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Utilization of low rank coal as oxidation catalyst by controllable removal of its carbonaceous component



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ABSTRACT

Controlled removal of carbonaceous component in low rank coal by sulfonation followed by calcination demonstrated that it is a simple and effective method to utilize this material as catalyst in the oxidation of styrene. Low rank coal is one of the least utilized categories of coal. However, it shows excellent potential as a catalyst due to high concentrations of carbon and other elements, such as transition metals, which are embedded inside its structure. In this research, the low rank coal was treated by sulfonation followed by calcination in order to activate the transition metals embedded in it. The catalytic activity of the treated low rank coal was tested in the oxidation of styrene by aqueous hydrogen peroxide. The low rank coal showed high catalytic activity after sulfonation and calcination at 700 °C, with 3% of styrene conversion and 97% of selectivity toward benzaldehyde. The transition metal active sites in low rank coal that play the most important role in the oxidation of styrene were determined by coal mimicking models. The presence of cobalt oxide and titanium oxide active sites in the low rank coal plays the most significant role in the oxidation of styrene by aqueous hydrogen peroxide.

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1. Introduction

Coal is one of the most abundant fossil fuel derived energy sources in the world. Coal plays an important role as a source of energy in many countries, such as in Indonesia. The total coal reserves in Indonesia are estimated at 21.13 billion tons, which contributes to around 3% of the world's total coal reserves. Coals from Indonesia consist of approximately 24% of low-rank coal, 62% of medium-rank coals, 13% of high rank coals and only 1% of very high rank coals [1]. Since low-rank coal is readily-available from approximately 50% of world's coal reserves and has a low economic value [2,3], it is of interest to convert it into a value-added products.

Coal contains a relatively high concentration of trace elements when compared with other geological materials [4]. Besides carbon, hydrogen and oxygen as the main elements, some transition metals can also be found in coal. Transition metals are usually embedded in the structure of coal and form coordination bonds with aqua mono- and multi-nuclear hydroxyl transition metal complexes [5]. Some minerals in coal, such as illite, pyrite, magnetite, pyrrhotite, jarosite, hematite and siderite, have been known to have catalytic effects in various coal utilization processes [6]. For catalytic purposes, coal usually undergoes pyrolysis in order to extract its carbon and then the extracted carbon is functionalized with different active sites in order to be used as catalysts [7–14]. To the best of our knowledge, there has not been any research on the utilization of low rank coal with naturally present metal catalytic active sites as catalyst.

In this research, low rank coal used was obtained from Batuah, Loajannan, Kutai Kartanegara, East Kalimantan, Indonesia. It was used and treated by sulfonation followed by calcination in order to relocate the catalytic active sites (transition metal oxides) that are

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embedded inside the carbonaceous component to the surface. The mimicking of low rank coal after calcination was also done in order to determine the active sites in coal, which influenced the catalytic activity in the oxidation of styrene with aqueous hydrogen peroxide. It is expected that this research can increase the value and also the usage versatility of low rank coal, by showing that low rank coal itself is an active catalyst, even without any addition of active sites to it.

2. Experimental

2.1. Raw materials

The low rank coal obtained from Batuah, Loajannan, Kutai Kartanegara, East Kalimantan, Indonesia, was used as the raw material. The chemical composition and physical properties from the low rank coal were investigated by using 1 kW wavelength dispersive X-ray fluorescence (WDXRF) and thermogravimetric analysis (TGA). WDXRF was used to determine elements that are present in the low rank coal. The weight loss in the lignite coal with increasing temperature was determined by using thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The thermal experiments were carried out using a Mettler Toledo TGA-DTA STAR SW.8.10 thermal analyzer with a heating rate of 10 °C/min, temperature range of 0 to 800 °C and under nitrogen atmosphere. The investigation of weight loss in the low rank coal was used to control the amount of carbon while increasing the temperature.

2.2. Sample preparation

The sulfonation of the low rank coal (denoted Coal) was carried out by adding sulfuric acid (6 ml, 98%, JT Baker) per gram of coal. The mixture was stirred intermittently in an oil bath at 90 °C for 24 h. Subsequently, the mixture was washed with distilled water to remove any loosely bound acid. Then it was dried overnight at 110 °C [15]. Sulfonated low rank coal was denoted as SO₃H/Coal. For the thermal activation, SO₃H/Coal (5 g) was calcined at the following temperatures, namely 350, 500, 700 and 900 °C, in a VULCAN™ 3–550 muffle furnace. Catalysts were labeled as SO₃H/Coal-Y; where SO₃H/Coal refers to the sulfonated low rank coal and Y refers to calcination temperature employed. For example, SO₃H/Coal-500 represents the low rank coal catalyst that underwent sulfonation and calcined at 500 °C. A complete list of the codes and treatments used in this study is presented in Table 1.

2.3. Samples characterization

The low rank coal, sulfonated low rank coal and calcined sulfonated low rank coal were characterized by Fourier transform infrared (FTIR) spectroscopy using a Perkin Elmer (Model Spectrum One) spectrometer, with a spectral resolution of 2 cm⁻¹, scanning of 10 s, at 20 °C. Crystallinity and phase content of the solid materials were investigated using a Bruker AXS Advance D8 X-ray diffractometer (XRD) with the Cu K_α (λ = 1.5406 Å) radiation as the

diffracted monochromatic beam at 40 kV and 40 mA. The pattern was scanned in the 2θ range, of 2 and 60° at a gradual increment of 0.05° and step time of 1 s. The hydrophobicity of all catalysts was determined using the water adsorption technique [16]. 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 min. The percentage of adsorbed water as a function of time was determined by $((m_t - m_o)/m_o) \times 100\%$, where m_t represents the sample mass after adsorption of water and m_o represents the initial mass of the sample [17]. Scanning electron microscopy images were obtained by using JEOL JSM-6390LV instrument with an accelerating voltage of 15 kV. X-ray photoelectron spectrometer (XPS), Kratos, Shimadzu Axis Ultra DLD was used for measuring the element composition on the surface of catalysts. The nitrogen adsorption-desorption isotherms were measured at 77 K using a Micromeritics ASAP 2020 V4.00 instrument. The apparent surface areas were calculated from the nitrogen adsorption data in the 0.01–0.2 relative pressure range, according to the Brunauer-Emmett-Teller (BET) equation. The total pore volume was obtained from the amount of N₂ adsorbed at a relative pressure of 0.976. The micropore volume was determined using the t-plot method. The pore size distributions (PDS) based on the nitrogen isotherms were calculated by applying the Barrett-Joyner-Halenda (BJH) model. Samples were degassed at 150 °C for 12 h prior to analysis.

2.4. Catalytic testing

The catalytic activities of the prepared catalysts were tested out in the oxidation of styrene with aqueous H₂O₂ (30%, Merck) as the oxidant. Styrene (5 mmol, Aldrich), aqueous H₂O₂ (5 mmol, 30%, Merck), acetonitrile (4.5 ml, Merck) and catalyst (100 mg) were mixed in a sample bottle and stirred at room temperature for 24 h [18]. The products were then separated from the catalysts by centrifugation. A portion of the resulting liquid mixture was withdrawn and analyzed by GC-2014 Shimadzu-gas chromatograph equipped with a BPX5 column (30 m × 0.25 mm × 0.25 μm), a flame ionization detector (FID) and nitrogen as the carrier gas. The temperatures of the injector and detector were programed at 250 and 260 °C, respectively. The temperature of the column oven was programed to increase from 80 to 140 °C, at a rate of 10 °C/min.

2.5. Preparation of mimicked coals

In order to study the effects of different metals on the catalytic activity of low rank coal, low rank coal was mimicked using different precursors. SiO₂ was used as the silica source, Fe(NO₃)₃·9H₂O as the iron source, Ti(SO₄)₂ as the titanium source, Co(CH₃COO)₂·4H₂O as the cobalt source and sucrose (C₁₁H₂₂O₁₁), as the carbon source. The mimicking of SO₃H/Coal was created by mixing all the precursors mentioned above with the same amount contained in the original low rank coal, before undergoing

Table 1
Codes and treatments done to the samples.

Code	Type of treatment	Duration of sulfonation (h)	Temperature of calcinations (°C)	Duration of calcination (h)
Coal	–	–	–	–
Coal-700	–	–	700	2
SO ₃ H/Coal	Sulfonation	24	–	–
SO ₃ H/Coal-350	Sulfonation	24	350	2
SO ₃ H/Coal-500	Sulfonation	24	500	2
SO ₃ H/Coal-700	Sulfonation	24	700	2
SO ₃ H/Coal-900	Sulfonation	24	900	2

pyrolysis at 400 °C for 2 h as the carbonization process. The formulation was based on the chemical composition obtained by XPS of SO₃H/Coal-700. Five different types of mimicked coal were prepared. The first type was prepared with the same metal compositions with SO₃H/Coal-700 and labeled as MCoal (mimicked coal). In a typical experiment, SiO₂ (Fluka Chemika, 3.15 g), Fe(NO₃)₃·9H₂O (Merck, 0.26 g), Ti(SO₄)₂ (Kanto chemical, 0.16 g), Co(CH₃COO)₂·4H₂O (QRec, 0.37 g) and C₁₁H₂₂O₁₁ (sucrose, 1.95 g), were dispersed in deionized water (20 ml), heated at 80 °C until all water evaporated, and pyrolyzed under a nitrogen atmosphere at 400 °C for 2 h to allow carbonization. The second type of mimicked coal was synthesized with the exact procedures as the first type, but without the addition of Fe precursor, while the third was prepared without using the Ti precursor. Cobalt as a precursor was excluded during the preparation of the fourth type of mimicked coal, while the fifth was formulated without C precursor. These mimicked coals were denoted as MCoal(x), where x represents the precursors added during the preparation.

3. Results and discussion

3.1. Physical properties

The thermogravimetric analysis curves of the low rank coal are displayed in Fig. 1. The weight loss of the low rank coal was obtained in two steps. In the first step, the weight loss began at 28 °C, reached midpoint at 64 °C and continued until 130 °C. This step was caused by the release of water from the sample. The weight loss in the second step started at 349 °C and ended at 657 °C, with a midpoint of 463 °C, which was due to the decomposition of organic compounds. The result from thermogravimetric analysis is used to determine the temperature calcination at range 350–900 °C of the low rank coal.

The results from wavelength dispersive X-ray fluorescence (WDXRF) show that the low rank coal consisted of major elements like calcium (Ca), ferum (Fe), silicon (Si) and aluminium (Al). Various transition elements also were found inside in the coal sample such as titanium (Ti), copper (Cu), manganese (Mn), nickel (Ni) and zinc (Zn). The complete list of elements and compounds is displayed in Table 2.

Elemental analysis of the bulk sample using XRF is important to determine the elements available on the sample. However, not all elements present influence the catalytic activity of the coal, as only the elements on the surface play vital roles in catalytic reactions. Thus elemental analysis on the surface of the coal by using XPS

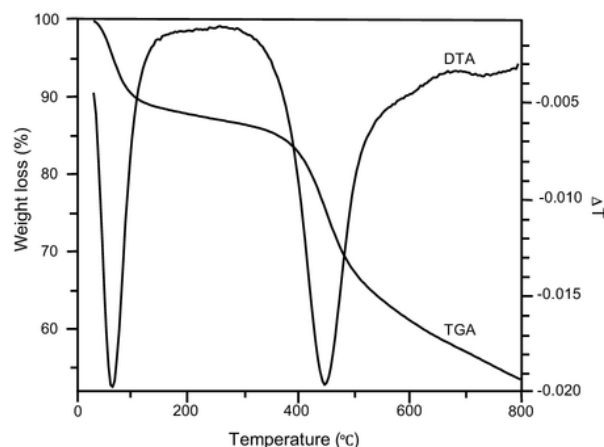


Fig. 1. TGA and DTA curves of the low rank coal used.

Table 2
Elements analysis of the low rank coal obtained using WDXRF.

Element	wt%	Element	wt%
Ca	24.7	P	1.6
Fe	21.7	Na	0.8
Si	19.3	Ru	0.3
Al	12.0	Cl	0.3
S	5.6	Mo	0.2
Ti	3.8	Cu	0.2
Sr	3.7	Mn	0.2
Mg	2.1	Ni	0.1
Ba	1.7	Zn	0.1
K	1.7		

also extremely important. The full XPS report from the low rank coal is shown in Table 3. The main elements on the low rank coal surface were C, O, N, C, S, Al and Fe. They were indicated by binding energies of 282, 530, 398, 348, 101, 73 and 712 eV, respectively. It should be highlighted that during the elemental analysis using WDXRF and also the proximate analysis, Co was not detected in low rank coal. This is due to the fact that the analyses were done on the bulk structure, where the concentration of Co was very low. The Co was only detectable by XPS surface analysis after sulfonation and calcination, as the active sites (Co) has been successfully relocated to the surface.

Fig. 2 shows the FTIR spectra of sulfonated low rank coal and sulfonated low rank coal that had been calcined at various temperatures. The adsorption bands at 1166, 1026, and 595 cm⁻¹ were related to the attachment of -SO₃H groups. The adsorption band at 1166 indicated O=S=O symmetric stretching mode in -SO₃H and 1026 cm⁻¹ assigned SO₃⁻ stretching mode. The SO₂ deformation frequency was detected in the region of 592 cm⁻¹ [19,20]. The -SO₃H groups vanished after the samples were calcined at temperature higher than 350 °C presumably due to release and evaporation of SO₂ and H₂O. The adsorption band at 1095, 799, 779 and 481 cm⁻¹ were attributed to symmetric stretching vibrations of Si-O-Si, while the adsorption at 481 cm⁻¹ is assigned to the bending mode of Si-O [21,22]. The adsorptions at 1095, 799, 779 and 481 cm⁻¹ indicate the presence of quartz. The adsorption band at 1626 cm⁻¹ was assigned to aromatic ring like C-C stretching mode in polyaromatics [20]. The absorption bands at 2920 and 2846 cm⁻¹ were related to the symmetric and asymmetric stretching modes of aromatic and aliphatic C-H sp³ groups of the organic template [23]. The intensity of the absorption band at 2920, 2846 and 1626 cm⁻¹ were reduced, which is in line with the reduction of carbon from aromatic and aliphatic compounds in the low rank coal, with increasing calcination temperatures. The absorption band at 3394 cm⁻¹ correlated to O-H stretching vibration of -COOH and phenolic OH groups, indicating the presence of -OH groups before and after sulfonation [20]. The intensity of O-H stretching decreased during calcination due to -COOH and -OH groups being released from sulfonated low rank coal as CO, CO₂ and H₂O.

Fig. 3 displays the XRD patterns of the low rank coal and sulfonated low rank coal (SO₃H/Coal) with recorded at different calcination temperatures. It was observed that majority of the peaks displayed by the low rank coal were broad and weak diffractions in the 2θ range of 10–30°. These peaks were attributed

Table 3
Elements analysis of coal and SO₃H/C-700 using XPS.

Sample	Element concentration (wt%)										
	C	O	N	Ca	Si	Al	Fe	Co	Ti	K	S
Coal	72.3	22.0	1.8	0.5	1.8	1.2	0.5	-	-	-	-
SO ₃ H/Coal-700	8.2	62.5	-	1.6	14.8	9.1	0.4	0.9	0.3	0.4	1.5

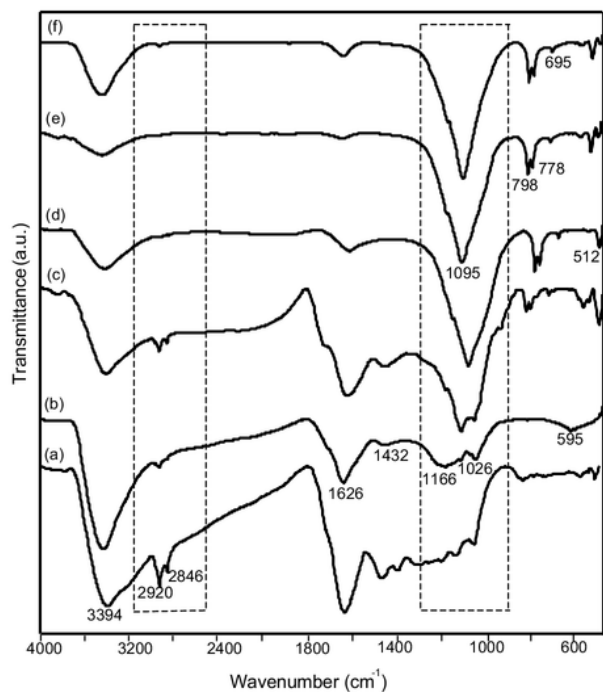


Fig. 2. FTIR spectra of (a) Coal, (b) $\text{SO}_3\text{H}/\text{Coal}$, (c) $\text{SO}_3\text{H}/\text{Coal-350}$, (d) $\text{SO}_3\text{H}/\text{Coal-500}$, (e) $\text{SO}_3\text{H}/\text{Coal-700}$ and (f) $\text{SO}_3\text{H}/\text{Coal-900}$.

to the amorphous carbon from the aromatic compounds [24] and only showed small crystallinity at 2θ angle of 26.5° . The XRD pattern for sample $\text{SO}_3\text{H}/\text{Coal}$ showed that it was composed mostly of amorphous carbon with low crystallinity. When $\text{SO}_3\text{H}/\text{Coal}$ was calcined at 350°C ($\text{SO}_3\text{H}/\text{Coal-350}$), the fraction of amorphous carbon decreased and the crystallinity increased. When the calcination temperature increased (500 to 900°C), $\text{SO}_3\text{H}/\text{Coal}$ turned to a fully crystalline sample with complete loss of its amorphous carbon. The dominant peaks at 2θ angle of 26.5° that existed in every pattern indicated the presence of quartz. The quartz phase could also be identified by the peaks at 2θ angles of 20.6 , 40.1 , 49.8 and 59.7° , with the peaks being most prominent after being calcined at 700°C . The peaks at 2θ angle of 19.6 and 25.1° were assigned to the crystalline muscovite [25].

Fig. 4 shows the amount of adsorbed water on low rank coal, and the $\text{SO}_3\text{H}/\text{Coal}$ before and after calcination. The amount of adsorbed water can be attributed to hydrophobicity of the samples. The lower the amount of water adsorbed, the higher is the hydrophobicity of sample. The order of hydrophobicity from high to low is as follows: $\text{SO}_3\text{H}/\text{Coal-900} > \text{SO}_3\text{H}/\text{Coal-700} > \text{Coal} > \text{SO}_3\text{H}/\text{Coal-500} > \text{SO}_3\text{H}/\text{Coal-350} > \text{SO}_3\text{H}/\text{Coal}$, with average percentage of water adsorption of 1.1, 2.8, 9.8, 12.9, 13.9 and 25.4%, respectively. The sulfuric acid treatment caused significant changes in low rank coal surface chemistry. Sulfuric acid solution produced oxygenated functional groups (SO_3H , COOH and OH groups), CO_2 and CO , which caused the catalyst's surface to be hydrophilic and have significant effect on the oxidation of organic compounds, such as in the oxidation of styrene with H_2O_2 , and conversion processes [22]. However, when the calcination temperature increased, functional groups, namely CO_2 and CO , will be released together with the carbon from low rank coal's surface, which then caused an increase in hydrophobicity. The increase in hydrophobicity is caused by the hydrophilic nature of those functional groups, hence losing them also decreases the hydrophilicity.

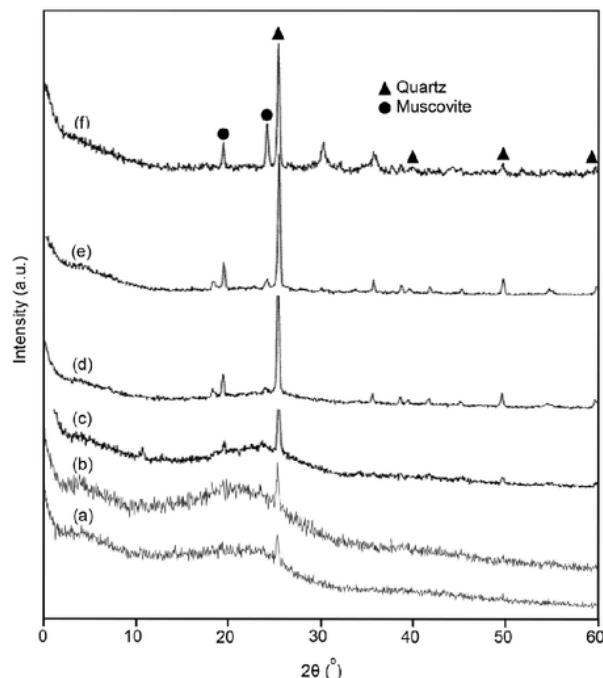


Fig. 3. XRD patterns for (a) Coal, (b) $\text{SO}_3\text{H}/\text{Coal}$, (c) $\text{SO}_3\text{H}/\text{Coal-350}$, (d) $\text{SO}_3\text{H}/\text{Coal-500}$, (e) $\text{SO}_3\text{H}/\text{Coal-700}$ and (f) $\text{SO}_3\text{H}/\text{Coal-900}$.

It is clear that sulfonation and calcination affected the carbon deposition process. In order to further investigate the effects of these processes, the morphologies of the low rank coal before and after sulfonation followed by calcination were investigated using SEM.

Fig. 5 shows the SEM images of Coal, $\text{SO}_3\text{H}/\text{Coal}$ and calcined $\text{SO}_3\text{H}/\text{Coal}$ at different temperatures. From the images shown in Fig. 5a, it can be seen that the low rank coal had a smooth and flat surface with large particles, which indicated the presence of bulk carbon. Fig. 5b represents the SEM image of low rank coal after the sulfonation process, which shows rough surfaces. It also indicates that carbonization occurred in low rank coal, which was assisted

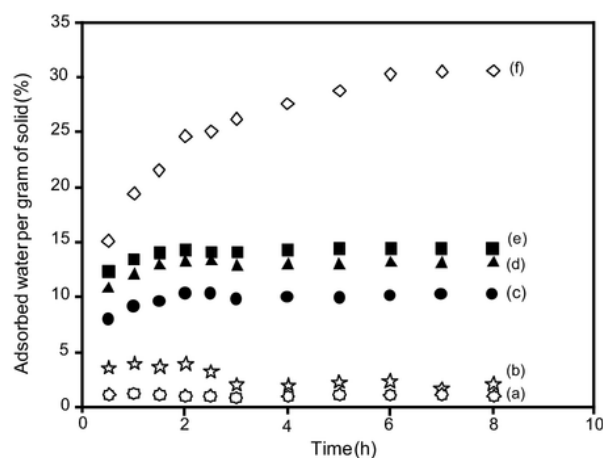


Fig. 4. Water adsorption percentage for (a) $\text{SO}_3\text{H}/\text{Coal}$, (b) $\text{SO}_3\text{H}/\text{Coal-350}$, (c) $\text{SO}_3\text{H}/\text{Coal-500}$, (d) Coal, (e) $\text{SO}_3\text{H}/\text{Coal-700}$ and (f) $\text{SO}_3\text{H}/\text{Coal-900}$.

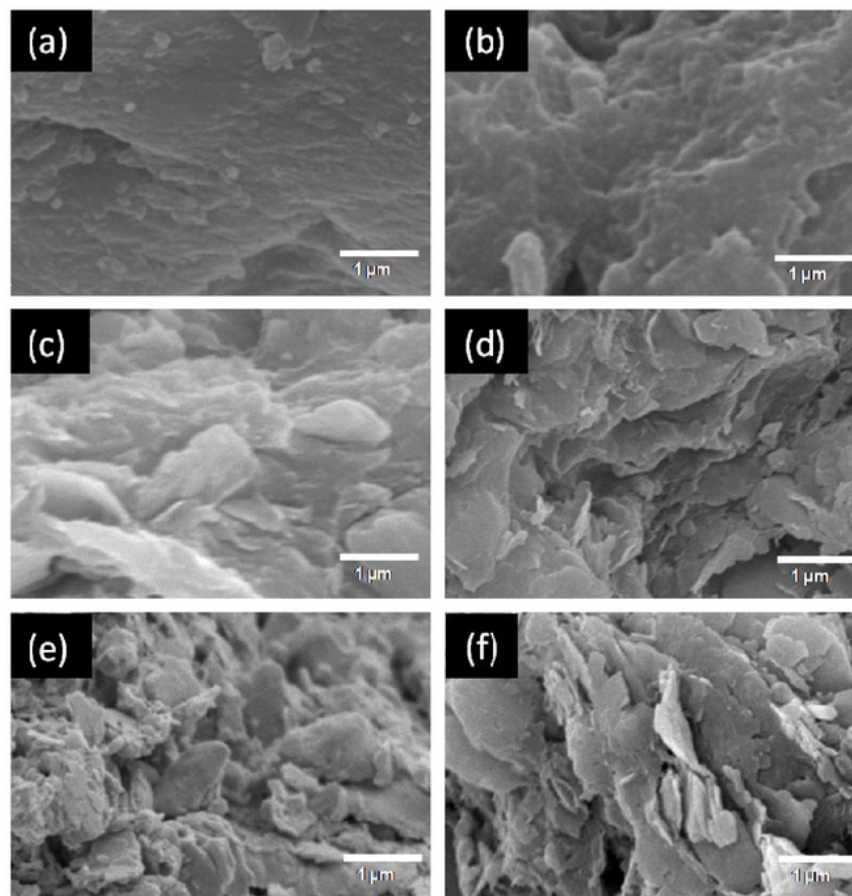


Fig. 5. SEM images of (a) Coal, (b) $\text{SO}_3\text{H}/\text{Coal}$, (c) $\text{SO}_3\text{H}/\text{Coal-350}$, (d) $\text{SO}_3\text{H}/\text{Coal-500}$, (e) $\text{SO}_3\text{H}/\text{Coal-700}$ and (f) $\text{SO}_3\text{H}/\text{Coal-900}$.

by the sulfonation process. Fig. 5c and d shows the SEM images of $\text{SO}_3\text{H}/\text{Coal}$ after being calcined at 350 and 500 °C. From these SEM images, it can be seen that the surfaces were also rough. While the SEM image for sample $\text{SO}_3\text{H}/\text{Coal-700}$ shown in Fig. 5e, the surface appears to have a more significant roughness, which correspond to metals in the low rank coal after calcination. This suggests that the metals in the low rank coal are more exposed after calcination.

The N_2 adsorption-desorption isotherms and corresponding pore size distribution curves (using the BJH method) for low rank coal and $\text{SO}_3\text{H}/\text{Coal-700}$ are shown in Fig. 6. The isotherm of low rank coal is of type IV with a type H-2 hysteresis loop [26] in the relative pressure range of 0.3–0.99. The BET surface area, the total pore volume and the t-plot micropore volume analyses show the following values; 4.0 m^2/g , 0.004764 cm^3/g and $-0.000917 \text{ cm}^3/\text{g}$, respectively. The negative value from t-plot micropore volume exhibited by low rank coal proved that the material does not contain any micropores. This was further supported by the pore size distribution curve that shows the presence of uniform mesopores ($\sim 50.4 \text{ \AA}$). The isotherm of $\text{SO}_3\text{H}/\text{Coal-700}$ is of type V with a type H-3 hysteresis loop in the very narrow relative pressure range of 0.9–0.99 [26]. The BET surface area, the total pore volume and the t-plot micropore volume analyses show the following values; 56.7 m^2/g , 0.15883 cm^3/g and 0.00123 cm^3/g , respectively. The pore size distribution indicates the presence of uniform mesopores ($\sim 27.5 \text{ \AA}$) in $\text{SO}_3\text{H}/\text{Coal-700}$ and also some

microporosity, based on the t-plot micropore volume. These results showed that calcination of low rank coal led to the increase in BET surface area, the total pore volume and the rise of micropore structure for the carbonaceous component in low rank coal.

3.2. Catalytic activity

Oxidation of styrene with aqueous hydrogen peroxide as the oxidant was used to test the catalytic activity of low rank coal, sulfonated low rank coal before and after being calcined at varying temperatures. By using authentic samples of the products and GC analysis, the products of styrene oxidation were benzaldehyde, styrene oxide and phenylacetaldehyde, which is in agreement with previous study [27]. Benzaldehyde was found to be the main product in the styrene oxidation.

Fig. 7 shows the histogram of the conversion and selectivity of products from the oxidation of styrene catalyzed by Coal, Coal-700, $\text{SO}_3\text{H}/\text{Coal}$ and $\text{SO}_3\text{H}/\text{Coal}$ after being calcined at different temperatures. It can be observed that the conversion of styrene and selectivity of benzaldehyde were only 0.7% and 60% when the low rank coal alone was used as the catalyst (Fig. 7b), which values were lower than when no catalyst was used (Fig. 7a). The catalytic activity shown by Coal-700 (Fig. 7c) was also lower than when no catalyst was used, confirming that calcination alone is not sufficient to relocate the catalytic active sites in low rank coal.

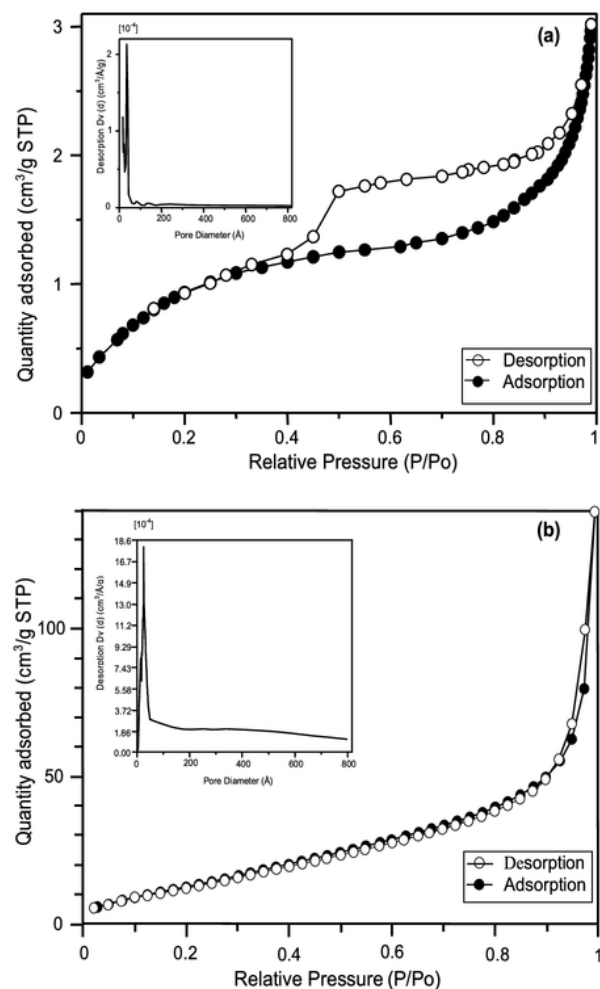


Fig. 6. Nitrogen adsorption-desorption isotherms and pore size distribution patterns (inset) of (a) Coal and (b) $\text{SO}_3\text{H}/\text{Coal-700}$.

The $\text{SO}_3\text{H}/\text{Coal}$ exhibited increased catalytic activity with conversion of styrene and selectivity of benzaldehyde of 1.5% and 79%, respectively (Fig. 7d). This is due to the presence of $-\text{SO}_3\text{H}$ groups on the low rank coal surface. When $\text{SO}_3\text{H}/\text{Coal}$ was calcined at 350°C , a small decrease in the catalytic activity was observed, most probably due to the release of some $-\text{SO}_3\text{H}$ groups from the surface (Fig. 7e). On the other hand, $\text{SO}_3\text{H}/\text{C}$ calcined at 500 , 700 and 900°C exhibited obvious increases in catalytic activity (Fig. 7f–h). The conversion of styrene using $\text{SO}_3\text{H}/\text{Coal-500}$, $\text{SO}_3\text{H}/\text{Coal-700}$ and $\text{SO}_3\text{H}/\text{Coal-900}$ as the catalysts reached 2, 3 and 2.0%, respectively. $\text{SO}_3\text{H}/\text{Coal}$ calcined at 700°C had the best activity of all the catalysts used, with more than 300% increase in the catalytic activity, as compared to those of the low rank coal alone. These improvements in catalytic activity might be due to increased access to the assessment of the metal active sites by substrate in the low rank coal, as reported in the XRF and XPS results. The hydrophobicity and the carbon deposition in the low rank coal during the calcination process also may have contributed to these improvements. Apart from that, it was also shown (Fig. 6) that the surface area of the low rank coal increased after calcination, which may have led to the enhancement in the catalytic activity.

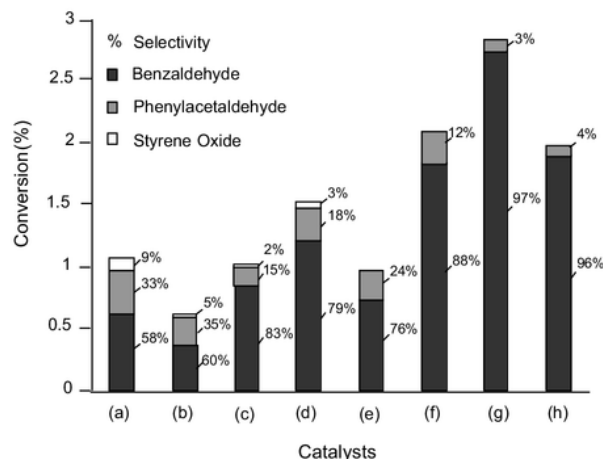


Fig. 7. The conversion of styrene and selectivity of products from the oxidation of styrene using (a) no catalyst, (b) Coal, (c) Coal-700, (d) $\text{SO}_3\text{H}/\text{Coal}$, (e) $\text{SO}_3\text{H}/\text{Coal-350}$, (f) $\text{SO}_3\text{H}/\text{Coal-500}$, (g) $\text{SO}_3\text{H}/\text{Coal-700}$ and (h) $\text{SO}_3\text{H}/\text{Coal-900}$ as the catalysts. The reactions were carried out at room temperature for 20 h with styrene (5 mmol), 30% H_2O_2 (5 mmol) and catalyst (100 mg).

It is generally known that carbon is present as polycyclic aromatic hydrocarbons in low rank coal. When low rank coals containing minerals were activated by the sulfonation, the polycyclic aromatic hydrocarbons compounds were carbonized. The deposition of carbon in low rank coal during thermal treatment also influenced the active sites in the low rank coal. The catalytic active sites were embedded in the low rank coal when the amount of carbon was still abundant. Along with the increase in temperature, the amount of carbon declined, followed by the appearance of more active sites on the surface. As shown in Table 3, many active sites can be found using XPS analysis, such as cobalt, iron and titanium oxides, which play an important role in accelerating styrene oxidation.

3.3. The mimicking of coal

The mimicking of low rank coal was carried out to investigate the combination of active sites in the low rank coal, which plays an important role in styrene oxidation. Coal mimics were formulated in five types.

Fig. 8 shows the histogram of the conversion of styrene, the selectivity of benzaldehyde and phenyl acetaldehyde catalyzed by the mimicked low rank coals. The illustrations of the combination of active sites in the mimicked low rank coals are also given. For comparison purpose, only the conversion of styrene and the selectivity of benzaldehyde were used, as it was the main product in this reaction. It was observed that $\text{SO}_3\text{H}/\text{Coal-700}$ and the mimicked low rank coal $\text{MCoal}(\text{Si},\text{Fe},\text{Co},\text{Ti},\text{C})$ showed almost similar conversion of styrene and selectivity of benzaldehyde. This indicates that the mimicked low rank coal has comparable characteristics as the original low rank coal. The catalytic activities of the combination of active sites in mimicked low rank coal catalysts follow the trend of: $\text{MCoal}(\text{Si},\text{Co},\text{Ti},\text{C}) > \text{MCoal}(\text{Si},\text{Co},\text{Fe},\text{C}) > \text{MCoal}(\text{Si},\text{Co},\text{Fe},\text{Ti}) > \text{MCoal}(\text{Si},\text{Fe},\text{Co},\text{Ti},\text{C}) > \text{MCoal}(\text{Si},\text{Fe},\text{Ti},\text{C})$. Based on the trend of the catalytic activities showed in Fig. 8, the absence of Fe in the mimicked catalyst shows the highest conversion of styrene. This indicates that the presence of Fe in low rank coal give a negative effect in the oxidation of styrene. The reason of this phenomenon is still being investigated in our laboratory.

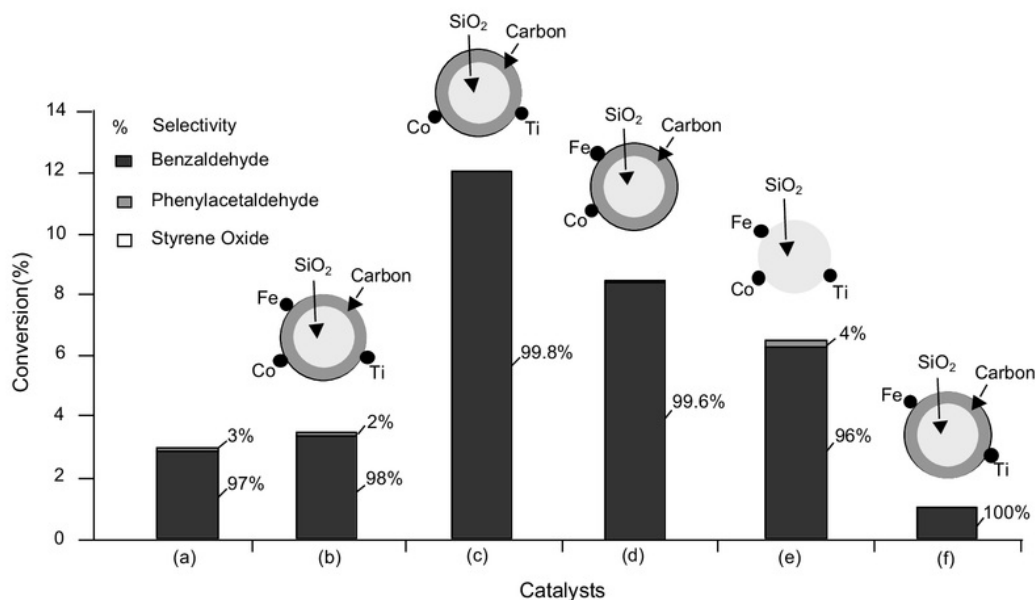


Fig. 8. The conversion of styrene and selectivity of products in the oxidation of styrene using different types of mimicked coals (a) $\text{SO}_3\text{H}/\text{Coal-700}$, (b) $\text{MCoal}(\text{Si,Fe,Co,Ti,C})$, (c) $\text{MCoal}(\text{Si,Co,Ti,C})$, (d) $\text{MCoal}(\text{Si,Co,Fe,C})$, (e) $\text{MCoal}(\text{Si,Co,Fe,Ti})$ and (f) $\text{MCoal}(\text{Si,Fe,Ti,C})$ as the catalysts, together with the illustration of the active sites present in the mimicked coals. The reactions were carried out at room temperature for 20 h with styrene (5 mmol), 30% H_2O_2 (5 mmol) and catalyst (100 mg).

4. Conclusions

Many transition elements such as Fe, Ti, Cu, Mn, Ni, and Zn were found embedded in the low rank coal with carbon as the main component. The amount of carbon and transition metal active sites in low rank coal were influenced by sulfonation and calcination processes, which then gave effects to its catalytic activity. If high amount of carbon is present, the metal active sites will be embedded and shielded. Yet certain amount of carbon is still needed to maintain the attachments of these metal active sites. Low rank coal which was sulfonated for 24 h and calcined at 700 °C possesses excellent catalytic activity in the oxidation of styrene. This is caused by the many active sites on the surface, which are cobalt oxide, titanium dioxide and iron oxide. Based on the coal mimicking models, combination cobalt oxide and titanium oxide active sites played the most important role in this catalytic reaction.

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