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Titanium Dioxide-Supported Sulfonated Low Rank Coal as Catalysts in the Oxidation of Styrene with Aqueous Hydrogen Peroxide

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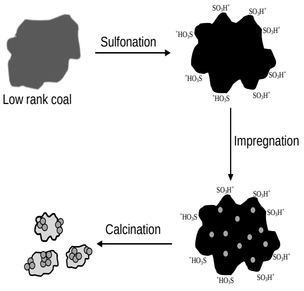
Graphical abstract



Abstract

Titanium dioxide supported sulfonated low rank coal catalyst possesses high catalytic activity in liquid phase oxidation of styrene with aqueous hydrogen peroxide at room temperature. The catalysts were prepared by sulfonation with concentrated sulfuric acid and impregnation of titanium dioxide (500-2500 µmol). The effect of titanium dioxide impregnation and calcinations on the catalysts were studied by X-ray diffraction, UV-vis diffuse reflectance spectroscopy, Fourier transform infrared spectroscopy, BET surface area, field emission scanning electron microscopy and hydrophobicity measurement. The catalytic activity of the catalysts in the oxidation of styrene by aqueous H_2O_2 without calcination increased when the amount of titanium dioxide increased. Meanwhile, the catalytic activity of the catalyst calcined at 500ºC for 2 h was lower than before calcination. It is suggested that the agglomeration of titanium dioxide and hydrophobicity play important role in the catalytic activity of titanium dioxide-supported sulfonated low rank coal in the oxidation of styrene with aqueous H_2O_2.

Keywords: Styrene; oxidation; coal; sulfonation; benzaldehyde; phenyl acetadehyde; styrene oxide

Abstrak

Mangkin titanium dioksida disokong arang batu kelas rendah tersulfonasi mempunyai keaktifan pemangkinan tinggi dalam pengoksidaan fasa cecair stirena dengan hidrogen peroksida akueus pada suhu bilik. Mangkin disediakan melalui sulfonasi dengan asid sulfurik pekat dan pengisitepuan dengan titanium dioksida (500-2500 µmol). Kesan pengisitepuan dan pengkalsinan terhadap mangkin dikaji menggunakan pembelauan sinar-X, UV-vis meresap pantulan spektroskopi, spektroskopi inframerah transformasi Fourier, luas permukaan BET, pelepasan medan mikroskop imbasan elektron dan kehidrofobikan. Keaktifan pemangkinan oleh mangkin dalam pengoksidaan stirena dengan H_2O_2 akueus tanpa pengkalsinan meningkat apabila jumlah titanium dioksida ditingkatkan. Aktiviti pemangkinan oleh mangkin yang dikalsin pada 500ºC selama 2 jam adalah lebih rendah berbanding sebelum dikalsin. Ini menunjukkan bahawa pengaglomeratan titanium dioksida dan kehidrofobikan memainkan peranan penting dalam keaktifan pemangkinan daripada mangkin titanium dioksida disokong arang batu kelas rendah tersulfonasi dalam pengoksidaan stirena dengan hidrogen peroksida akueus.

Keywords: Stirena; pengoksidaan; arang batu; sulfonasi; benzaldehida; fenilasetaldehida; stirena oksida

■1.0 INTRODUCTION

Coal is an energy and carbon source derived from fossil fuels which numbers are abundant in the world. It is grouped into four groups; lignite, subbituminous, bituminous, and anthracite. Approximately 50% of coal is composed of low rank coals, including lignite or brown coal and sub bituminous [1,2].

Coal is one of the most complex carbon compounds with oxygenic functional groups such as carboxyl groups (COOH) and phenolic hydroxyl (OH) groups. It can be converted to amorphous carbon with high density of hydrophilic functional groups bound to carbon sheet by using sulfonation [3]. Sulfonation will lead to the incorporation of hydrophilic molecules, that provide good access for reactants in solution to the SO_3H groups and hence, this will result in higher catalytic performance [4].

Carbon is most commonly utilized as a support. This is due to its characteristic such as inexpensive, inertness, stability, elevated external span, porosity and can raise the catalytic ability of frail catalyst [5]. Coal is also a suitable support catalyst due to its natural resources of carbonaceous materials in various forms and low cost [6].

Benzaldehyde, phenyl acetaldehyde, and styrene oxide that produced from styrene epoxidation are of interest at academic and commercial levels [7]. They are important chemical intermediates in the fine chemicals industry. Therefore, the catalytic epoxidation of styrene or substituted styrene is an important reaction in organic synthesis. Silica supported titanium, particularly TS-1, has been widely investigated due to of its remarkable catalytic performance in the selective oxidation of styrene with hydrogen peroxide under mild conditions. Several factors including the preparation method, crystallite size, impurities, solvent, *etc.*, could affect the catalytic performance.

In the last two decades, many catalyst supports have been developed to improve the activity and selectivity of titanium dioxide catalyst in the oxidation of styrene by using hydrogen peroxide as the oxidant, such as SiO_2 [8], MCM-41 [9], TS-1 [10], and carbon [11]. However, these kinds of catalysts are usually very costly for extensive application.

To the best of our knowledge, there are still no research publications based on the study of modified low rank coal by both sulfonation and titanium dioxide impregnation, as catalyst in the oxidation of styrene with hydrogen peroxide as the oxidant. The purpose of the present work is to investigate the effects of sulfonation, different amount of titanium and calcination on the structure and catalytic performance of the titanium dioxide-supported sulfonated low rank coal, as ways to optimize the conditions for the oxidation of styrene.

■2.0 EXPERIMENTAL

2.1 Preparation of Catalyst

The low rank coal sample (denoted as Coal) was obtained from Batuah, Loajannan, Kutai Kartanegara, East Kalimantan, Indonesia. It was pulverized to particle size of 200 mesh. The proximate and ultimate elemental analysis of the low rank coal were conducted by ASTM method and the results are presented in Table 1.

The sulfonation of the low rank coal was carried out according to the modification procedure reported previously [12]. In a typical procedure, 1 g of the low rank coal was immersed in 12 mL of concentrated sulfuric acid (98%, JT. Baker) and treated in an oil bath at 90 ± 2°C for 6 h with stirring. Then, the mixture was filtered and washed with distilled water to remove any excess acid, before drying at 110 °C for overnight. The sulfonated low rank coal was labeled as SO_3H/Coal. Next, each 1 g of SO_3H/Coal was immersed in 10 mL of toluene (Merck) containing of titanium(IV) isopropoxide (Aldrich) (500, 1000, 1500, 2000 and 2500 μmol) and stirred until all the toluene was completely evaporated. The solid was washed with ethanol (QRec) to remove the residual toluene and subsequently dried at 110 °C for overnight. The sulfonated low rank coal which has been impregnated was labeled as Ti(X)-SO_3H/Coal; where SO_3H/Coal represents sulfonated low rank coal and X indicates the amount of titanium(IV) isopropoxide. As an example, Ti(500)-SO_3H/Coal represents a coal catalyst that was prepared from sulfonated coal which has been impregnated with 500 μmol of titanium(IV) isopropoxide. Then, Ti(X)-SO_3H/Coal was calcined at 500°C for 2 h and labeled as Ti(X)-SO_3H/Coal-500. The complete procedures for preparing titanium dioxide-supported sulfonated low rank coal catalyst is shown in Table 2.

2.2 Samples Characterization

X-ray diffraction (XRD) patterns were obtained with a Bruker Advance D8 transmission difractometer using the Cu K_α (λ = 1.5406 Å) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. The patterns ware scanned in the 2θ range of 2-60° at a step size of 0.050 and step time of 1 s. UV-vis diffuse reflectance (DR UV-vis) spectras were recorded under ambient conditions using a Perkin-Elmer Lambda 900 UV/VIS/NIR spectrometer and monitored in the range of 190–600 nm. Fourier transform infrared (FTIR) spectra of the samples were collected on a Perkin-Elmer Fourier Transform Infrared (FTIR) spectrometer using KBr technique, with a spectral resolution of 2 cm^{-1}, scan of 10 s, at temperature of 20°C. Thermal gravimetric analysis (TGA) was carried out starting from room temperature to 800°C (heating rate of 10°C/min), under nitrogen atmosphere using Mettler Toledo TGA-DTA STAR SW.8.10 instrument. 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 was determined by the amount of water adsorbed on the samples. In a typical experiment, samples (0.1 g) were dried in an oven at 110°C overnight to remove all physically adsorbed water. Distilled water (0.75 l) was filled into desiccators for overnight. After dehydration, the samples were exposed to water vapor by placing them into the water-filled desiccators at room temperature and weighed every 30 minute. The percentage of adsorbed water as a function of time was determined by $((m_t–m_0)/m_0)$ x 100 %, where m_t represents the sample mass after adsorption of water and m_0 represents the initial mass of the sample. Field emission scanning electron microscopy (FESEM) images and mapping elements were determined by using a JSM-6701F and Energy dispersive X-ray analyzer (EDX) JEOL-JED 2300.

2.3 Catalytic Testing

All coal catalysts were investigated in the oxidation of styrene using 30 % aqueous H_2O_2 (Merck) as the oxidant. The oxidation of styrene was carried out in a glass tube at room temperature for 20 h with 5 mmol of styrene (Aldrich), 5 mmol of 30 % aqueous H_2O_2 (Merck), 4.5 mL of acetonitrile (Merck) and 50 mg of catalyst [13]. The catalyst was separated from the oxidation product by centrifugation. The amount of the products was determined with a GC-2014 Shimadzu-gas chromatograph instrument by using BPX5 columns, (serial number: 1286043), maximum column temperature: 360°C, column length: 30 m, inner diameter: 0.25 mm and film thickness: 0.25 μm. The temperature of the injector and detector were programmed at 250°C and 260°C, respectively. The temperature of the column oven was programmed with: the initial temperature of 80°C and it was maintained for 1 min with heating rate of 10 °C/min. Then, the temperature was raised to 110 °C for 0.5 min. Lastly, the temperature reached 150 °C and it was held for 0.5 min. The heating rate of 10 °C/min was applied throughout the temperature program. The yields of products were calculated in mmol. The styrene conversion, products selectivity and turnover number were calculated as follows: conversion = (∑mmol of all the products / (mmol of $styrene_{final}$ + ∑mmol of all the products)) x 100, Selectivity = (mmol of every product/ ∑mmol of all the products)x100 and TON = (mmol of the particular $\text{product}_{\text{final}}$ / mmol of Ti(IV) present in the catalyst).

Table 1 Proximate and ultimate analysis results of the low rank coal

Proximate analysis	Wt. (%)	Ultimate analysis	Wt. (%)	Gross calorific value(Kcal/kg)
Total moisture	13.67	Carbon	65.4	6342
Inherent moisture	11.91	Hydrogen	4.88	
Ash content	4.10	Nitrogen	1.16	
Volatile matter	37.99	Oxygen	12.29	
Fixed carbon	46.00			
Total sulfur	0.26			

Table 2 Codes of samples and treatments done.

Code	Type of treatment	Duration of sulfonation (h)	The amount of titanium dioxide (μmol)	Temperature of treatment (°C)	Duration of thermal treatment (h)
TiO_2[a]	-	-	-	-	-
Coal[b]	-	-	-	-	-
SO_3H/Coal [c]	Sulfonation	6	-	-	-
Ti(500)-SO_3H/Coal [d]	Sulfonation	6	500	-	-
Ti(1000)-SO_3H/Coal[d]	Sulfonation	6	1000	-	-
Ti(1500)-SO_3H/Coal[d]	Sulfonation	6	1500	-	-
Ti(2000)-SO_3H/Coal[d]	Sulfonation	6	2000	-	-
Ti(2500)-SO_3H/Coal[d]	Sulfonation	6	2500	-	-
Ti(500)-SO_3H/Coal500[e]	Sulfonation	6	500	500	2
Ti(1000)-SO_3H/Coal500[e]	Sulfonation	6	1000	500	2
Ti(1500)-SO_3H/Coal500[e]	Sulfonation	6	1500	500	2
Ti(2000)-SO_3H/Coal500[e]	Sulfonation	6	2000	500	2
Ti(2500)-SO_3H/Coal500[e]	Sulfonation	6	2500	500	2

[a] Titanium dioxide

[b] Coal from Batuah Loajannan, Kalimantan Timur, Indonesia

[c] Coal (200 mesh) was mixed with 12 mL of H_2SO_4 (98%) and was stirred at 90 °C for 6 h. The mixture was washed with distilled water to remove any excessive acid subsequently. It was dried at 105 °C for 3 h.

[d] Sulfonated low rank coal was impregnated with $Ti(PrO)_4$ in 5 mL of toluene with stirring until the solvent dried, followed by washing with ethanol to remove the toluene left.

[e] Sulfonated coal was impregnated with $Ti(PrO)_4$ in 5 mL of toluene by stirring until the solvent dried. It was then washed with ethanol to remove the toluene. Sulfonated coal impregnated with titanium dioxide was calcined at 500 °C for 2 h.

■3.0 RESULTS AND DISCUSSION

3.1 Physical Properties

The XRD pattern of the low rank coal (Coal), sulfonated low rank coal (SO_3H/Coal), Ti(500)-SO_3H/Coal, Ti(1000)-SO_3H/Coal, Ti(1500)-SO_3H/Coal, Ti(2000)-SO_3H/Coal and Ti(2500)-SO_3H/Coal are shown in Figure 1 (a)–(g), respectively. All XRD patterns were subjugated by broad peaks in the 2θ range of 10-30°, which are attributed to amorphous carbon composed of aromatic carbon [4]. A small crystalline phase was found in all XRD patterns at 26.5 °, which is assigned to crystalline quartz.

The XRD patterns of all titanium dioxide-supported sulfonated low rank coal after being calcined at 500°C for 2 h (Figure 2) were dominated by quartz and TiO_2 anatase crystalline structure. The quartz stucture is indicated by the major peaks that appeared at 2θ = 26.5° and its intensity decreases as the amount of impregated titanium dioxide was increased. The TiO_2 crystalline anatase structure was observed from the dominant peak at 25.4° and other peaks at 2θ = 37.9, 48.1, 54.1 and 55.2°. The intensity of TiO_2 peaks increase as the amount of impregnated titanium dioxide increased. The size of titanium dioxide was determined by using Scherrer's equation. The average size of TiO_2 crystalline anatase from Ti(500)-SO_3H/Coal, Ti(1000)-SO_3H/Coal, Ti(1500)-SO_3H/Coal, Ti(2000)-SO_3H/Coal and Ti(2500)-SO_3H/Coal calculated were 4.9, 6.1, 7.9, 8.0 and 8.1 nm, respectively.

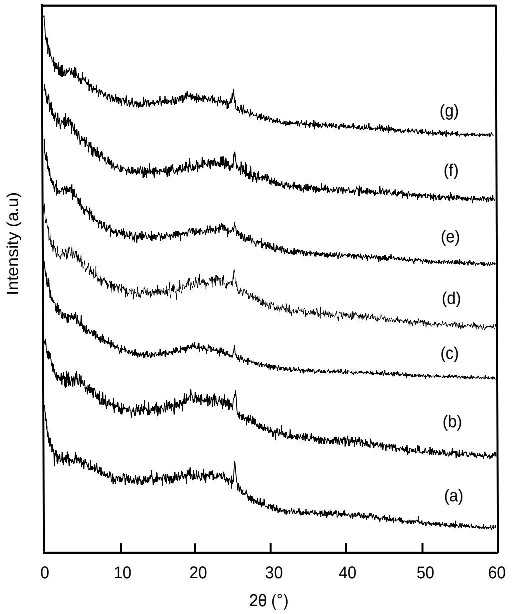


Figure 1 XRD patterns of (a) Coal, (b) SO_3H/Coal, (c) Ti(500)-SO_3H/Coal, (d) Ti(1000)-SO_3H/Coal, (e) Ti(1500)-SO_3H/Coal, (f) Ti(2000)-SO_3H/Coal and (g) Ti(2500)-SO_3H/Coal

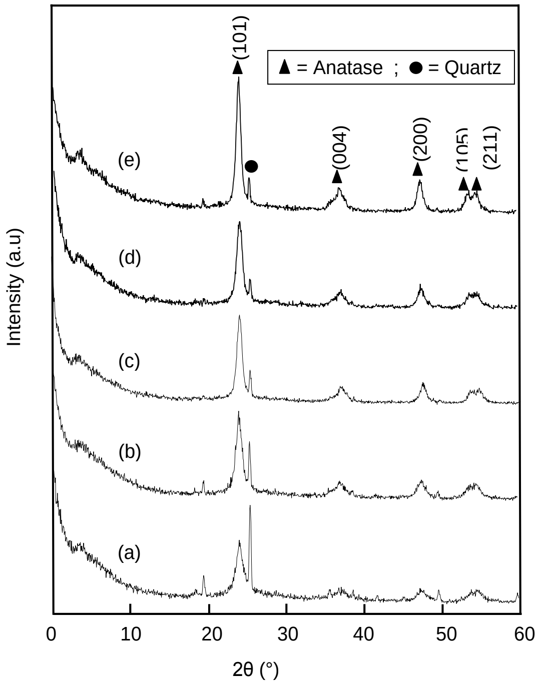


Figure 2 XRD patterns of (a) Ti(500)-SO_3H/Coal500, (b) Ti(1000)-SO_3H/Coal500, (c) Ti(1500)-SO_3H/Coal500, (d) Ti(2000)-SO_3H/Coal500 and (e) Ti(2500)-SO_3H/Coal500

The FTIR spectra of Coal, SO_3H/Coal, Ti(500)-SO_3H/Coal, Ti(1000)-SO_3H/Coal, Ti(1500)-SO_3H/Coal, Ti(2000)-SO_3H/Coal and Ti(2500)-SO_3H/Coal catalysts are presented in Figure 3(a)-(g). The FTIR spectra was used to confirm the degree of sulfonation and the presence of the characteristic bands at for sulfonic, carboxylic, poly aromatic carbon and titania. The broad peak around 3392 cm^{-1} is assigned to O-H stretching mode of –COOH and phenolic OH groups [14]. The bands at 2923 cm^{-1} can be attributed to symmetric and asymmetric stretching mode of the aromatic and aliphatic C-H [3,15]. The corresponding bending mode of C-H is observed at 1432 cm^{-1}. The band at 1701 cm^{-1} is attributed to the C=O stretching vibration of COOH and –COO- groups [16]. Similarly, absorption band at 1614 cm^{-1} can be assigned to aromatic ring vibration of C=C stretching modes in polyaromatics and graphite-like materials [16]. The influence of -SO_3H group (Figure 3(b)) is observed from the presence of three absorption bands at 592, 1031 and 1166 cm^{-1}. The SO_2 deformation frequency is found in the region of 592 cm^{-1}. The peak at 1031 cm^{-1} is assigned to S=O symmetric stretching mode and the absorption band at 1166 cm^{-1} is due to the O=S=O symmetric stretching mode in SO_3H [15,17].

The spectra for titanium dioxide-supported sulfonated low rank coal with a different amount of titanium dioxide impregnated are shown in Figure 3(c-g). The local stretching mode of [TiO_4] and/or [O_3TiOH] and titanyl [Ti = O] vibration are indicated by the broad peak around 900 – 1000 cm^{-1}[18].

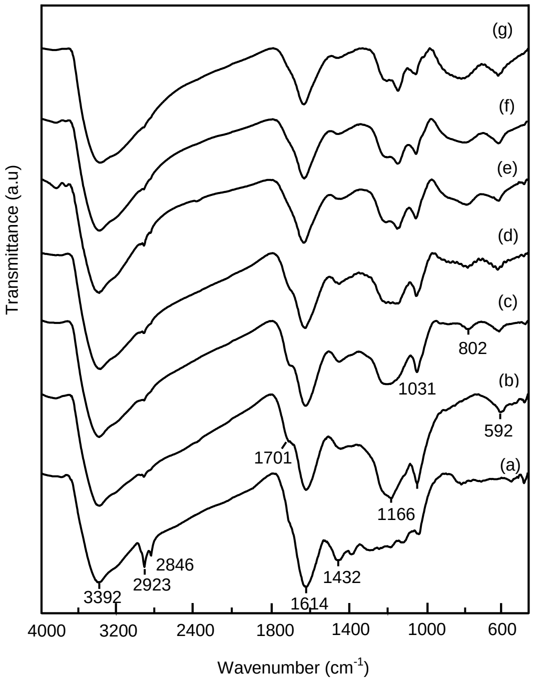


Figure 3 FTIR spectra of (a) Coal, (b) SO_3H/Coal, (c) Ti(500)-SO_3H/Coal, (d) Ti(1000)-SO_3H/Coal, (e) Ti(1500)-SO_3H/Coal, (f) Ti(2000)-SO_3H/Coal and (g) Ti(2500)-SO_3H/Coal

The infrared spectra of all titanium dioxide-supported sulfonated low rank coal after being calcined have similar FTIR spectra (Figure 4). The broad peak around 3401 cm^{-1} is characteristics of the terminal silanol hydroxyl groups and hydroxyl groups with hydrogen bonding of water molecule with silanol groups [19]. The absorption band at around 2917 and 2857 cm^{-1} are identified as the symmetric and asymmetric stretching mode of the C-H groups of the aromatic and aliphatic organic template. A prominent peak that appeared at 1095 cm^{-1} is due to the Si-O-Si asymmetric stretching of silica framework in coal [19,20]. According to Flanigen, the absorption bands around 1100, 800 and 450 cm^{-1} are lattice modes associated with internal linkages in tetrahedral SiO_4 (or AlO_4) and are insensitive to structural changes [21].

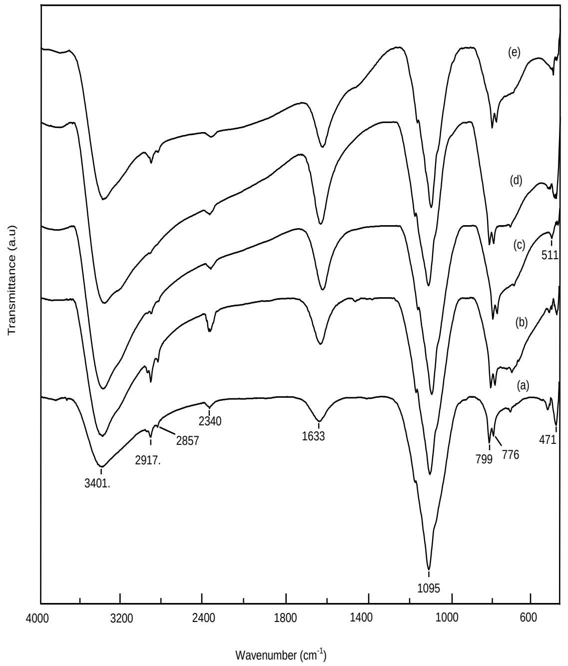


Figure 4 FTIR spectra of (a) Ti(500)-SO_3H/Coal500, (b) Ti(1000)-SO_3H/Coal500, (c) Ti(1500)-SO_3H/Coal500, (d) Ti(2000)-SO_3H/Coal500 and (e) Ti(2500)-SO_3H/Coal500

The DR UV-vis spectra of titanium dioxide-supported sulfonated low rank coal after being calcined are shown in Figure 5. The adsorption peak at 230-300 nm is considered as isolated or low polymerization Ti(IV) species that shows Ti-O-Ti bonding in titanium dioxide-sulfonated low rank coal [22]. The absorption peak around 220 nm indicates a characteristic of partially overlapping $O^{2-} \rightarrow Ti^{4+}$ charge transfer (CT) of tetrahedral titanium environment while octahedral titanium environment is revealed at around 270 nm. All spectra showed the increase in the intensity of absorption peak around 220 nm and this indicates the occurrence of transformation in some of the octahedral titanium framework to the tetrahedral structure during the impregnation of titanium dioxide [23,24]. The presence of anatase and rutile phase can be seen from the absorption above 300 nm [25]. The anatase absorption is observed at around 370 nm and rutile at around 410 nm. The samples were dominated by anatase due to the absence of the absorption peak around 410 nm for rutile.

The percentage amount of adsorbed water on the low rank coal and sulfonated low rank coal before and after being impregnated with titanium dioxide is displayed in Figure 6. The figure shows that the sulfonated low rank coal possesses the highest hydrophilic properties compared to the low rank coal and titanium dioxide-support sulfonated low rank coal. This is due to the functional groups such as COOH, OH and SO_3H, on the surface. The average percentage of adsorbed water the samples before calcination for Ti(500)-SO_3H/Coal, Ti(1000)-SO_3H/Coal, Ti(1500)-SO_3H/Coal, Ti(2000)-SO_3H/Coal and Ti(2500)-SO_3H/Coal are 16.9, 16.5, 13.9, 13.4 and 13.3, respectively. The water adsorption capacity ware slightly decreased as some functional groups have been replaced by titanium dioxide and released during the impregnation process.

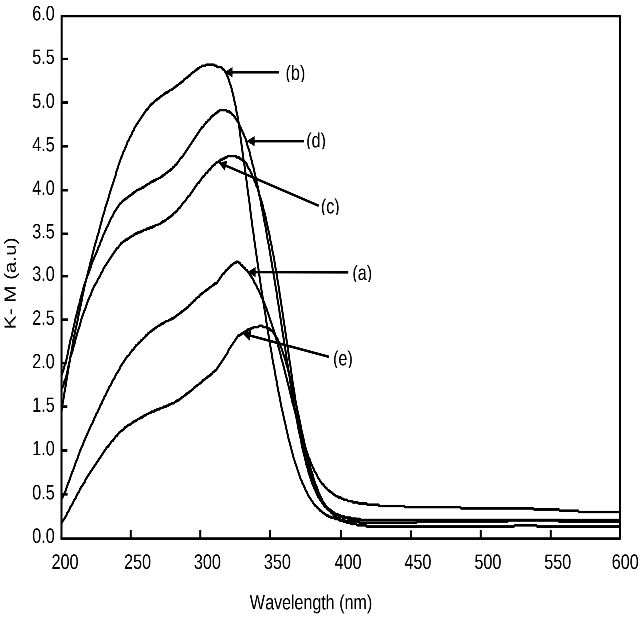


Figure 5 UV-vis spectra of (a) Ti(500)-SO_3H/Coal500, (b) Ti(1000)-SO_3H/Coal500, (c) Ti(1500)-SO_3H/Coal500, (d) Ti(2000)-SO_3H/Coal500 and (e) Ti(2500)-SO_3H/Coal500

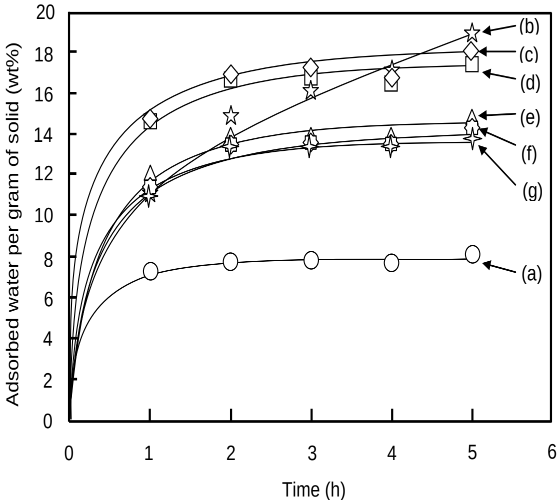


Figure 6 Percentage of adsorbed water on the surface of (a) Coal, (b) SO_3H/Coal, (c) Ti(500)-SO_3H/Coal, (d) Ti(1000)-SO_3H/Coal, (e) Ti(1500)-SO_3H/Coal, (f) Ti(2000)-SO_3H/Coal and (g) Ti(2500)-SO_3H/Coal

The average of percentage of adsorbed water on the samples after being calcined for Ti(500)-SO_3H/Coal500, Ti(1000)-SO_3H/Coal500, Ti(1500)-SO_3H/Coal500, Ti(2000)-SO_3H/Coal500 and Ti(2500)-SO_3H/Coal500 were 4.2, 6.1, 8.4, 9.5 and 10.7, respectively. The samples are more hydrophobic after calcination as functional groups such as COOH, OH and SO_3H, were released from the surface during the calcination process. The hydrophobicity of the samples after calcination completely is shown in Figure 7.

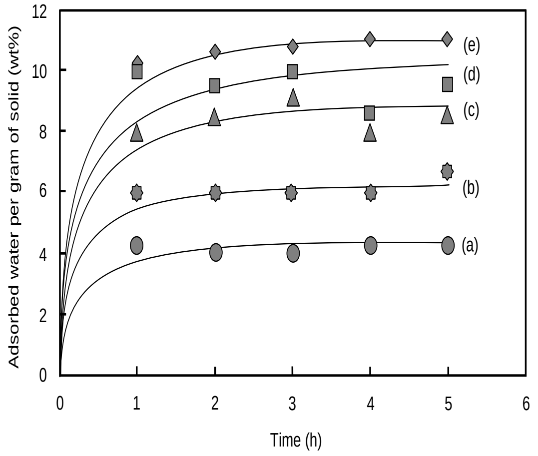


Figure 7 Percentage of adsorbed water on the surface of (a) Ti(500)-SO_3H/Coal500, (b) Ti(1000)-SO_3H/Coal500, (c) Ti(1500)-SO_3H/Coal500, (d) Ti(2000)-SO_3H/Coal500 and (e) Ti(2500)-SO_3H/Coal500

The thermalgravimetric (TG) profile of the low rank coal, Ti(1500)-SO_3H/Coal and Ti(1500)-SO_3H/Coal500 samples are shown in Figure 8. Generally, TG analysis is used to illustrate the amount of carbon that is released from samples. TG analysis of the low rank coal displayed a two-stage weight loss. In the first-stage, the weight loss (around 12.1%) was due to desorption water and adsorption of gas molecules (<200 °C). In the second stage, the weight loss (~33.63%) was caused by carbon materials from organic compounds that decomposed at 200 – 800 °C. TG analysis of Ti(1500)-SO_3H/Coal consists of a single-stage weight loss of about 51%, which is caused by the carbonation process by concentrate sulfuric acid, leading to easy removal of carbon. Meanwhile, Ti(1500)-SO_3H/Coal500 also revealed a two-stage weight loss. The first-stage loss (~7%) was caused by the desorption of water and adsorption of gas molecules (<200 °C). In the second stage (around 8%) the weight loss at 200 – 800 °C is from released as carbon from organic compound remain.

The nitrogen adsorption-desorption isotherms and corresponding BJH pore size distributions of Ti(2500)-SO_3H/Coal and Ti(2500)-SO_3H/Coal500 are shown in Figure 9. Both isotherms are type V in the IUPAC classifications, which is typical for mesoporous materials. The isotherms exhibited clear hysteresis loops in the relative pressure range of ~0.5-1.0. The pore size distribution (Figure 9(b)) indicated the presence of uniform mesopores (~117.4 Å). The pore characteristic of the sample, surface area by BET plot, pore volume by the t-plot method and pore size estimated from desorption average pore width (4V/A by Langmuir).

The BET surface area of the samples before calcination Ti(2500)-SO_3H/Coal (64.8 m^2/g) was lower than sample after calcination/ Ti(2500)-SO_3H/Coal500 (98.2 m^2/g). Similarly, the pore volume of Ti(2500)-SO_3H/Coal (0.0006 cm^3/g) was also lower than that of Ti(2500)-SO_3H/Coal500 (0.0019 cm^3/g). Likewise, the pore size of Ti(2500)-SO_3H/Coal (117.4 Å) was lower than Ti(2500)-SO_3H/Coal500 (143.6 Å).

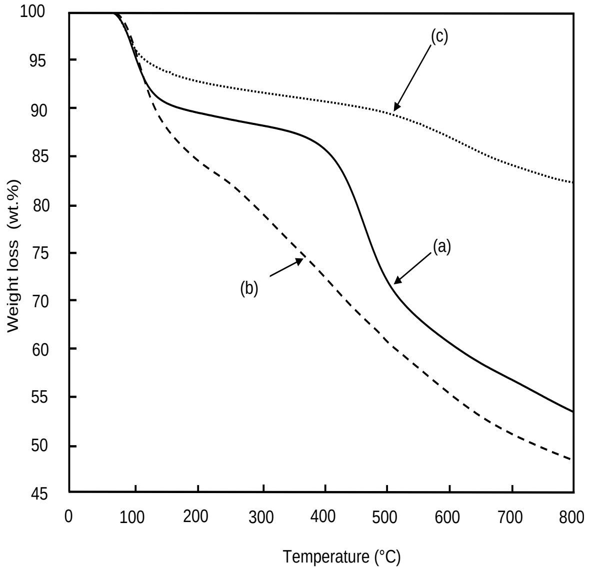


Figure 8 TGA curves of (a) coal, (b) Ti(1500)-SO_3H/Coal and (c) Ti(1500)-SO_3H/Coal500

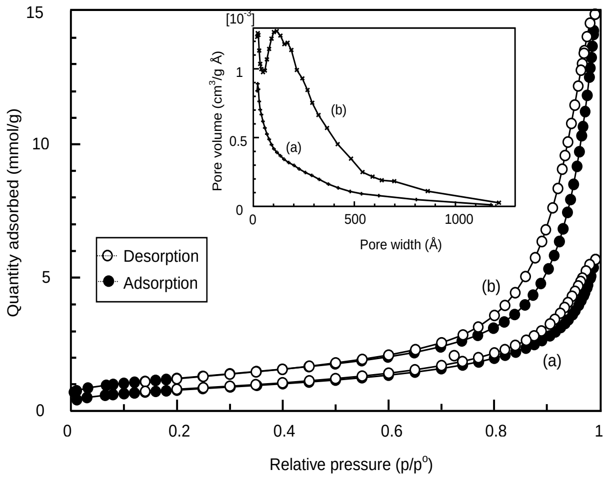
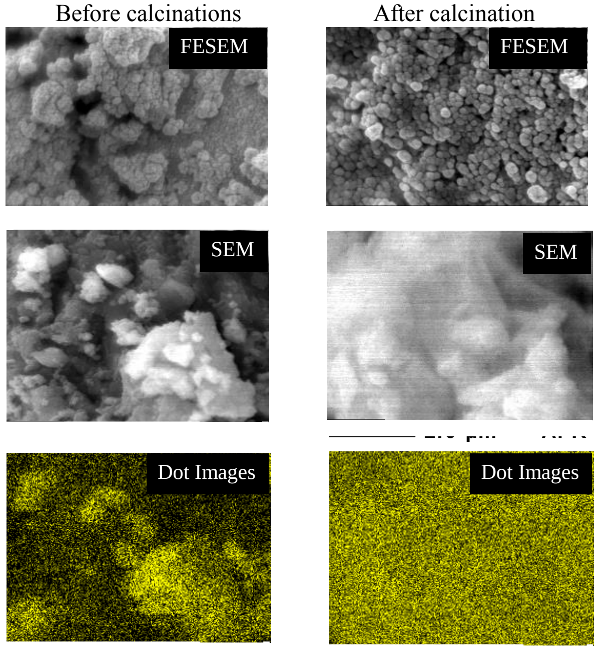


Figure 9 N_2 adsorption isotherms and pore size distribution of (a) Ti(2500)-SO_3H/Coal and (b) Ti(2500)-SO_3H/Coal500

FESEM images of Ti(1500)-SO_3H/Coal and Ti(1500)-SO_3H/Coal500 for the catalysts before and after being calcined are shown in Figure 10. The images reveals the differences in surface morphology among the samples. The images showed spherical structures and the agglomeration of titanium dioxide on the catalysts surface. FESEM image of Ti(1500)-SO_3H/Coal showed no clearly the spherical structure and the agglomeration of titanium dioxide that covered most of the carbon surface. On the other hand, the FESEM image of Ti(1500)-SO_3H/Coal500 shows the spherical structure and the agglomeration of titanium dioxide that covered almost on of carbons surface appeared more clearly and sharper.



(a) (b)

Figure 10 FESEM images of (a) Ti(1500)-SO_3H/Coal and (b) Ti(2500)-SO_3H/Coal500

The formation of Ti(1500)-SO_3H/Coal and Ti(1500)-SO_3H/Coal500 were confirmed by EDX analysis. The EDX spectra of Ti(1500)-SO_3H/Coal and Ti(1500)-SO_3H/Coal500 are shown in Fig. 11 and EDX measurement result are listed in Table 3. Ti(2500)-SO_3H/Coal catalyst contains carbon (46.6%), oxygen (27.0%), aluminium (1.9%), silicon (6.7%), sulfur (3.3%) and titanium (13.5%). Some elements of Ti(1500)-SO_3H/Coal500 decreased in percentage such as carbon (13.1%), aluminium (0.9%), silicon (3.9%) and sulfur (0.6%). Only titanium and oxygen increased with 44.7% and 35.4%, respectively.

Table 3 The elements in Ti(1500)-SO_3H/Coal and Ti(1500)-SO_3H/Coal500 from EDX measurement

Elements	**Ti(1500)-SO_3H/Coal (%)**	**Ti(1500)-SO_3H/Coal500 (%)**
C	51.43	7.63
O	29.49	33.25
Al	0.74	1.27
Si	2.31	4.06
S	3.35	0.67
Ti	11.78	53.37

3.2 Catalytic Activity

Figure 11 shows the histogram of yields of benzaldehyde, phenyl acetaldehyde, and styrene oxide catalyzed by acid catalyst of titanium dioxide-supported sulfonated low rank coal. The amount of benzaldehyde was used as the basis for further explanation because it is the main product in this reaction. For comparison, TiO_2, C and SO_3H/C were also used as catalysts. It can be seen that the yield of benzaldehyde was 0.081 mmol when no catalyst was used and the yield of benzaldehyde did not change much when TiO_2 and C were used as the catalyst. This indicates that TiO_2 and C have low catalytic activities in this reaction. SO_3H/Coal exhibited higher catalytic activity with a benzaldehyde yield of 0.127 mmol due to the presence functional groups such as COOH, OH and SO_3H on the surface.

The catalytic activity of titanium dioxide-supported sulfonated low rank coal, before being calcined exhibited a higher yield when the amount of titanium active sites increased. The yields of benzaldehyde by Ti(500)-SO_3H/Coal, Ti(1000)-SO_3H/Coal, Ti(1500)-SO_3H/Coal, Ti(2000)-SO_3H/Coal and Ti(2500)-SO_3H/Coal improved with the value 0.196, 0.433, 0.783, 1.120, and 1.441 mmol while the selectivity were 88, 88, 89, 92 and 96%, respectively. The increase in oxidation products before calcination can be explained by the increasing in titanium active sites, which were impregnated on the carbon framework's surface in sulfonated low rank coal. Before calcination, the chemical bonds between carbon and the carbon in sulfonated coal are not yet destroyed. This bigger carbon framework can be used for titanium active sites to be well dispersed and attached on. The dominance of carbon in titanium dioxide-supported sulfonated low rank coal before calcination has already been proven by TGA and FESEM.

The catalytic activity of titanium dioxide-supported sulfonated low rank coal after calcination exhibited almost similar pattern. The yields of benzaldehyde of Ti(500)-SO_3H/Coal500, Ti(1000)-SO_3H/Coal500, Ti(1500)-SO_3H/Coal500, Ti(2000)-SO_3H/Coal500 and Ti(2500)-SO_3H/Coal500 reached 0.591, 0.613, 0.599, 0.623, and 0.611 mmol, respectively. The increasing amount of titanium active sites in the catalyst after calcination did not influence the yield of the products. This is caused by the carbon framework in sulfonated low rank coal that acts as a catalyst support, collapsed, decreased or released as carbon dioxide during the calcination process. Furthermore, agglomeration of the titanium dioxide occured after titanium dioxide-supported sulfonated low rank coal was calcined. The agglomeration of titanium dioxide and carbon reduction have already been proven by FESEM (Figure 10).

The catalytic activity was also investigated by using the conversion percentage and the turnover number (TON) of Ti(IV). Before calcination, the conversion and TON has increased when the amount of titanium dioxide impregnated on the sulfonated low rank coal increased. The highest conversion and TON was achieved by Ti(2500)-SO_3H/Coal (29.2% and 12.0, respectively). However, after calcination, the conversion and TON decreased, although the amount of titanium dioxide impregnated on the sulfonated low rank coal increased. The conversion of styrene by Ti(500)-SO_3H/C500 is 11% and TON is 24 which are higher than those of other catalysts. In addition, the selectivity of benzaldehyde also shows the same pattern. The selectivity increased before calcination and decreased after calcination when the amount of titanium impregnated on the sulfonated low rank coal increased. The complete data of the conversion, selectivity and TON are listed in Table 4.

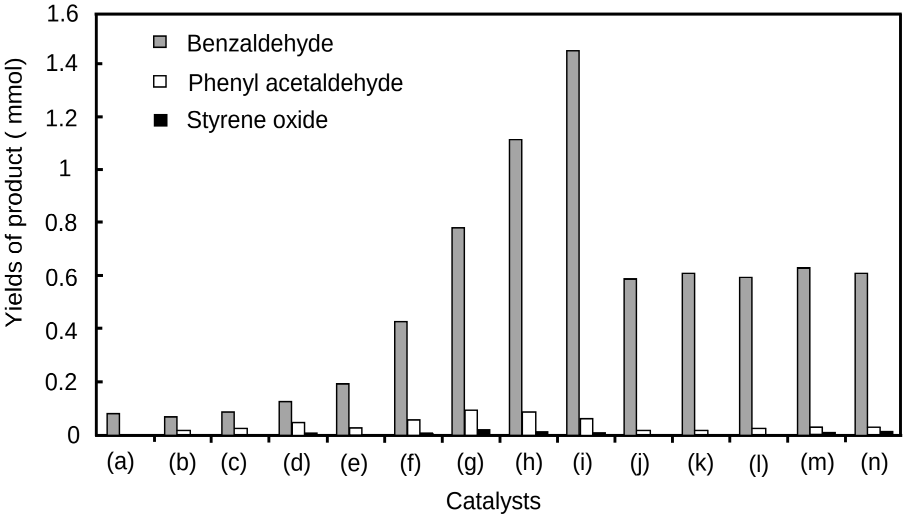


Figure 11 The absolute amount of benzaldehyde, phenyl acetaldehyde and styrene oxide from the oxidation of styrene using (a) no catalyst, (b) TiO_2 (c) Coal, (d) SO_3H/Coal, (e) Ti(500)-SO_3H/Coal, (f) Ti(1000)-SO_3H/Coal, (g) Ti(1500)-SO_3H/Coal, (h) Ti(2000)-SO_3H/Coal (i) Ti(2500)-SO_3H/Coal (j) Ti(500)-SO_3H/Coal500, (k) Ti(1000)-SO_3H/Coal500, (l) Ti(1500)-SO_3H/Coal500, (m) Ti(2000)-SO_3H/Coal500 and (n) Ti(2500)-SO_3H/Coal500 as catalysts. The reactions were carried out at room temperature for 20 h with styrene (5 mmol), 30% H_2O_2 (5 mmol) and catalyst (50 mg)

Table 4 Catalytic activity of the catalysts in the oxidation of styrene with 30% H_2O_2 as the oxidant

Catalyst	Conversion^a (%)	Selectivity^b (%)			TON^c
		Benzaldehyde	Phenylacetaldehyde	Styrene oxide	
No catalyst	5	100	0	0	0
TiO_2	1	86.0	12.6	1.4	0.1
Coal	0.1	81.4	16.7	1.9	0
SO_3H/Coal	0.5	72.3	24.9	2.8	0
Ti(500)- SO_3H/Coal	4.1	88.6	10.3	1.1	8.8
Ti(1000)- SO_3H/Coal	11.9	87.9	10.9	1.2	9.8
Ti(1500)- SO_3H/Coal	15.1	88.7	10.2	1.1	11.8
Ti(2000)- SO_3H/Coal	20.9	92.3	6.9	0.8	12.1
Ti(2500)- SO_3H/Coal	29.2	96.0	3.6	0.4	12.0
Ti(500)- SO_3H/Coal500	11.1	98.0	1.8	0.2	24.1
Ti(1000)- SO_3H/Coal500	10.6	97.4	2.3	0.3	12.6
Ti(1500)- SO_3H/Coal500	8.7	96.9	2.9	0.2	8.2
Ti(2000)- SO_3H/Coal500	13.5	94.9	3.9	1.2	6.5
Ti(2500)- SO_3H/Coal500	6.7	93.7	4.3	2.0	5.2

^{a}Conversion = (∑mmol of all the products / (mmol of styrene$_{final}$ + ∑mmol of all the products)) x 100 ,
^{b}Selectivity = (mmol of every product/ ∑mmol of all the products) x100
^{c}TON = (mmol of the particular product$_{final}$ / mmol of Ti(IV) present in the catalyst)

■4.0 CONCLUSION

In this research, titanium dioxide-supported sulfonated low rank coal was successfully synthesized by using the impregnation method, with titanium(IV) isopropoxide as the source of Ti. The structure of titanium dioxide-supported sulfonated low rank coal before calcination is amorphous and crystalline after calcination. Titanium dioxide-supported sulfonated low rank coal as a catalyst before calcinations is more active in the oxidation of styrene, giving benzaldehyde as the main product than after calcination. The existence of Ti(IV) active sites in sulfonated low rank coal before calcination is able to enhance the catalytic activity. As for sulfonated coal after calcination, the positive effect on Ti(IV) was lost, hence increasing amount of Ti did not contribute to the catalytic activity.

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