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Synthesis and characterization of SO_4^{2-}/KCC-1 catalyst as an alternative candidate for simultaneous esterification and transesterification reactions

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Abstracts

Sulfate-impregnated acid catalysts can be used to replace conventional homogeneous base catalysts which are very dangerous, corrosive and environmentally unfriendly. Sulfate impregnation on porous support material will increase the surface area of the catalyst. The use of KCC-1 as a supporting material can produce catalysts with excellent properties. The method used in this research is the hydrothermal method for the synthesis of KCC-1 and the direct impregnation method for the synthesis of SO_4^{2-}/KCC-1. Characterization of the resulting material using X-ray diffraction (XRD), FTIR spectrometer, and low temperature emission scanning electron microscope (SEM). The characterization results showed that the synthesis of KCC-1 and SO_4^{2-}/KCC-1 had been successfully carried out. This is evidenced by the formation of amorphous silica, the presence of peaks of silica and sulfate groups, and scanning electron microscope images showing nano-sized materials.

1. Introduction

The content of free fatty acids has a negative effect on the transesterification reaction in the manufacture of biodiesel [1]. Therefore, before starting the transesterification process, these free fatty acids must be removed by acid esterification to esters [2]. The use of solid (heterogeneous) acid or base catalysts can increase the good catalytic activity at low temperatures for the esterification and transesterification processes. Solid acid catalysts are more resistant to high concentrations of free fatty acids, and can trans esterify triglycerides and esterify free fatty acids into biodiesel. While alkaline catalysts have poor sensitivity to free fatty acid contaminants, so that they can cause suboptimal results [3].

Sulfate-impregnated acid catalysts can be used to replace conventional homogeneous base catalysts which are very dangerous, corrosive and environmentally unfriendly [3]. Its catalytic activity is highly depend on the strength of the acid and also the number of acid sites [4]. The addition of sulfate, which is a strong acid, will be able to increase the catalytic activity of the catalyst. In addition, the performance of solid acid catalysts in the simultaneous esterification and transesterification reactions also depends on the ease with which the reactants can reach the active site so that the reaction can be started [3]. Such accessibility can be increased by increasing the surface area of the catalyst. Increasing the surface area of the sulfate impregnated catalyst can be done by adding a catalyst support to keep the surface area of the active catalyst component large [5].

Mesoporous silica-based catalysts have been used for the esterification process because they have a very large surface area, are stable, have large pore sizes, and are very useful for reactions involving large molecules [6]. One of the silicas that has a large surface area and pores is fibrous silica (KCC-1) [7]. KCC-1 or commonly called fibrous silica has a unique shape, is porous, and the surface morphology is arranged fibrous in a three-dimensional structure to form a sphere. KCC-1 is surrounded by dendrimers (a structure consisting of branches around a central nucleus that can be changed in size and shape as desired) thus forming a fibrous morphology on top. KCC-1's unique morphology allows wide active site access so that it can improve performance for several applications such as producing advanced material properties (high mechanical and thermal stability, and excellent dispersion), so that these advantages can make KCC-1 quality increase. to be used as a catalyst support [8].

KCC-1 has been used for various applications such as nanocatalyst buffer for decarbonation reactions [9], catalyst buffer in CO methanation [10], photocatalysis, CO_2 capture conversion, sensing, ion detection and extraction, supercapacitors, drug delivery and other biomedical applications [11]. KCC-1 has better performance compared to other silica-based systems such as SBA-15 and MCM-41 in applications related to catalysis and/or adsorption [8]. Thus, it is expected that SO_4^{2-}/KCC-1 catalyst can be a better alternative candidate as a catalyst for simultaneous transesterification and esterification reactions than KCC-1 catalyst.

2. Experiments Procedure

Tools and Materials

The tools used in this research are oven, furnace, beaker glass, stirring rod, measuring glass, volume pipette, dropper pipette, filler, heating coat, thermometer, porcelain dish, measuring flask, burette, rotary evaporator, spatula, analytical balance, teflon hydrothermal, separating funnel, glass funnel, clamps and stands, erlenmeyer, magnetic stirrer, XRD Bruker D8 with Ni filtered Cu Kα radiation (k = 1.5418) at 40 kV and 20 mA, scanning angles from 10° to 90 ° with a scanning speed of 0.2°/min, FTIR Nicolet 360 with a range of 500-4000 cm^{-1} with KBr pellets, and a low temperature SEM Hitachi SU8230 operated at 2 kV.

The materials used in this study were TEOS (tetraethyl orthosilicate) (Merck), demineralized water, n-butanol (Merck), toluene (Merck pa), urea (Merck pa), CTAB (cetyl trimethyl ammonium bromide microemulsion) (Sigma Aldrich) , 1 M H_2SO_4 solution, distilled water, Whattman filter paper, coarse filter paper, deionized water, 0.1 N KOH solution, 96% ethanol, and phenolphtalein indicator.

Synthesis of Fibrous Silica (KCC-1)

A total of 2.5 g of TEOS was put into glass A, then 1.5 mL of butanol and 30 mL of toluene were added, then stirred until homogeneous. A total of 0.6 g of urea, 1 g of CTAB and 40 mL of demineralized water were put into glass B, then stirred for 3 hours. Glass A and B were mixed and stirred at room temperature for 45 minutes then heated for 5 hours at 120^0C in a hydrothermal Teflon reactor. After that, the mixture was centrifuged and rinsed with distilled water and

dried in an oven at 100^0C overnight, then calcined at 550^0C for 5 hours. [12].

Synthesis of SO₄²⁻/KCC-1 Catalyst

SO₄²⁻/KCC-1 catalyst was prepared by direct impregnation method. 1 M H_2SO_4 solution was mixed with KCC-1 (15 mL/g) at room temperature for 1 hour, then filtered using Whattman filter paper. After that the mixture was dried at a temperature of 105°C for 24 hours and calcined at a temperature of 500-550°C for 4 hours [6].

Characterization of Catalyst

Characterization was carried out on KCC-1 and SO₄²⁻/KCC-1 using X-ray diffraction (XRD) to determine the crystallinity, electron microscopy (SEM) to determine particle morphology, elemental composition and spatial distribution, and FTIR to determine the functional groups present in catalyst.

3. Result and Discussion

The process of making KCC-1 begins with mixing TEOS as a silica precursor, butanol as a co-surfactant and toluene as a solvent (solution A). The mixture then mixed with CTAB which functions as a template or as a guiding molecule, urea, and demineralized water (solution B). The use of CTAB as a framework is due to its less toxic nature when compared to other organic frameworks [12], [13].

Alcohol (in this study n-butanol) will cooperate with CTAB at the micellar interface to form inverted micelles in the KCC-1 mixture, then after the reverse micelle interface is formed, TEOS which in this study is used as silica precursor, will be hydrolyzed by urea. Then the positive charge of CTAB interacts with the negative charge of silica (SiO_3^{2-}) using electrostatic interactions to form fibrous silica. The calcination process at a temperature of 550°C serves to produce a more stable fibrous silica morphology, and also to remove the skeleton that is still present in the product [12].

XRD Analysis

KCC-1 diffraction pattern in Figure 1 shows a wide peak at a value of 2θ around 23°. This result indicates that the synthesis of the KCC-1 in this study, carried out successfully because of the similarity with the result of XRD analysis of KCC-1 which was carried out by Abdullah [8]. The broad peak indicates that the resulting KCC-1 is an amorphous structure [12], [14], [15]. Salman *et al.* [16] and Kalapathy *et al.* [17] stated that the synthesized silica and silica sulfate samples generally have an amorphous structure. This is indicated by a diffraction pattern that widens at 2θ around 21-23° (d= 3,9 Å).
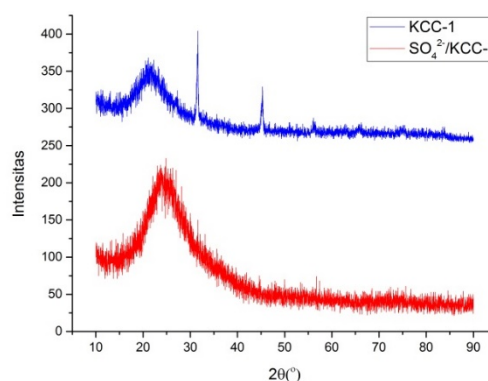

Figure 1. Diffractogram KCC-1 and SO₄²⁻/KCC-1

The diffraction pattern of SO₄²⁻/KCC-1 when compared with the diffraction pattern of KCC-1 in Figure 1, shows a decrease in the crystallinity of the material due to the loss of sharp peaks in the SO₄²⁻/KCC-1 diffraction pattern. The pattern seen after the addition of SO₄²⁻ actually widened (broadening). These results indicate that the added SO₄²⁻ spreads smoothly on the KCC-1 surface [6]. yang menyatakan bahwa adanya penambahan zat aktif (bahan) lain pada silika berserat (KCC-1) menyebabkan kristalinitas dari silika berserat (KCC-1) menurun These results are also supported by research conducted by AbouAitah & Farghali [18] which states that the addition of other active substances (materials) to fibrous silica (KCC-1) causes the crystallinity of fibrous silica (KCC-1) to decrease.

SEM Analysis

Figure 2 explains that KCC-1 has been successfully synthesized because it shows uniform and monodispersed microspheres. This is in accordance with research conducted by Mohammadbagheri & Chermahini [19]. Figure 2 also shows that the KCC-1 sample has a particle diameter size range of 270-410 nm. These results are in accordance with the research of Febriyanti, *et al.* [13] which states that the KCC-1 material has spherical particles with a diameter between 250-450 nm. However, the shape of the fibers in the material is not clearly visible on the image due to the density being too high or the physical shape of the material being too fine [13].
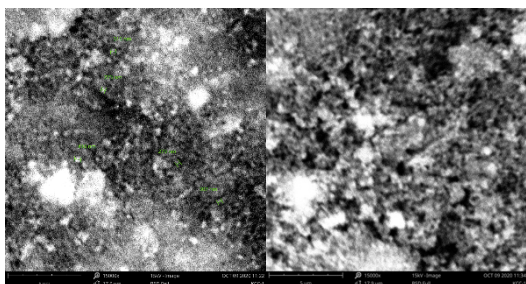

Figure 2. Image of KCC-1

Infra-red Spectrum (FTIR) Analysis

The infrared spectrum of the KCC-1 sample shown in Figure 3 shows the absorption band appears at wave number 3446.28 cm^{-1} which indicates the stretching vibration of the –OH group of Si-OH, the absorption 1636.05 cm^{-1} shows a bending vibration of –OH group of Si-OH, absorption 1088.83 cm^{-1} shows asymmetric stretching vibrations of Si-O group of Si-O-Si, absorption 805.10 cm^{-1} shows stretching vibration of symmetry of Si-O group of Si- O-Si, and the absorption of 464.35 cm^{-1} shows the bending vibration of the Si-O group of Si-O-Si. These results are in accordance with previous studies which stated that the widening band in the range of 3300 - 3500 cm^{-1} showed a water-bound -OH strain (Si-OH), which was confirmed by a peak in the wave number in the range of 1635 cm^{-1} which is a bending vibration. water molecules, and there is a peak in the wave number in the range of 1100 cm^{-1} which indicates the asymmetric vibration of the silica

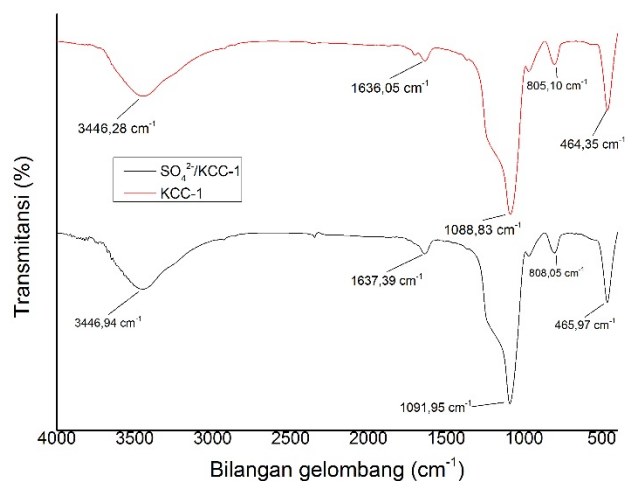atoms present in the siloxane (Si-O-Si) [14], [20]–[22].

Figure 3. Infra-red spectrum of KCC-1 and SO_4^{2-}/KCC-1

The infrared spectrum of the SO_4^{2-}/KCC-1 sample has a very similar peak pattern, in fact there is only a slight shift from the peak of the wave number obtained by the KCC-1 sample (Figure 3). This is because the functional group of SO_4^{2-}/KCC-1 is similar to the functional group of KCC-1, such as silica. In addition, the SO_4^{2-}/KCC-1 catalyst also has the S=O functional group of sulfuric acid. The peaks of the S=O group appear in the range of wave numbers 1140-1200 cm^{-1} and 1300-1375 cm^{-1} which coincide and are even covered or overlapped by the vibrations of the Si-O asymmetry groups of Si-O-Si [16], [21], [23]. Therefore, the results of the infrared spectra of the sample SO_4^{2-}/KCC-1 did not show a very clear vibration of the S=O group.

4. Conclusion

This study revealed that the synthesis of KCC-1 and SO_4^{2-}/KCC-1 was successfully carried out. This can be proven by the results of X-ray analysis which shows the diffraction pattern that forms amorphous silica, infrared spectra showing the peaks of silica and sulfate groups, and scanning electron microscopy which shows the material is already nano-sized. However, the crystallinity of SO_4^{2-}/KCC-1 samples decreased

compared to KCC-1 due to the addition of SO_4^{2-} on the surface of KCC-1 which spreads smoothly. The decrease in crystallinity in SO_4^{2-}/KCC-1 is expected to provide better catalyst activity for simultaneous esterification and transesterification reactions compared to KCC-1.

Acknowledgment

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