# Epoxidation of 1-Octene with hydrogen peroxide aqueous catalyzed by titania supported sulfonated coal

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# Epoxidation of 1-Octene with Hydrogen Peroxide Aqueous Catalyzed by Titania Supported Sulfonated Coal

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**Abstract.** Titania supported sulfonated coal was created as heterogeneous catalyst for epoxidation of 1-octene with aqueous hydrogen peroxide as oxidant at room temperature. The catalysts were prepared from coal that was sulfonated with $H_2SO_4$ (97%) and impregnated 7.2%wt with titanium(IV) isopropoxide $(Ti(PrO)_4)$. All catalysts coal (C), CS, Ti(7.2)-CS and Ti(7.2)-CSC were characterized by FTIR. The catalytic performance was tested for epoxidation of 1-octene with $H_2O_2$ aqueous as oxidant. It is found that Ti(7.2)-CS possessed the best catalytic performance and it gave the highest 1,2 epoxyoctene 322 µmol.

## INTRODUCTION

Carbon is one of materials that used as catalyst support. Coal is one source of carbon because it is the most complex carbon compounds which have chemical composition namely oxygenic functional groups such as carbonyl groups, phenolic hydroxyl (OH) groups. Amorphous carbon can be created by sulfonation process that incorporated large amount of hydrophilic molecules for provide good access of reactant to the $SO_3H$ groups, so it give high catalytic performance [1]. Indonesia has abundant coal resources that can be found almost all over the islands. Indonesian's coal is approximately 115.18 billion tons that dominated by low rank coal include lignite and sub-bituminous [2, 3].

Many reseachers have developed a lot of supports to improve catalytic performance and selectivity of titania catalyst in epoxidation 1-octene by using hydrogen peroxide as oxidant. Several titania catalysts have been created such as TS-1 [4], $TiO_2@SiO_2$ [5], Ti-TUD-1 [6], Ti-NaY [7]. In the other hand, these kinds of catalysts are very costly for extensive application.

In this research, coal can be considered as the suitable catalyst support due to it was natural resources of carbonaceous material in various forms and low costly [8]. Coal modified by sulfonation to create sulfonated coal (CS). Furthermore, sulfonated coal was impregnated by tinania and calcined to form Ti(7.2)-CS and Ti(7.2)-CSC. All materials were investigated its catalytic performance in epoxidation 1-octene by aqueous hydrogen peroxide as oxidant.

## EXPERIMENTAL

The raw material of coal obtained from Batuah, Loajannan, Kutai Kartanegara, East Kalimantan, Indonesia. Previous research, the coal classed in low rank coal [9, 10]. Firstly, the coal was pulverized to 200 mesh. The sulfonated coal was created by immersing 1 g of coal with 12 mL of concentrated sulfuric acid (98%, JT. Beker) and treated in oil bath at $90 \pm 2$ °C for 6 h with intermittent stirring. After that, the mixture was filtered and washed with distilled water to remove any loosely bound acid, before drying at 110 °C for overnight. The sulfonated coal was symbolized as CS. Then, 1 g of CS was added in 10 mL of toluene that contained 7.2 %wt of titanium (IV) isopropoxide (Aldrich) and stirred until toluene was completely evaporated. The sample was washed with ethanol to

remove residual toluene and next dried at 110 °C for overnight to remove ethanol. The sulfonated coal which has been impregnated was labeled as Ti(X)-CS; where CS represents sulfonated coal and X indicates the amount of titanium(IV) isopropoxide. As an example, Ti(7.2)-CS represents a coal catalyst that was prepared from sulfonated coal which has been impregnated with 7.2 %wt of titanium(IV) isopropoxide. Finally, Ti(7,2)-CS was calcined at 500 °C and it labeled as Ti(7.2)-CSC

The catalysts were characterized by Fourier transform infrared (FTIR) spectrometer. 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.

Catalytic performance was investigated in the epoxidation of 1-octane using aqueous $H_2O_2$ (30%, Merck) as the oxidant. 1-octane (4 mL, Merck), aqueous $H_2O_2$ (1 mL, 30%, Merck) and catalyst (50 mg) were mixed in a sample bottle and stirred at room temperature for 24 h [11]. The products were then separated from the catalysts by centrifugation. The resulting products were withdrawn and analyzed with GC-2014 Shimadzu-gas chromatograph.

## RESULT AND DISCUSSION

**FIGURE 1** shows the infrared spectra of coal before sulfonation (C) and coal after sulfonation (CS). Both samples showed a broad band centered at 3410 cm$^{-1}$ and was assigned to the –OH stretching vibration mode of the –COOH group. The strong adsorption band at around ~1614 cm$^{-1}$ was assigned to the C=C stretching mode in polyaromatics. The adsorptions band at 2920 and 2850 cm$^{-1}$ were related to the symmetric and asymmetric stretching modes of aromatic and aliphatic –CH$_2$ groups. The main difference is exhibited in the adsorption band at 1186, 1033 and 592 cm$^{-1}$due to the attachment of –SO$_3$H groups. The adsorption band at 1186 cm$^{-1}$ indicated O=S=O symmetric stretching in –SO$_3$H and 1033 cm$^{-1}$ was related SO$_3^-$ stretching mode. The adsorption band in region 592 cm$^{-1}$ was detected as deformation frequency of SO$_2$.
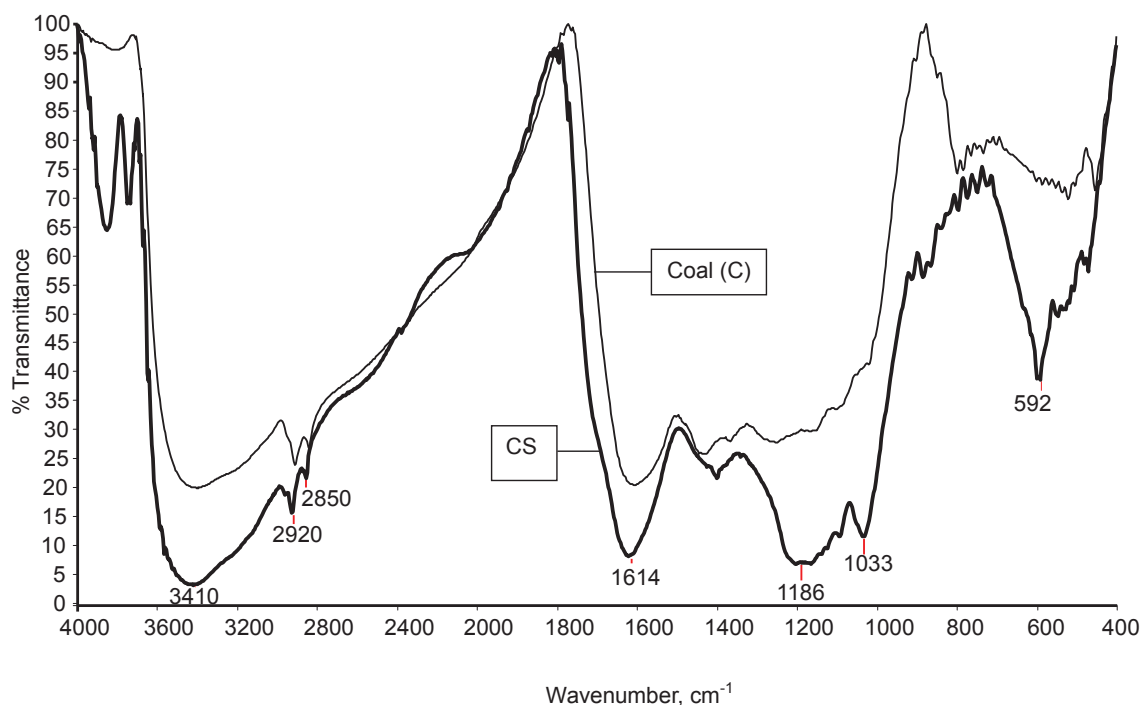


**FIGURE 1.** Infrared spectra of coal (C) and sulfonated coal (CS)

**FIGURE 2** showed the effect of calcination process to Ti(7.2)-CS sample. The intensity of adsorption band at 3410 and 1614 cm$^{-1}$ were decreased due to the –OH stretching vibration mode of the –COOH group and the C=C stretching mode in polyaromatics were released as CO, CO$_2$ and H$_2$O when Ti(7.2)-CS was calcined. The adsorption band at 1186, 1033 and 592 cm$^{-1}$ were assigned –SO$_3$H groups were loss after calcination process due to it released

as SO$_2$ gas. The adsorption band at 1095, 799, 776 and 511 cm$^{-1}$ were attributed to symmetric stretching vibrations of Si–O–Si, while the adsorption at 511 cm$^{-1}$ is assigned to the bending mode of Si–O. The adsorption band at 1095, 799, 776 and 511 cm$^{-1}$ were indicated the presence quartz. The quartz become dominant in the infrared spectra of Ti(7.2)-CSS than Ti(7.2)-CS.

Titanium with tetrahedral structure [TiO$_4$] and titanyl [Ti=O] should be identified by an absorption band in the 900-975 cm$^{-1}$ region in FTIR spectra. But infrared spectra of Ti(7.2)-CS and Ti(7.2)-CSC, the peak around 900-975 cm$^{-1}$ not perform due to amount of titanium very small.
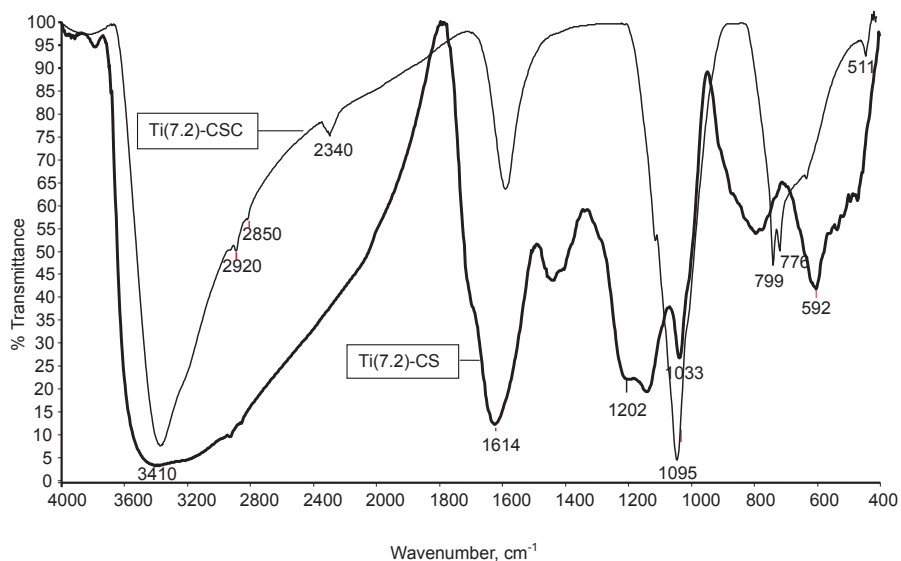


**FIGURE 2.** Infrared spectra of Ti(7.2)-CS and Ti(7.2)-CSC

Catalytic performance of titania supported sulfonated coal catalysts were tested to oxidation of 1-octane with aqueous hydrogen peroxide as the oxidant. Based on agreement with previous study, the products of 1-octane oxidation have included 1,2 epoxyoctene, 2-octanol and 1,2 octanediol which based on the authentic samples of the product and GC analysis [12]. Nevertheless, 1,2 epoxyoctene was found to be the important product in the 1-octane oxidation in this research.
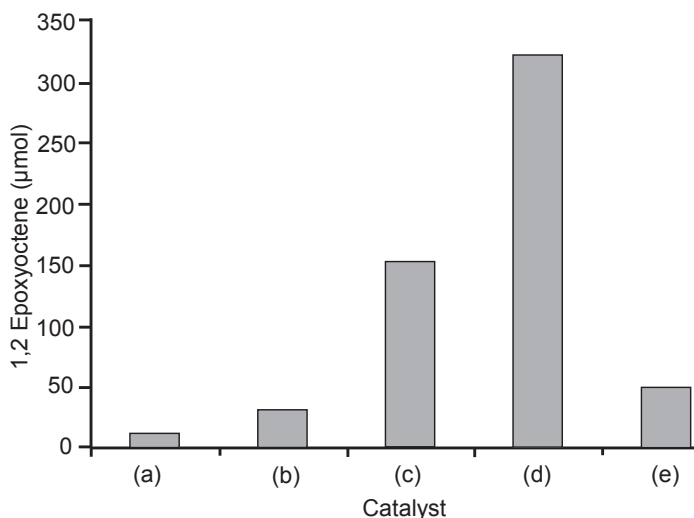


**FIGURE 3.** Epoxidation activity of (a) no catalyst, (b) Coal, (c) CS, (d) Ti(7.2)-CS and (e) Ti(7.2)-CSC

**FIGURE 3** shows the histogram of product of epoxidation 1-octane catalyzed by titania supported sulfonated coal composites. As comparison, Coal, CS and Ti(7.2)-CSC were also applied as the catalysts in the epoxidation 1-octane. We could see that the amount of 1,2 epoxyoctene was 13 µmol without catalyst, and 1,2 epoxyoctene increased slightly when coal was used as catalyst, indicating that coal have low catalytic performance in this reaction. CS exhibited rather high catalytic performance with the yield of 1,2 epoxyoctene was 154 µmol because the presence of the –SO$_3$H groups. In addition to that, Ti(7.2)-CS exhibited obvious high catalytic performance in the epoxidation 1-octane with hydrogen peroxide as oxidant. The yield of 1,2 epoxyoctene on Ti(7.2)-CS reached 322 µmol which was almost twice higher than those on CS. Ti(7.2)-CSC had relatively low catalytic performance and the corresponding yield of 1,2 epoxyoctene was 50 µmol. Decreasing catalytic performance of Ti(7.2)-CSC catalyst correlated with the releasing carbon elements and –SO$_3$H groups during calcination process.

## CONCLUSIONS

Coal can be used as the catalyst support of titania by sulfonation and impregnation process. Titania supported sulfonated coal without calcination process as Ti(7.2)-CS composite possesses high catalytic performance in epoxidation 1-octane with hydrogen peroxide as oxidant.

## ACKNOWLEDGEMENTS

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