

Utilization Low Rank Coal Bottom Ash as TiO₂ Support for Oxidation Catalyst of Styrene with Hydrogen Peroxide Aqueous

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Keywords: Styrene; Oxidation; Low rank coal, Bottom ash; Calcination

Abstract. One of the coal combustion ashes is coal bottom ash. Low rank coal bottom ash can act as TiO₂ catalyst's support which was calcined at varying temperature, has been created. The low rank coal bottom ash model was collected from low rank coal which burned in muffle furnace at 800 °C for 2 h. Subsequently, the low rank coal bottom ash was impregnated with titanium(IV) isopropoxide (Ti(PrO)₄) 500 μmol, and then calcined at variation temperature of 300, 400, 500, 600 and 700 °C. The modified physiochemical property of catalysts were determined UV-vis spectroscopy, N₂ adsorption-desorption and hydrophobicity test. The performances of the catalysts were tested for styrene oxidation with H₂O₂ aqueous as oxidant. It is found that the low rank coal bottom ash was as good catalyst support, whereby TiO₂ supported low rank coal bottom ash which calcined at 400 °C possessed the best catalytic activity with styrene conversion 45% and selectivity 87%.

Introduction

Coal is very economical, readily obtainable and most abundant resource in Indonesia. Coal resource in this country is predicted to reach about 21.13 billion short tons and it is dominated by low rank coal which involves of lignite and sub-bituminous. Thus, Indonesia has become the second largest coal exporter in the world. [1].

Utilization of coal in the world was dominated for power generation and industrial sectors. However, one of the major problems today is the pollution mainly caused by ashes yield from the coal utilization. The pollution which discharged as the by-products of coal combustion, such as coal fly ash (60%), inorganic sulfur and organic sulfur (24%), coal bottom ash (12%) and boiler slag (4%). The yield of pollutant has tendency to be increased when the low rank coal was used [2].

Many studies have been carried out to investigate the utilization of the by-products from coal combustion as catalysts. Some applications of the by-products from coal combustion as catalysts, including utilize of coal fly ash as a nano-crystalline solid acid catalyst for liquid phase esterification of salicylic acid with acetic anhydride and methanol [3]. Coal fly ash, such as calcium oxide, for recyclable solid base catalyst for Knoevenagel condensation reaction [4]. Coal fly ash as solid base catalyst for Claisen-Schmidt condensation between cyclohexanone and benzaldehyde [5] was also conducted. Coal fly ash can be used to be a support of titanium catalyst which possesses good performance for removal NO gas in the photocatalytic activity [6].

Two kinds of pollutant ashes from coal combustion namely coal fly ash and coal bottom ash. Previous research was more focused only on the utilization of coal fly ash. Therefore, in the present work, we have elaborated utilization low rank coal bottom ash as supporters of TiO₂ as a catalyst for the oxidation of styrene with H₂O₂, as an oxidant, and have investigated the influence of the calcination temperature variations on the activity of the catalyst.

Experimental

The raw material of the low rank coal obtained from Batuah, Loajannan, Kutai Kartanegara, East Kalimantan, Indonesia. Firstly, the low rank coal was ground to 200 mesh. The model of bottom ash was created by calcination process of low rank coal at 800 °C for 2 h, in VULCANTM 3-550 muffle

furnace. Furthermore, the low rank coal bottom ash was labeled BA. A series of catalysts were prepared by impregnation of titanium(IV) isopropoxide ($\text{Ti}(\text{PrO})_4$) 500 μmol on low rank coal bottom ash. Catalysts were calcined at variation of temperatures, i.e. 300, 400, 500, 600 and 700 $^\circ\text{C}$ for 2 h. Catalysts were labeled as Ti-BA(X); where X refers to calcination temperature employed. For example, Ti-BA(500) represents the low rank coal bottom ash which impregnated by using titanium(IV) isopropoxide ($\text{Ti}(\text{PrO})_4$) 500 μmol and it underwent calcined at 500 $^\circ\text{C}$.

The catalysts were characterized by using UV-vis spectra were collected on a Perkin Elmer Lambda 35 UV-visible-NIR spectrometer. Nitrogen adsorption-desorption isotherms were measured at 77 K using a Micromaritics ASAP 2020 V4.00 instrument. The pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) model. The hydrophobicity of all catalysts was determined using the water adsorption technique.

Catalytic testing was carried out in the oxidation of styrene using aqueous H_2O_2 (30%, Merck) as the oxidant. Styrene (5 mmol, Aldrich), aqueous H_2O_2 (5 mmol, 30%, Merck), acetonitrile (4.5 ml, Merck) and catalyst (50 mg) were mixed in a reflux and stirred at 60 $^\circ\text{C}$ for 24 h [7]. The products were then separated from the catalysts by centrifugation. The resulting products were withdrawn and analyzed with GC-2014 Shimadzu-gas chromatograph, using BPX5 column, with the column's maximum temperature of 360 $^\circ\text{C}$, column length of 30 m, inner diameter of 0.25 mm and film thickness of 0.25 μm .

Results and discussion

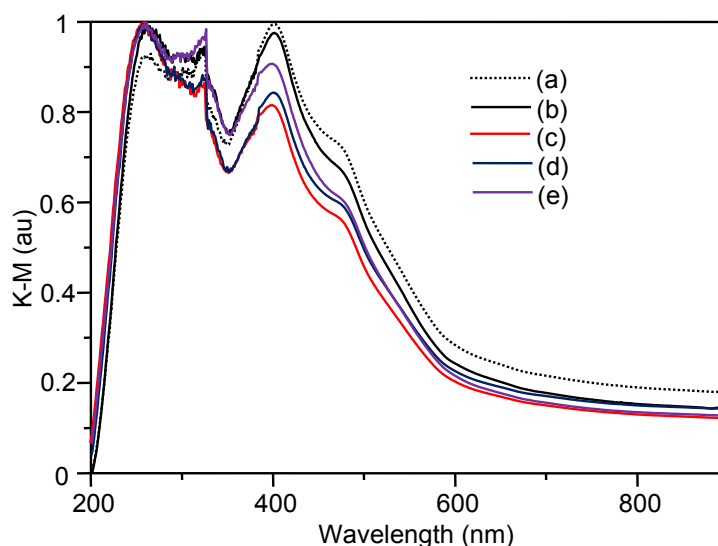


Fig. 1 UV-vis spectra of (a) Ti-BA(300), (b) Ti-BA(400), (c) Ti-BA(500), (d) Ti-BA(600) and (e) Ti-BA(700).

The central Ti(IV) atoms were expected in the UV-visible region. For oxo species of Ti(IV), strong absorptions caused charge transfer (CT) transitions between O^{2-} . Framework Ti(IV) in a tetrahedral coordinated was assigned with absorption at 240 nm, pent-coordinated at 250 nm and an octahedral coordinated at 330 nm. For bulk TiO_2 , the adsorption threshold of anatase was investigated near 370 nm, rutile near 410 nm and TiO_2 oligomer near 480 nm [8]. Fig 1 depicts the UV-vis spectra recorded for (a) Ti-BA(300), (b) Ti-BA(400), (c) Ti-BA(500), (d) Ti-BA(600) and Ti-BA(700) samples. All UV spectra were dominated by a strong band at near 250, 330, 410 and 480 nm, assigned to the presence of titanium sites in higher coordination number and having Ti–O–Ti bonds. UV absorption band at 250 nm is usually ascribed to the presence of isolated pent-coordinated titanium sites, 330 nm assigned of isolated octahedral coordinated. The presence of bulk TiO_2 in rutile phase and oligomer shown by signals located at wavelengths near 410 nm and 480 nm [9].

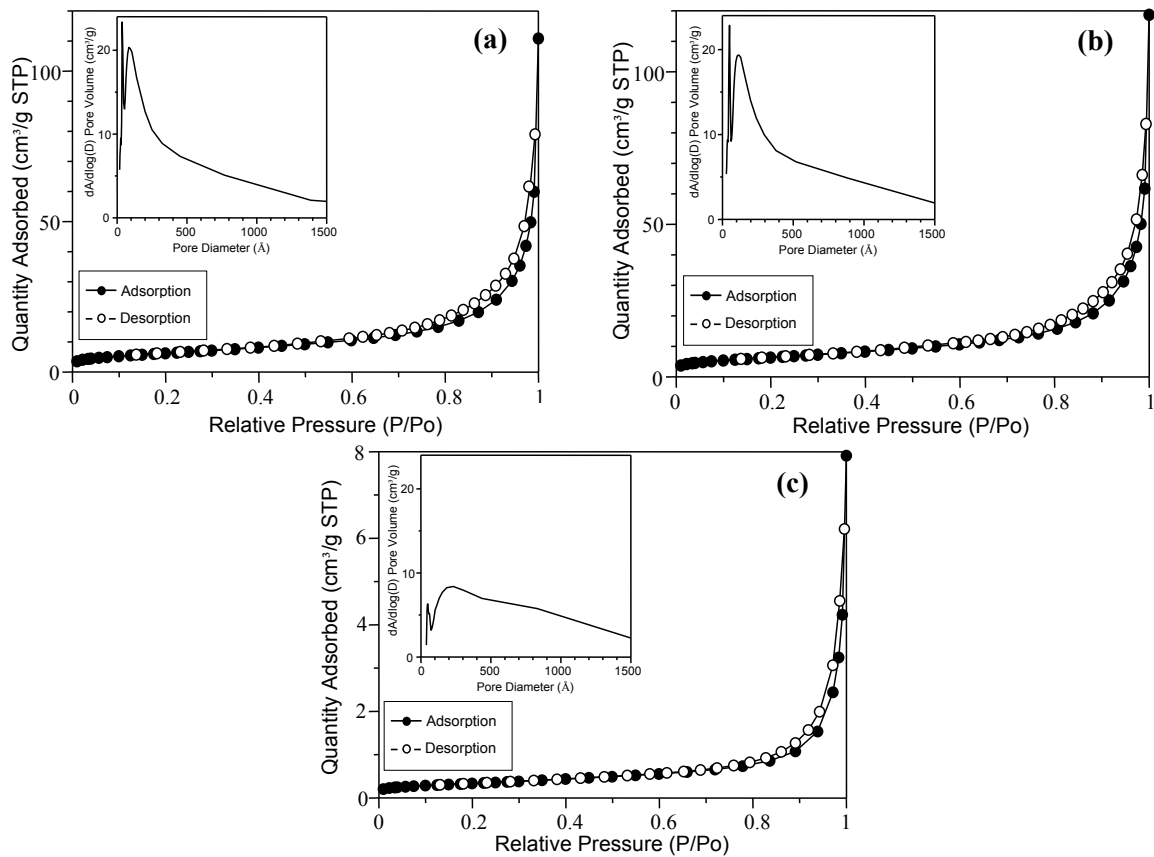


Fig. 2 N₂ adsorption-desorption isotherms and BJH pore distribution of (a) Ti-BA(300), (b) Ti-BA(400) and (c) Ti-BA(700).

Fig. 2 shows N₂ adsorption-desorption isotherms and correlated BJH pore distribution of samples. The isotherms of samples were type V with H₃ hysteresis loop. The pore size distribution indicates the presence of uniform mesoporous ~ 84.2 Å for Ti-BA(300), ~ 107.0 Å for Ti-BA(400) and ~ 29.1 Å for Ti-BA(700). The BET surface area obtained were 22.1 m² g⁻¹ for Ti-BA(300), 22.4 m² g⁻¹ for Ti-BA(400) and 11.9 m² g⁻¹ for Ti-BA(700). The decreasing of BET surface area of Ti-BA(400) to Ti-BA(700) after calcination at 700 °C caused by the pores collapsing.

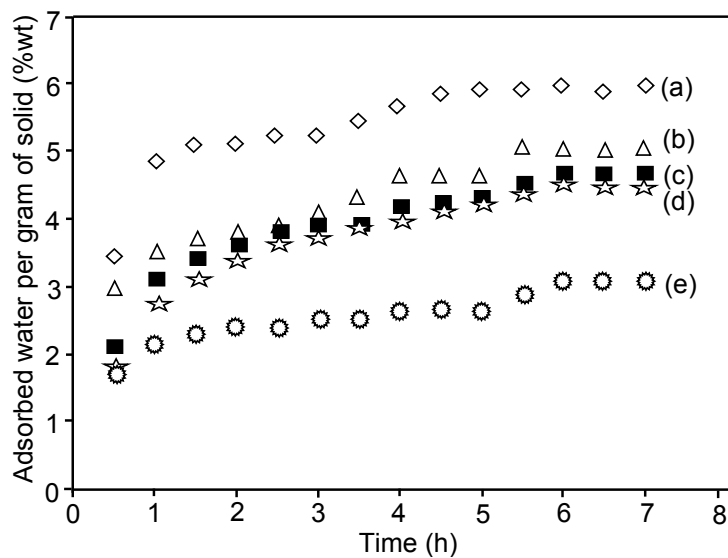


Fig. 3 Water adsorption percentage for (a) Ti-BA(300), (b) Ti-BA(400), (c) Ti-BA(500), (d) Ti-BA(600) and (e) Ti-BA(700).

Fig. 3 shows the amount of adsorbed water on Ti-BA(300), Ti-BA(400), Ti-BA(500), Ti-BA(600) and Ti-BA(700). One suggests that the amount of adsorbed water can be attributed to hydrophobicity and hydrophilicity of the samples. The lower is the amount of water adsorbed, the higher is the hydrophobicity of sample. The order of hydrophobicity from high to low is as follows: Ti-BA(700)>Ti-BA(600)>Ti-BA(500)>Ti-BA(400)>Ti-BA(300), with average percentage of water adsorption of 2.6, 3.7, 3.9, 4.3 and 5.4%wt, respectively. The calcination treatment caused significant changes in Ti-BA(T) surface chemistry. The calcination temperature increased, the functional groups, CO₂ and CO will be released together with carbon from low rank coal's surface, decreasing the hydrophobicity.

Catalytic performance of titanium supported low rank coal bottom ash (Ti-BA(T)) catalysts which calcined at varying temperatures were tested to oxidation of styrene with aqueous hydrogen peroxide as the oxidant. Base on agreement with previous study, the products of styrene oxidation have included benzaldehyde, phenylacetaldehyde, styrene oxide and other products, such as acetophenone, benzoic acid, phenylketene, phenylacetic acid, benzene which based on the authentic samples of the products and GC analysis [10]. Nonetheless, benzaldehyde was found to be the main product in the styrene oxidation in this research.

Table 1 Catalytic performance of catalyst in the Oxidation of Styrene^a.

Catalyst	Styrene conversion (%)	Selectivity (%)			
		BzA ^b	PhA ^c	SO ^d	Oth ^e
No catalyst	5	82	1	15	2
BA	7	76	1	20	3
Ti-BA(300)	27	83	1	8	8
Ti-BA(400)	45	87	1	11	1
Ti-BA(500)	43	71	1	24	4
Ti-BA(600)	32	70	1	25	4
Ti-BA(700)	11	82	1	12	5

^a **Reaction conditions:** The reactions were carried out at room temperature for 20 h with styrene (5 mmol), 30% H₂O₂ (5 mmol) and catalyst (50 mg). BzA^b = benzaldehyde, PhA^c = phenylacetaldehyde, SO^d = styrene oxide and Oth^e = other products

The conversion and selectivity of products from oxidation styrene that were catalyzed by low rank coal bottom ash (BA) and titanium supported bottom ash such as Ti-BA(300), Ti-BA(400), Ti-BA(500), Ti-BA(600) and Ti-BA(700) can be shown in Table 1. It can be observed that the conversion of styrene and selectivity to benzaldehyde were 7% and 76%, respectively, when BA was used as catalyst, which its percentage was more slightly higher than no catalyst was used. The influencing of varied calcination temperatures to the catalytic activity can be seen when Ti-BA(300), Ti-BA(400), Ti-BA(500), Ti-BA(600) and Ti-BA(700) as catalysts. The catalytic activities exhibited the conversion of styrene and selectivity to benzaldehyde were 27% and 83% when Ti-BA(300) was used. The highest catalytic activities 45% as the conversion of styrene and 87% as selectivity of benzaldehyde were reached when a catalyst was calcined at 400 °C (Ti-BA(400)). The increasing of catalytic performance when the calcination temperature increased from 300 to 400 °C, this most probably due to the increasing of the presence of isolated pent-coordinated titanium sites in the catalyst samples. The conversion of styrene decreased from 43% to 11% when the calcination temperatures were increased from 500 °C to 700 °C, this most correlated with decreasing of surface area of the catalyst samples from 22.4 m² g⁻¹ to 11.9 m² g⁻¹.

Conclusions

Low rank coal bottom ash can be used as the catalyst support of titanium while the calcination temperatures have influenced to the catalytic activities. The increasing of calcination temperatures could cause the decreasing of surface area of the catalysts. The catalyst which calcined at 400 °C possesses an excellent catalytic activity in the oxidation of styrene.

Acknowledgements

The author is grateful acknowledge government of East Kalimantan Province, Indonesia.

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