatalytic performance compared to the untreated m-SiO_2/ZrO_2 (19%) This is due to the higher tetragonal phase of zirconia and higher surface area. In addition, a higher amount of oxygen vacancy contributed to the narrowing of its band gap which can lead to a decrease in electron-hole recombination rate [17, 18].

The possibility of recycling a catalyst is receiving a lot of attention since it has the potential to lower operating costs, which in turn encourages photocatalysis as an effective method for the treatment of wastewater [19]. As a result, several different studies have been carried out to assess the catalyst's resistance to BPA photodegradation (Figure 5). After five cycles, there was only a slight drop in the percentage of photodegradation, which indicated that the catalysts have outstanding photoactivity and reusability.

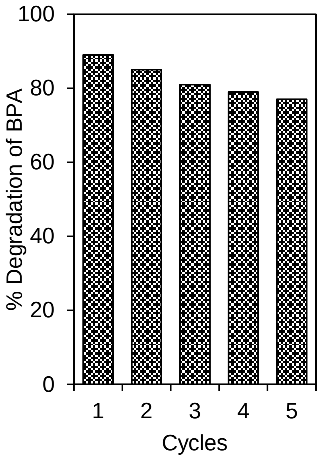

Figure 5 Regeneration studies of calcined m-SiO_2/ZrO_2 catalyst ([BPA] = 10 mgL^{-1}, W= 0.375 g L^{-1}, pH=7).

4. CONCLUSION

In this study, the mesoporous silica zirconia (m-SiO_2/ZrO_2) was successfully synthesized through a microwave method and studied the effect of the calcination process, which half of the sample was left untreated (labeled "untreated sample"), while other half was calcined at 850 °C for 3 hours in an air atmosphere in a muffle furnace to get rid of the CTAB. The synthesized catalysts were characterized by XRD, FTIR, UV-DRS, N_2 adsorption-desorption, and ESR spectroscopy. The characterization data showed that the calcination process induced the formation of oxygen vacancies and increased the surface area, which affected the photocatalytic activity. In terms of photocatalytic activity, the calcined m-SiO_2/ZrO_2 (80%) catalyst outperformed the untreated m-SiO_2/ZrO_2 (19%). The increased surface area and occurrence of the tetragonal phase of zirconia are responsible for higher photoactivity. In addition, a smaller band gap and lower electron-hole recombination rate can result from a greater amount of oxygen vacancy. The calcined m-SiO_2/ZrO_2 catalyst maintained photocatalytic activity after five cycles.

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CONFLICT OF INTEREST

The authors confirm that there are no known conflicts of interest associated with this publication.

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