

# E-03

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**Submission date:** 21-Nov-2018 10:19PM (UTC+0700)

**Submission ID:** 1043186744

**File name:** E-03\_Paper.docx (896.35K)

**Word count:** 2737

**Character count:** 14836

# Synthesis of <sup>1</sup> Solid Acid Catalyst from Fly Ash for Eugenol Esterification

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## Abstract

A series of fly ash-based heterogeneous acid catalysts were prepared by chemical and thermal treatment. Fly ash was chemically activated using sulfuric acid and followed by thermal activation. Characterization methods of XRD, BET, SEM-EDX, and the performance in esterification of eugenyl acetate production was carried out to reveal the physical and chemical characteristics of prepared catalysts. Activated catalyst showed high silica content (96.5%) and possessed high BET surface area of 70 m<sup>2</sup>g<sup>-1</sup>. The catalyst was proven to be highly active solid acid catalyst for liquid phase esterification of eugenol with acetic acid yielding eugenyl acetate. A yield of 43-48% was obtained with activated fly ash catalysts for 90 minutes reaction. These catalysts may replace beneficially the conventional homogenous liquid acid to the eco-friendly heterogeneous one.

<sup>7</sup>  
**Keywords:** fly ash, solid acid catalyst, esterification, eugenyl acetate.

## 1. Introduction

<sup>6</sup>  
Coal fly ash is an inorganic deposit and a waste product arising from the coal combustion processes in coal-fired power station or steam production. Bulky quantities of coal fly ash are kept in the form of waste deposits which contaminate the environment as inorganic pollution and cause deleterious effects on human health. Fly ash physically is in the form of fine particles with an average size of less than 20  $\mu\text{m}$  and has low to medium bulk density (0.54–0.86 gcm<sup>-3</sup>), high surface area 300–500 m<sup>2</sup>kg<sup>-1</sup> and light texture [1]. The acidity depends on the ratio of alkaline and acid-forming element in the ash but mostly it tends to alkaline [2]. Fly ash has a complex heterogeneous mixture of amorphous and crystalline phases with oxides of Si, Al, Ca, Mg and Na as major components [3].

Fly ash has been proven its suitability for applications variety such as admixture in cement/concrete, brick and potential materials for some chemical industries. However, in some countries the percentages utilization of total produced is still low [4]. The other applications of fly ash is still developed for examples as catalyst and catalyst support for catalytic cracking [5], esterification [6], trans-esterification [7], dehydration [8], oxidation [9] etc.

Esterification reaction are used to produce chemicals such as drugs [10], biodiesel [11], and for food industry [12,13]. Typically, esterification is performed using homogeneous catalysts such  $H_2SO_4$ ,  $H_3PO_4$  and  $HF$  [14]. However these acids are destructive, environmentally harmful and difficult to recover from the reaction mixture. On-going efforts involve the use of solid acid catalyst: amberlyst-15 [15], Al-alginat [14], and zirconia UDCaT-5 [16], allowing for efficient catalyst separation and recovery and minimizing corrosion effects. Esterification of eugenol to eugenyl ester have been carried out using zirconia UDCaT-5 [16], molecular sieve  $4\text{\AA}$  and amberlite XAD-16 [17]. High conversion (90%) has been achieved for two hours reaction by using amberlite XAD-16.

Application for fly ash has developed, more importantly in its roles in catalytic oxidation, chlorination, as a synthetic derivative of 2-mercaptobenzothiazole, and as a solid acid catalyst for esterification. Fly ash was activated chemically to increase the composition of silicon up to 80% and is used to support zirconium sulfate as a catalyst in benzylation reactions. The use of fly ash does not just aid in cutting down catalyst expenses but also to show high acid levels and enlarge the catalytic activities in benzylation reactions from benzene and toluene [18]. The catalyst fly ash- $H_2SO_4$  poses an ability to increase efficiency for synthesizing chalcones by reaction of chalcones aldol-flow condensation [19]. In the present work, sulfonated fly ash catalysts have been prepared with different calcination time and tested their activity for esterification of eugenol present in clove leaf oil.

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## 2. Materials and Methods

### 2.1 Materials

Acetic acid and sulfuric acid were supplied from Merck. Clove leaf oil was purchased from local market in Boyolali. All the received chemicals were used without any further purification. The fly ash was a solid waste obtained from Petrokimia Gresik chemical company.

## 2.2 Catalyst Preparation

Grey fly ash in the form of powder with a size of 50-110  $\mu\text{m}$  was washed with distilled water. Fifty grams of fly ash was impregnated with 100 ml of sulfuric acid solution for 24 hours. The fly ash was then separated from the solution. The acquired solid was washed with distilled water until the pH was neutral. It was then dried at a temperature of 100°C to remove the water content found on the surface. Next, the remaining fly ash was calcinated at 400°C for a specific time (2, 4, 6, or 8 hours).

## 2.3 Catalyst Characterization

The surface areas and pore size of the prepared catalysts were determined by using the Brunauer Emmett Teller (BET) method. The data were acquired on Quantachrome NovaWin Analyzer (Quantachrome Instruments) and nitrogen physical adsorption at liquid nitrogen temperature -195°C. XRD analysis was used to determine the shape of structure and the crystallinity of fly ash catalyst. Diffractogram was obtained from the diffractometer Philips XPert MPD at the  $2\theta$  angle ranging from 10 to 90° and wavelength,  $\lambda = 0.154$  nm. SEM-EDAX observation was performed on FEI Inspect s50 model. The catalytic activity was identified by eugenol conversion to eugenyl acetate. Esterification reactions were carried out in 500 mL three-neck glass equipped with a condenser and magnetic stirrer. Reactions were performed with eugenol to acetic acid of 1:1 ratio using 3% sulfated fly ash for 90 minutes. After the reaction, the catalyst was separated from the liquor and the unreacted acetic acid was titrated using NaOH solution.

## 3. Result and Discussion

### 3.1 SEM-EDAX Analysis

The morphology of untreated and activated fly ash were examined using scanning electron microanalyzer equipped with energy dispersive X-ray spectroscopy (EDAX) which identifies constituent atoms and approximate amount of atoms. Figures 1 and 2 show the SEM micrograph of original fly ash and activated fly ash, respectively.

The SEM image of surface of untreated fly ash (Figure 1a) was observed to have a smooth surface and wide range in diameter size. The widest diameter is more than 5  $\mu\text{m}$ . On the other hand, after treating with acid and calcination process, their appearance are slightly rougher (Figure 2a). Some particles aggregate, but some also shrink to sizes less than 5  $\mu\text{m}$ . EDAX spectra of raw fly ash represents high percentages of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  as the major constituents and small amounts of

Fe<sub>2</sub>O<sub>3</sub>, MgO, Na<sub>2</sub>O, MoO<sub>3</sub> and In<sub>2</sub>O<sub>3</sub>. Acid treatment and high temperature heating for 4 hours leech out some constituents and rise SiO<sub>2</sub> content. The silica composition is doubled from 14 to 31%w. It was reported that SEM analysis on the manufacturing of fly ash sulfonation as a catalyst in the synthesis of free solvents from aryl chalcones that increased silica levels after chemical activation was due to the loss of a large number of other components during impregnation by H<sub>2</sub>SO<sub>4</sub> [19]. Apart from that, the surface of the particles has been slightly corroded by H<sub>2</sub>SO<sub>4</sub>.

### 3.2 XRD Analysis

The purpose of XRD analysis is to obtain information about the change of mineral and crystalline structure characteristics from raw materials and products in the course of synthesis process. Figure 3 shows XRD patterns sulfonated fly ash catalysts at different calcination time. Diffractograms of untreated fly ash exhibit typical diffraction peak at 2θ of 26.60° and 50.12°. These characteristic peaks show the predominant quartz phase (SiO<sub>2</sub>) with a major peak at 2θ of 26.60° and then also identified the less intense phase for MgO dan Al<sub>6</sub>O<sub>18</sub>. Impregnation and calcination causes the characteristic peak at 2θ of 20.7-20.9° and 50.11° to be clearly identified, which shows the peak of crystalline quartz. Treated fly ash shows that SiO<sub>2</sub> quartz is the dominant phase from 60% up to almost 100%. Mazumder et al. reported that fly ash activated with o-phosphoric acid induce dissolving some of the crystalline component of raw fly ash by acid [6]. Therefore, the crystallinity of fly ash was reduced during acid and heating treatment, consequently the amorphous of fly ash was increased.

### 3.3 BET (*Brunauer Emmet Teller*)

BET test results are shown in Table 1. Untreated fly ash has a BET surface area of around 5 m<sup>2</sup>/g. Impregnation with sulfuric acid and calcination at 400°C causes the surface area to multiply by 9-14, ranging from 49.05 – 70.13 m<sup>2</sup>/gr. The time of calcination can affect the surface area particles. A high duration of calcination can decrease the BET surface area. This shrinking of surface area is caused by the agglomeration process of particles. During calcination, particles undergo condensation until hydroxyl groups are released, and the binding and rearranging of particles result in a more stable configuration [21]. Other studies reveal the same results, that solid acid fly ash catalyst that were synthesized with o-phosphoric acid and calcinated at a temperature of 300°C for 3 hours had an increased surface area from 0.09 to 21.92 m<sup>2</sup>g<sup>-1</sup> [6].



The N<sub>2</sub> adsorption and desorption isotherms obtained showed that untreated fly ash and two hours treated fly ash form micropores at around 15.53 Å and 16.94 Å. Extended calcination time results in mesopores volume, 29.56-49.06 Å. The nitrogen adsorption-desorption isotherm is presented in Figure 4. The lower adsorption volume on the untreated fly ash indicates a low surface area.

### 3.4 Conversion of Eugenol to Eugenyl Acetate

To find out the performance of sulfuric-acid-activated fly ash catalyst, synthesis from eugenol to eugenol acetate is carried out by esterification of eugenol within clove oil and acetate acid. This reaction is operated at a temperature of 60°C. Conversion from eugenol to eugenyl acetate as function of time is shown on Figure 5.

The conversion from eugenol to eugenyl acetate with activated fly ash catalyst goes to show that all catalysts with different time preparation for calcination display almost the same performance. After the reaction has been carried out for 90 minutes, eugenol conversion was 43-48% completed. To get a higher level of conversion, a much longer time is needed for eugenol esterification. The performance of catalyst is comparable with the acidic zirconia and Amberlite ZAD-16 catalyst. Yadav and Yadav reported that conversion 30% were obtained by esterification of eugenol with benzoic acid over a solid super acidic modified zirconia catalyst at temperature of 80°C for 90 minute reaction [16]. High conversion at around 90% was achieved when temperature was increased up to 110 °C for 240 minutes reaction. Using Amberlite XAD-16 reaction eugenol and acetic anhydride to form eugenyl acetate achieved 85% and 98.6% conversion for reaction time 180 and 360 minutes, respectively and molar ratio 1:3 [17]. Other result [23] inform us that eugenyl acetate by enzymatic esterification of Novozym 435 as catalyst which come from the catalyst and the conversion of eugenyl acetate of 99.87%. An optimum condition from eugenyl acetate at temperature of 60°C, the ratio molar of clove oils and acetic anhydric 1:5, and 10% of catalyst for catalyst from the total enzymes for two hours reaction.

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## TABLE CAPTIONS

Table 1. BET surface area of fly ash catalyst



## FIGURE CAPTIONS

Figure 1. SEM images (a) and EDAX spectra of untreated fly ash (b)

Figure 2. SEM images (a) and EDAX spectra of activated fly ash (b)

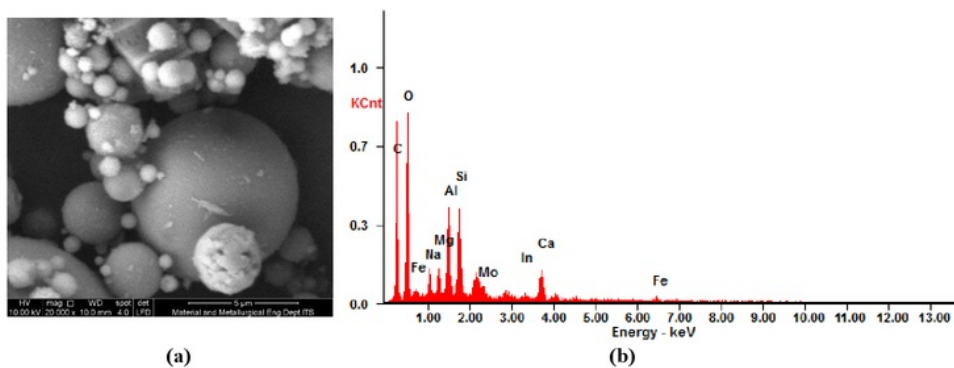
Figure 3. XRD pattern for the effect of calcination time on fly ash formation.

Figure 4. Nitrogen adsorption-desorption isotherm of untreated and treated fly ash

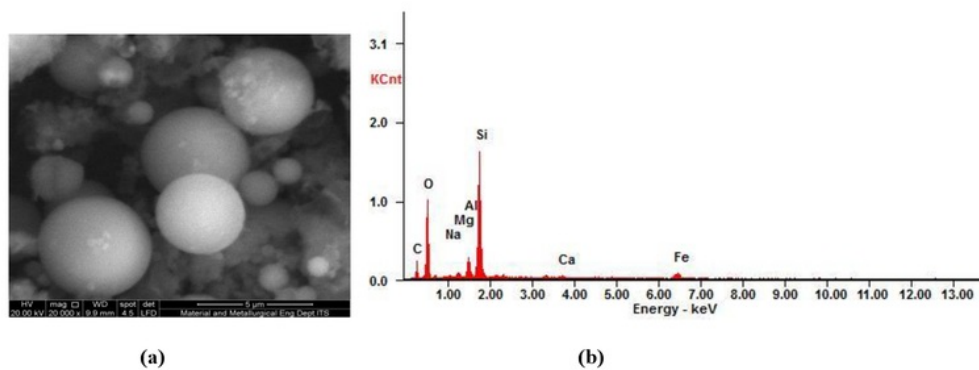
Figure 5. Eugenol conversion on sulfonated fly ash catalysts

**Table 1.** BET surface area of fly ash catalyst

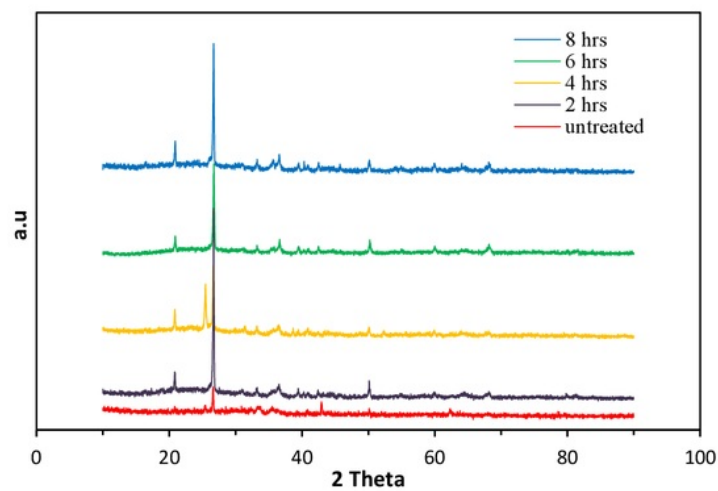
Calcination time (h)	Surface area ( $\text{m}^2\text{g}^{-1}$ )
Untreated	5.08
2	70.13
4	69.80
6	56.31
8	49.05



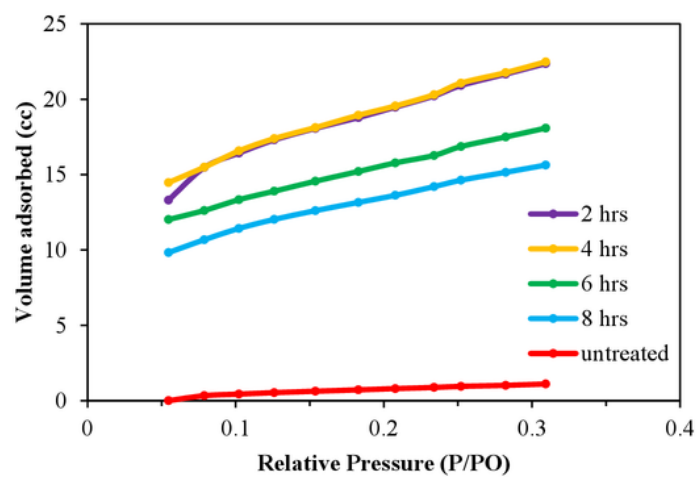
**Figure 1.** SEM images (a) and EDAX spectra of untreated fly ash (b)



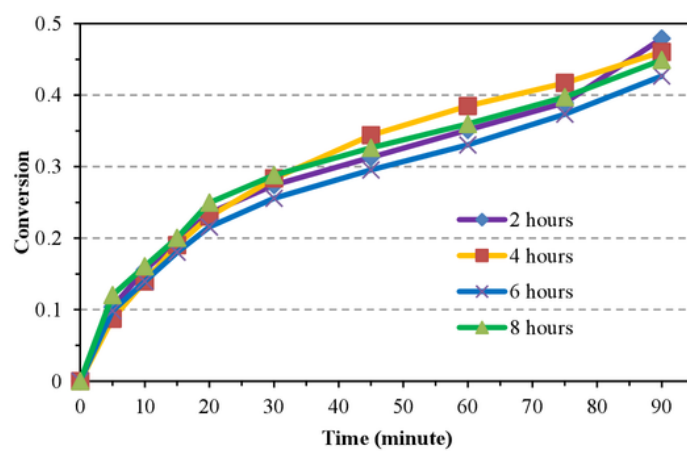
**Figure 2.** SEM images (a) and EDAX spectra of activated fly ash (b)



**Figure 3.** XRD pattern for the effect of calcination time on fly ash formation.



**Figure 4.** Nitrogen adsorption-desorption isotherm of untreated and treated fly ash



**Figure 5.** Eugenol conversion on sulfonated fly ash catalysts

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