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

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 actives 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 SO_3H/Coal. For the thermal activation, SO_3H/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 SO_3H/Coal-Y; where SO_3H/Coal refers to the sulfonated low rank coal and Y refers to calcination temperature employed. For example, SO_3H/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 difractometer (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. Distillated 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 mt represents the sample mass after adsorption of water and mo 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 N_2 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 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 (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. SiO_2 was used as the silica source, $Fe(NO_3)_3 \cdot 9H_2O$ as the iron source, $Ti(SO_4)_2$ as the titanium source, $Co(CH_3COO)_2 \cdot 4H_2O$ as the cobalt source and sucrose ($C_{11}H_{22}O_{11}$), as the carbon source. The mimicking of SO_3H/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_3H/Coal	Sulfonation	24	–	–
SO_3H/Coal-350	Sulfonation	24	350	2
SO_3H/Coal-500	Sulfonation	24	500	2
SO_3H/Coal-700	Sulfonation	24	700	2
SO_3H/Coal-900	Sulfonation	24	900	2