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Research Article

Catalytic Performance of TiO_2–Carbon Mesoporous-Derived from Fish Bones in Styrene Oxidation with Aqueous Hydrogen Peroxide as an Oxidant

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Abstract

The catalytic performance of titania-supported carbon mesoporous-derived from fish bones (TiO_2/CFB) has been investigated in styrene oxidation with aqueous H_2O_2. The preparation steps of (TiO_2/CFB) catalyst involved the carbonization of fish bones powder at 500 °C for 2 h. followed by impregnation of titania using titanium(IV) isopropoxide (500 µmol) precursor, and calcined at 350 °C for 3 h. The physical properties of the adsorbents were characterized using Fourier transform infrared, X-ray diffraction (XRD), Scanning electron microscopy with energy dispersive X-ray (SEM-EDX), and nitrogen adsorption-desorption studies. The catalytic test was carried out using styrene oxidation with H_2O_2 as an oxidant at room temperature for 24 h. Its catalytic activity was compared with Fe_2O_3/CFB, CuO/CFB, TiO_2, and CFB catalysts. It is demonstrated that the catalytic activity of TiO_2/CFB catalyst has the highest compared to Fe_2O_3/CFB, CuO/CFB, TiO_2, and CFB catalysts in the oxidation of styrene with styrene conversion ~23% and benzaldehyde selectivity ~90%. Kinetics of TiO_2/CFB catalyzed oxidation of styrene has been investigated and mechanism for oxidation of styrene has been proposed.

Keywords: Titania; Fish bones; Carbon; Oxidation; Styrene; Hydrogen peroxide

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1. Introduction

Styrene oxidation is one of the vital reactions in the oxidation of olefin for the production of various fine chemicals, such as: benzaldehyde, phenyl acetaldehyde, and styrene epoxide. Benzaldehyde produced in this reaction has attracted interest due to this compound is used for the production of perfumes, pharmaceuticals, and agrochemicals [1]. Oxidation styrene with hydrogen peroxide as an oxidant is highly

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advocated, because it is bestowed with advantages, such as: an environmentally friendly, high atom economy, and only water as the by-product. Many heterogeneous catalysts have been developed to increase yield product in styrene oxidation with H_2O_2. Multifarious efforts have been taken, including metal-supported mesoporous materials [2–6], metal-supported carbon material [7,8] and single-component metal oxides such as Fe_2O_3 [9] and Fe_3O_4 [10]. However, those catalysts, in general, involve complicated preparation methods, high production costs, and environmentally unfriendly.

Titanium dioxide (TiO_2) or titania is a very well-researched materials catalysts that exhibit high efficiency in the oxidation reaction due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties. In nature, titania can be found in four polymorphs minerals form such as rutile, anatase, and brookite and titanium dioxide (B) or TiO_2(B) [11,12]. Anatase and rutile were commonly used in the oxidation reaction due to commercial availability, large amounts of reactive oxygen species like hydroxyl (•OH) radicals, hydroperoxy radicals (•OOH) and superoxide ($•O_2^-$) radical anion onto TiO_2 surface [1]. However, titania has low product yields if it is used without supported by catalyst support [13,14].

A support or a carrier is the inert substance that spreading out an expensive catalyst ingredient for its most effective use, expressly, the supports allow catalysts deposition or distribution homogeneously onto their surface, thus maximizing the number of catalytic active sites for reactions. Carbon can be considered as the potential catalyst supports, which can be used for catalyst reaction, but the support itself is nonreactive [6]. Waste from fish bones can be used as a particular alternative precursor for producing mesoporous carbon with a straightforward method [15].

Herein, we have developed a heterogeneous oxidation catalyst, a combination of titania as an active catalytic site and carbon mesoporous-derived fishbone as catalyst support. This catalyst system, titania supported carbon mesoporous-derived fishbone, has advantages such as cheaper, non-toxic, and environmentally friendly. The catalytic performance of this system was compared to the other transition metals supported carbon derived fish bones such as iron (Fe_2O_3) and copper. The oxidation styrene with aqueous H_2O_2 as an oxidant was used as a model reaction.

2. Materials and Methods

2.1 Carbonization Process

The waste of fish bones was collected from many food companies around Samarinda, East Kalimantan, Indonesia. The fish bone was washed with boiling water to remove impurities. Then, it was dried in the oven at 110 °C overnight. The dried fish bone was crushed to powder and carbonized in a furnace at 500 °C for 2 h. The carbon-derived from fish bone is labeled as CFB.

2.2 Titania Impregnation

One gram CFB was immersed in 10 mL toluene (Merck) that containing titanium(IV) isopropoxide (500 µmol, Sigma Aldrich) and stirred until all of the toluene solvent completely evaporated. The sample was washed with ethanol (Merck) to remove the residual toluene and subsequently dried at 110 °C overnight. Then the sample was calcined at 350 °C for 2 h. The carbon of fish bone, which has been impregnated was labeled as TiO_2/CFB. As a comparison, 1 g samples were impregnated by copper nitrate trihydrate (500 µmol, 10 mL, Merck) and Iron (III) nitrate nonahydrate (500 µmol, 10 mL, Sigma Aldrich). Furthermore, both samples were calcined at 350 °C for 2 h, and the catalysts were notated as CuO/CFB and Fe_2O_3/CFB.

2.3 Catalysts Characterizations

The functional groups in the catalyst were identified by using the FTIR spectrometer (IR−Prestige−21 Shimadzu). The XRD (Phillips PANalytical X'Pert PRO type was used to investigate the crystallinity and phase content of the catalyst with the Cu K_α (λ = 1.5406 Å) radiation and range of 2θ (°) from 7 to 60. The surface morphology of the catalyst was investigated by using SEM images obtained from a FEI Inspect S50 instrument. The surface area, pore-volume, and pore size distribution were determined by nitrogen adsorption-desorption isotherms that were created from the data collected from a Quantachrome nova 1200e instrument.

2.4 Catalytic Activity Test

Catalytic activity of the catalysts was carried by styrene (Merck) oxidation reaction with aqueous hydrogen peroxide (H_2O_2 30%, Merck) as an oxidant. The catalytic reactions were carried out with a similar procedure reported pre-

viously [13,14,16]. All reactions were performed with mixing styrene (5 mmol), 30 % aqueous H_2O_2 (5 mmol), acetonitrile (4.5 mL), and catalyst (50 mg) with stirring for 24 h at room temperature. The GC-2014 Shimadzu was used to analyze the product of the reaction.

3. Results and Discussions

3.1 Physical Properties of Catalysts

Figure 1 shows the FTIR spectra of (a) CFB, (b) CuO, (c) Fe_2O_3, (d) TiO_2, (e) Fe_2O_3/CFB, (f) CuO/CFB and (g) TiO_2/CFB. The IR spectra of CFB show the absorption peaks at 3436 cm^{-1}, and 1632 cm^{-1} which indicating the O–H stretching. The C–O stretching vibration, which correlated to carbonate ion (CO_3^{2-}) substitution in the crystal lattice, was investigated by the absorption bands at 1435 cm^{-1} and 877 cm^{-1} [17,18]. The absorption bands at 1063 cm^{-1} and 564 cm^{-1} are assigned to the P–O stretching vibration in phosphate ion (PO_4^{3-}) groups [17,18]. The appearance of carbonate ion (CO_3^{2-}) and phosphate ion (PO_4^{3-}) groups are the evidence of the presence of hydroxyapatite. In the Fe_2O_3/CFB, CuO/CFB, and TiO_2/CFB catalysts, hydroxyapatite was assigned by the absorption band 1094 cm^{-1} and 591 cm^{-1}, which indicated the P–O stretching vibration in phosphate ion (PO_4^{3-}) groups. The O–H stretching was investigated by the absorption band at 672 cm^{-1}. After the impregnation of metal (Fe, Cu, Ti) and followed by the calcination process, the absorption band at 3436 cm^{-1} [17,18], which indicated as O–H stretching, was drastically decreasing. The IR spectra of (b) CuO, (c) Fe_2O_3 and (d) TiO_2 were used to identify Cu, Fe and Ti in the samples. The metals of Cu and Fe can be identified by Cu–O and Fe–O vibration with absorption peaks at 601 and 631 cm^{-1}, respectively. The existence of Ti framework was investigated by Ti–O vibration with an absorption broad peak at 700–950 cm^{-1}. The metals of Cu, Fe, and Ti are no detected in the IR spectra 1 (e-g) due to the amount of metal that impregnated so small.

The XRD pattern in Figure 2 illustrates that the crystallinity of (a) CuO, (b) Fe_2O_3, (c) TiO_2, (d) CFB, (e) Fe_2O_3/CFB, (f) CuO/CFB,

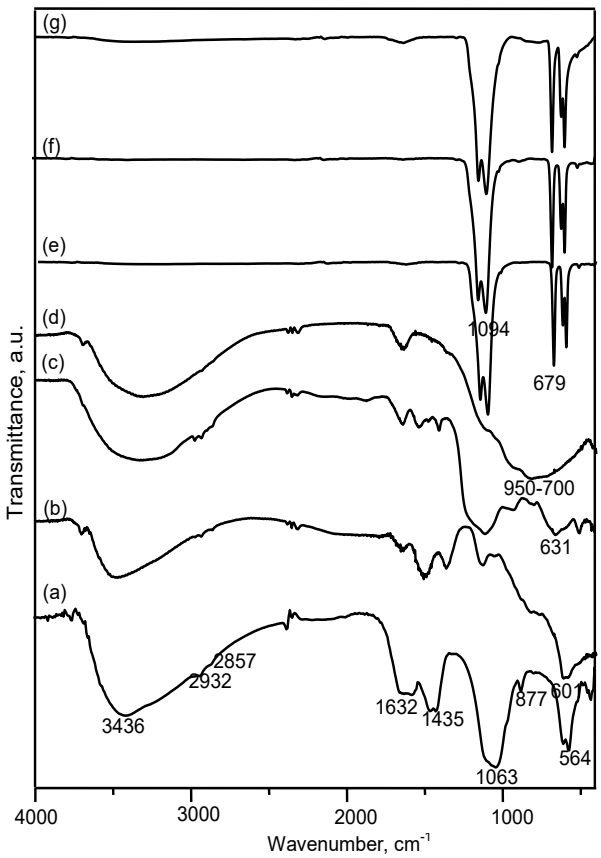


Figure 1. FTIR spectra of (a) CFB, (b) CuO, (c) Fe_2O_3, (d) TiO_2, (e) Fe_2O_3/CFB, (f) CuO/CFB and (g) TiO_2/CFB.

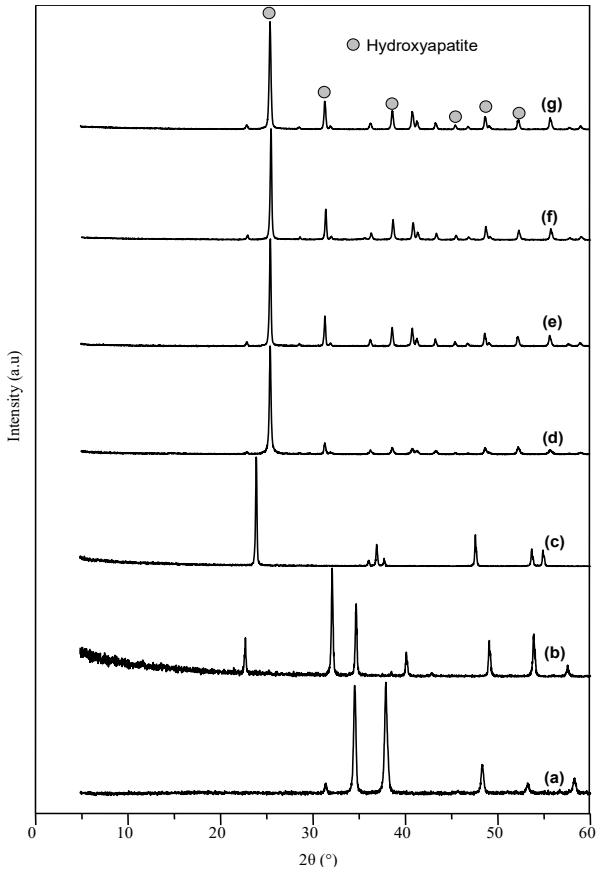
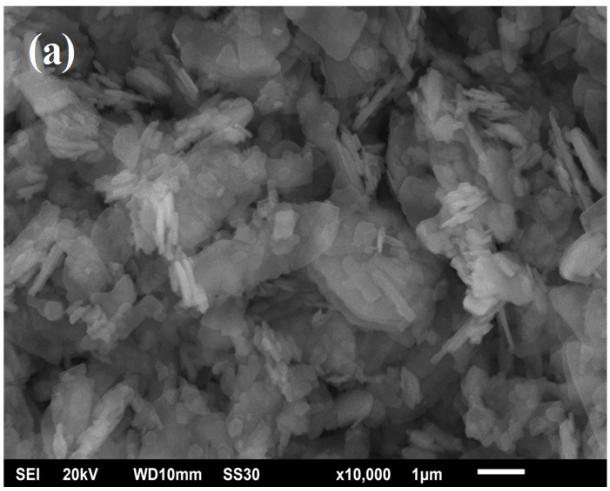
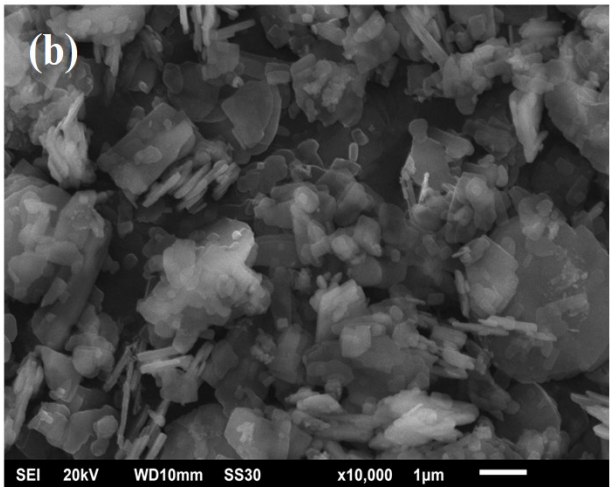


Figure 2. XRD pattern of (a) CuO, (b) Fe_2O_3, (c) TiO_2, (d) CFB, (e) Fe_2O_3/CFB, (f) CuO/CFB and (g) TiO_2/CFB.

and (g) TiO_2/CFB catalysts. The CFB shows the low crystallinity, but otherwise, the high crystallinity was shown by Fe_2O_3/CFB, CuO/CFB and TiO_2/CFB catalysts. Based on JCPDS 0760694, all catalysts contain hydroxyapatite, which proven by the diffraction peaks at 2θ = 25.9, 31.8, 46.8, 49.6, and 53.4. Based on JCPDS number 00-004-0477, the dominant diffraction peaks should be appeared at 2θ = 33.5 and 35.6 for Fe_2O_3; 35.5 and 38.9 for CuO and 25.2, 37.7 and 47.9 for TiO_2, but it did not appear in Figure 2 (e-g) due to its amount was very small (500 µmol).

The SEM images of Fe_2O_3/CFB, CuO/CFB, and TiO_2/CFB catalysts are exhibited in Figure 3. All the catalysts have rough surface morphology. The EDX results (Table 1) depict that all catalysts were dominated by many elements such as C, O, S, and Ca. The presence of Fe, Ti, and Cu are clearly observed in the EDX results. Figure 4 shows nitrogen adsorption-desorption isotherms of CFB, Fe_2O_3/CFB, CuO/CFB and TiO_2/CFB. All isotherms of catalysts were Type IV in the IUPAC classifications, which are a typical isotherm for mesoporous materials. The isotherms of all catalysts exhibited clear hysteresis loops. The BET surface area, pore-volume, and mean pore size of CFB, Fe_2O_3/CFB, CuO/CFB, and TiO_2/CFB were obtained from the nitrogen adsorption-desorption analysis. The complete data are listed in Table 2. The pore size distribution of CFB, Fe_2O_3/CFB, CuO/CFB, and TiO_2/CFB indicates the presence of uniform mesopores such as 4.4, 10.2, 10,4, and 7.7 nm, respectively. The





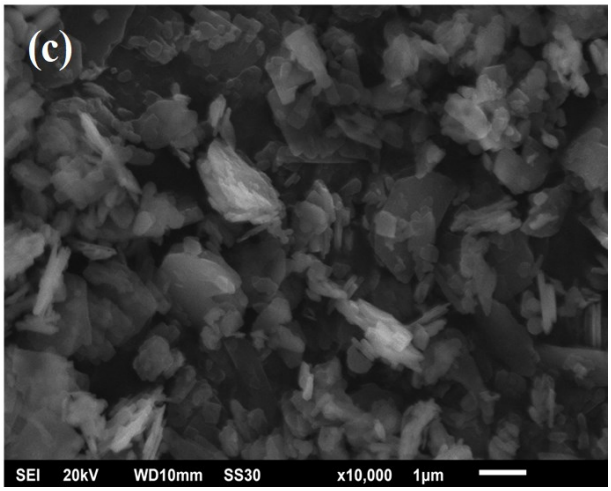


Figure 3. SEM images of (a) Fe_2O_3/CFB, (b) CuO/CFB and (c) TiO_2/CFB.

Table 1. Physical properties of SEM EDX of the catalysts.

Element	Wt%		
	Fe_2O_3/CFB	CuO/CFB	TiO_2/CFB
C	11.55	39.39	51.58
O	52.99	45.26	40.76
S	16.06	5.80	3.16
Ca	17.08	6.07	3.47
Ti	-	-	0.42
Fe	1.43	0.02	0.02
Cu	0.85	2.23	0.59
Zn	-	0.67	-
Zr	-	0.54	-

BET surface area and pore volume showed the following values: 158.8 $m^2.g^{-1}$, 0.350 $cm^3.g^{-1}$ for CFB; 7.610 $m^2.g^{-1}$, 0.039 $cm^3.g^{-1}$ for Fe_2O_3/CFB; 7.337 $m^2.g^{-1}$, 0.038 $cm^3.g^{-1}$ for CuO/CFB and 13.790 $m^2.g^{-1}$, 0.053 $cm^3.g^{-1}$ for TiO_2/CFB, respectively. The complete data were shown in Table 2. It can be seen that the BET surface area and pore volume drastically decrease when CFB was modified to be catalysts by the impregnation process.

3.2. Catalytic Activity of Catalysts

The histogram of product yields from styrene oxidation with H_2O_2 as oxidant catalyzed by TiO_2, CFB, Fe_2O_3/CFB, CuO/CFB, and TiO_2/CFB catalysts are shown in Figure 5. The styrene conversion over blank (without catalyst), TiO_2, CFB, Fe_2O_3/CFB, CuO/CFB and TiO_2/CFB catalysts are 1.43; 3.16; 0.41; 11.59; 0.49 and 22.99%, respectively. If compared to TiO_2 and CFB catalysts, the catalytic performance of Fe_2O_3/CFB (TON = 23.18) and TiO_2/CFB (TON = 45.98) catalysts are better than the others.

Titania and iron oxide on the surface of CFB was found as a suitable catalytic active site for the oxidation of styrene with aqueous H_2O_2 as an oxidant. Otherwise, the catalytic performance of CuO/CFB is lower than TiO_2 and almost the same with CFB catalyst support. It proves that the copper oxide was not active in the styrene oxidation with H_2O_2 as an oxidant. This might due to the H_2O_2 has adsorbed onto the catalytic surface of CuO/CFB but slow in H_2O_2 decomposition to form •OH radicals [19−21] It is demonstrated that, based on product conversion, the TiO_2/CFB catalyst is the best compared to the others. One considers that the Ti^{4+} in TiO_2/CFB catalyst has a higher amount of the electron vacancies in *d* orbital compared to Fe^{3+} and Cu^{2+}. So, Ti^{4+} ions in TiO_2/CFB catalyst can provide a large concentration of low energy electronic states and elec-

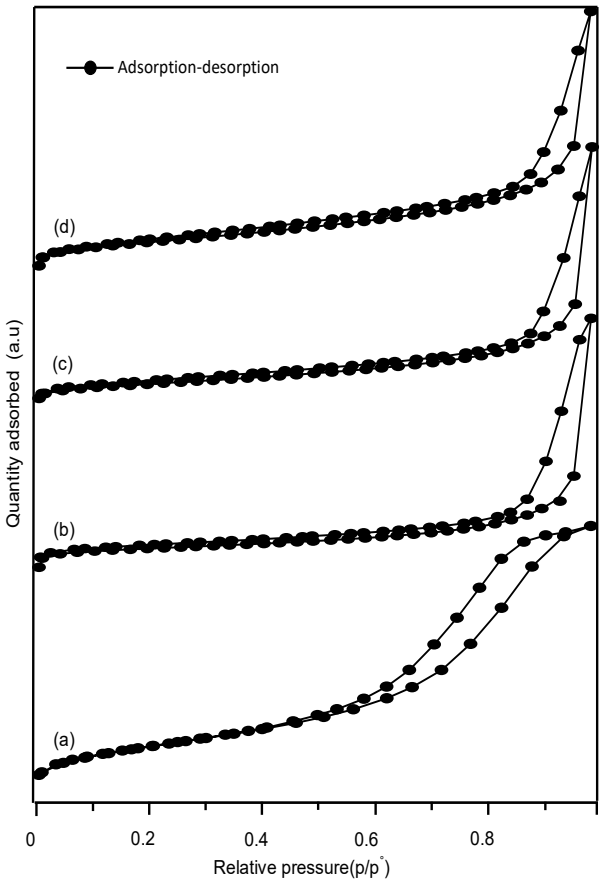


Figure 4. The physisorption isotherms of (a) CFB, (b) Fe_2O_3/CFB, (c) CuO/CFB and (d) TiO_2/CFB.

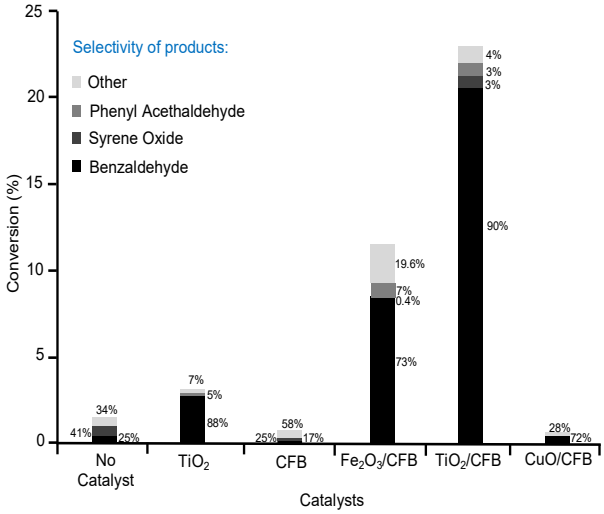


Figure 5. Comparison of catalytic performance of no catalyst, TiO_2, CFB, Fe_2O_3/CFB, TiO_2/CFB and CuO/CFB catalysts in the oxidation of styrene (5 mmol), 30% H_2O_2 (5 mmol) and catalyst (50 mg) at room temperature for 24 h.

Table 2. Physical properties of CFB, Fe_2O_3/CFB, CuO/CFB and TiO_2/CFB catalysts.

Samples	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Mean pore size (nm)
CFB	158.8	0.3500	4.41
Fe_2O_3/CFB	7.610	0.0386	10.16
CuO/CFB	7.337	0.0381	10.39
TiO_2/CFB	13.790	0.0532	7.70

tron vacancies states, so that it can facilitate the oxidation of styrene with H_2O_2 [17]. It is also reported that the formation of the titanium peroxo complex plays a vital role in the higher catalytic activity of TiO_2/CFB. The peroxo complexes might undergo homolytic cleavage on O-OH to form •OH radicals, which could further react with other H_2O_2 to form O_2•⁻ and •OOH radicals. Thus, TiO_2/CFB is more reactive in the oxidation of styrene using H_2O_2 [22]. By comparing Fe_2O_3/CFB and CuO/CFB, it is found that Fe_2O_3/CFB came before CuO/CFB because of CuO/CFB displays higher electronic configuration state and almost occupied electron vacancy state. The electronic configuration of Cu^{2+} is [Ar] $3d^9$; whereas Fe^{3+} is [Ar] $3d^5$, which indicates that Fe^{3+} has more empty orbitals for substrate accommodation in conjuncture of its half-filled orbital is more stable for catalyzing a reaction.

The surface area is one of the essential factors to be considered for the higher catalytic activity of TiO_2/CFB. It is clearly observed that the TiO_2/CFB catalyst has the highest surface area compared to Fe_2O_3/CFB and CuO/CFB catalysts. Nonetheless, the surface area of CFB reduced tremendously after the impregnation of TiO_2, CuO and Fe_2O_3 respectively. It is owing to the particles size of those three metal oxides are too large and almost cover the surface and pore volume of CFB, proven by the mean pore size shown in Table 2. Table 2 shows the mean pore sizes of Fe_2O_3/CFB is 10.16 nm, CuO/CFB is 10.39 nm and TiO_2/CFB is 7.70 nm, are larger than mean pore size of CFB. By considering TiO_2/CFB has the highest surface area compared to metal oxides/CFB, it can be summarized that the catalytic performance of TiO_2/CFB evidences the important function of the active site and surface area of the catalyst. From the histogram, it can be seen that the styrene conversion of TiO_2 (3.16%) and CFB (0.41%) increase drastically to be ~12% and ~23% when Fe_2O_3/CFB and TiO_2/CFB catalysts were used.

Benzaldehyde, phenyl acetaldehyde, and styrene oxide were the main products of styrene oxidation using H_2O_2 as an oxidant. It reveals that the products are selective to the formation of benzaldehyde. The benzaldehyde selectivity of blank (no catalyst), CFB, TiO_2, Fe_2O_3/CFB, CuO/CFB, and TiO_2/CFB catalysts was 25.2; 17.4; 88.3; 73.2; 72.4 and 90.1%, respectively.

3.3 Kinetic Model: the Power-Rate Law

A series kinetic experiment of styrene oxidation by H_2O_2 was carried out at room temperature with acetonitrile as solvent. The reaction mechanism scheme of styrene with H_2O_2, to produce benzaldehyde as the main product, is illustrated in Figure 6. This catalytic conversion reaction involves five steps: (1) At pre-equilibrium step, TiO_2/CFB reacts with H_2O_2 to generate titanium(IV) hydroperoxy species; (2)

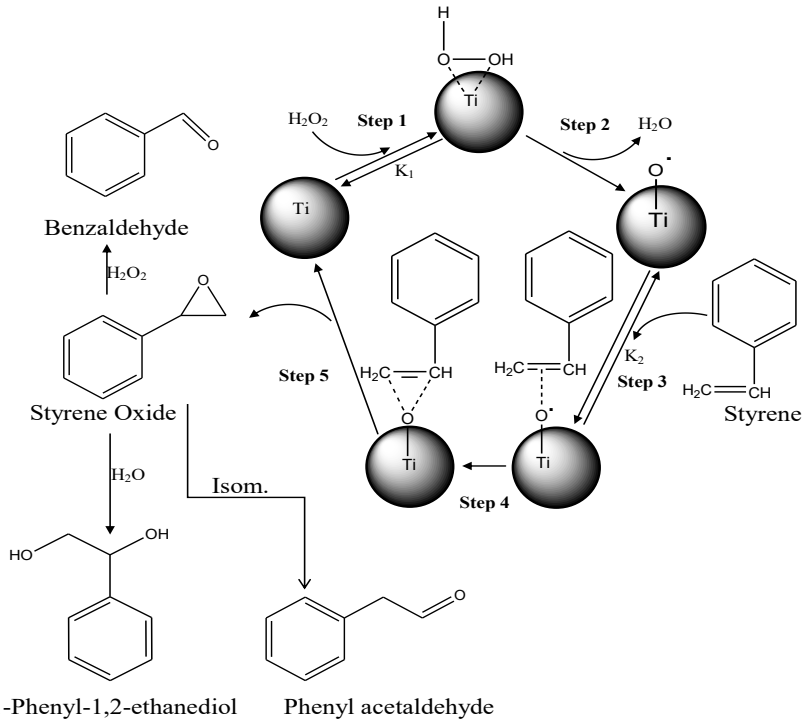


Figure 6. Reaction scheme of the styrene oxidation with H_2O_2 as oxidant [23,24].

Titanium(IV) hydroperoxy species are unstable, thus re-arranging themselves to form titanium(IV) oxo radicals by releasing water molecules as the by-product; (3) The highly active titanium(IV) oxo radicals collide with styrene at the second pre-equilibrium state to give π-bonded transient species; (4) Titanium(IV) oxo radicals transfer its oxygen to styrene by giving metalloepoxy intermediate species; (5) Titanium(IV) species in TiO_2/CFB regains its structure with the generation of styrene oxide. Since styrene oxide is an active intermediates, it can transform into several products, such as benzaldehyde (main product), 1-phenyl-1,2-ethanediol and phenyl acetaldehyde [23,24]. The proposed mechanism for the oxidation of styrene is consistent with the observation made in kinetic.

The kinetic model, such as: the power-rate law was used to best fit the results. The power-rate law can be represented as [25,26]:

$$r_i = -\frac{dC_i}{dt} = kK_1K_2\left[catalyst\right]\left[Styrene\right]\left[H_2O_2\right]^{1/2} \quad (1)$$

$$r_i = -\frac{d\left[C_0 - x\right]}{dt} = kK_1K_2\left[catalyst\right]\left[Styrene\right]\left[H_2O_2\right]^{1/2} \quad (2)$$

$$r_i = \frac{dx}{dt} = kK_1K_2\left[catalyst\right]\left[Styrene\right]\left[H_2O_2\right]^{1/2} \quad (3)$$

where r_i is the reaction rate of the styrene oxidation (mol.cm^{-3}.s^{-1}); k is the reaction rate constant (min^{-1}); C_i is styrene concentration after oxidation time t (mol.cm^{-3}); [catalyst] is concentration of TiO_2/CFB catalyst and K_1 and K_2 are preequilibrium constants of the step in the Scheme. If the total catalyst concentration is expressed as $[catalyst]_T$ and considering the steady state approach, which includes the concentration of all the intermediate catalyst species, the power-rate law can be given as:

$$r_i = \frac{kK_1K_2\left[catalyst\right]\left[Styrene\right]\left[H_2O_2\right]^{1/2}}{1 + K_1\left[H_2O_2\right]^{1/2} + K_1K_2\left[Styrene\right]\left[H_2O_2\right]^{1/2}} \quad (4)$$

$$\frac{\left[catalyst\right]_T}{r_i} = \frac{1 + K_1\left[H_2O_2\right]^{1/2} + K_1K_2\left[Styrene\right]\left[H_2O_2\right]^{1/2}}{kK_1K_2\left[Styrene\right]\left[H_2O_2\right]^{1/2}} \quad (5)$$

$$\frac{\left[catalyst\right]_T}{r_i} = \frac{1}{\left[Styrene\right]}\left\{\frac{1}{kK_1K_2\left[H_2O_2\right]^{1/2}} + \frac{1}{kK_2}\right\} + \frac{1}{k} \quad (6)$$

The value of rate constant k was determined of the intercept from the plot of $[catalyst]_T/r_i$ vs 1/[styrene]. The kinetics data obtained from styrene oxidation with H_2O_2 as oxidant onto TiO_2/CFB are recorded in Table 3. Base on the experiment results, the styrene oxidation onto TiO_2/CFB catalyst at room temperature obeys a first-order reaction model with the correlation coefficients $R^2 \sim 0.9002$ and the value of rate constant $k = 0.00081$ min^{-1}.

4. Conclusions

The use of carbon-derived fish bones (CFB) as catalyst support has been demonstrated in the styrene oxidation with aqueous H_2O_2 in this research. It is found that the combination of titania (TiO_2) and carbon-derived fish bones gave the highest catalytic activity compared to Fe_2O_3/CFB and CuO/CFB. The conversion and selectivity of styrene and benzaldehyde over TiO_2 was 3.16% and 88.3%; CFB is 0.41% and 17.4%; Fe_2O_3/CFB is 11.59% and 73.15%; CuO/CFB is 0.49% and 72.42%; and TiO_2/CFB is 22.99% and 90.1%. The highest catalytic activity of TiO_2/CFB was influenced by the electronic properties of Ti^{4+} and the high surface area of the catalyst. The kinetic of styrene oxidation by H_2O_2 fitted the first order with the rate constant $k = 8.1\times10^{-4}$ min^{-1}.

Acknowledgements

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Table 3. First order kinetics of styrene oxidation onto TiO_2/CFB catalysts.

Catalyst		Time (min)					First order	
		0	60	120	240	360	R^2	k_1 (min^{-1})
TiO_2/CFB	x	0	0.0159	0.0201	0.0386	0.0465	0.9002	0.00081
	C_i	0.8944	0.8785	0.8743	0.8558	0.8479		
	$\frac{\partial x}{\partial t}$	0	2.65×10^{-4}	1.675×10^{-4}	1.608×10^{-4}	1.291×10^{-4}		

(condition: 5mmol styrene = 0.5806 mL; 5mmol H_2O_2 = 0.5107 mL; Acetonitrile = 4.5 mL and catalyst = 50 mg)

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