SYNTHESIS AND CHARACTERIZATION OF ACETONITRILE LIGATED Cu(II)-COMPLEX AND ITS CATALYTIC APPLICATION FOR TRANSESTERIFICATION OF FRYING OIL IN HETEROGENEOUS PHASE

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Received October 5, 2012; Accepted December 17, 2012

ABSTRACT

Catalysts have played an important role in many industries because they allow the reaction occurs faster. The aim of this work were to synthesize and characterize a Cu(II)-acetonitrile complex immobilized on modified silica and to investigate its catalytic activity at optimal condition (catalyst concentration, stirring rate, and the duration of reaction) in transesterification of frying oil. Fourier Transform Infrared (FTIR) and Nano Laser-Particle Size Analyzer (NL-PSA) were used to characterized the catalyst obtained, metal loading and leaching of the copper content was measured by Atomic Absorption Spectroscopy (AAS) and the formation of product from transesterification reaction was analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS). FTIR spectra reveal a successful synthesis of modified silica and the immobilized Cu(II)-acetonitrile complex on it. NL-PSA Analysis showed that the catalyst possesed smaller particle size than the parent silica. Analysis with AAS confirms the stable catalysts formed because metal loading and leaching value were of 6.19 and 0.16%, respectively. The optimum conditions were found to be 0.80% catalyst concentration, 300 rpm stirring rate and 10 h duration of reaction.

***Keywords**: modified silica; immobilization; transesterification; methyl ester; Cu(II)-acetonitrile*

ABSTRAK

Katalis memainkan peranan penting dalam dunia industri karena memungkinkan reaksi berlansung lebih cepat. Pada penelitian ini telah dilakukan sintesis dan karakterisasi kompleks Cu(II)-acetonitril yang diamobilisasi pada silika modifikasi dan penentuan aktivitas katalitik dari katalis yang dihasilkan pada keadaaan optimum yaitu konsentrasi katalis, kecepatan pengadukan, dan lama pengadukan. FTIR dan Nano Laser-Particle Size Analyzer (NL-PSA) digunakan untuk mengkarakterisasi katalis yang dihasilkan; metal loading dan leaching kandungan tembaga diukur dengan AAS; dan pembentukan metil ester dari reaksi transesterifikasi dianalisis dengan GC-MS. Spektra FTIR menunjukan bahwa silika modifikasi dan katalis teramobilisasi sukses terbentuk. Analisis NL-PSA menunujukan bahwa ukuran partikel dari katalis lebih kecil dibandingkan silika induk dan silika modifikasi. Analisis dengan AAS memberikan informasi bahwa katalis yang terbentuk cukup stabil karena nilai metal loading dan leaching adalah of 6,19 dan 0,16%. Kondisi optimum dari reaksi transestrifikasi ditemukan pada konsentrasi katalis 0,80%, kecepatan pengadukan 300 rpm dan dengan lama pengadukan 10 jam.

***Kata Kunci**: modifikasi silika; amobilisasi; transesterifikasi; metil ester; Cu(II)-asetonitril*

INTRODUCTION

Catalyst is an important substance in synthesis process which is used to alter the rate of reactions. Based on it phase, there are homogeneous and heterogeneous catalysts. In comparison, homogeneous catalysts are better than that of the heterogeneous one to enhanced reactivity and selectivity but they are very difficult to separate from product [1-6]. On the other side, heterogeneous catalysts are more desirable in industrial process. These catalysts are easy to separate and recycle but they have drawbacks due to their lower catalytic activities [7,8].

Activity, selectivity, stability, yields and easy to regeneration are important parameters of catalysts to describe a good and stable catalyst [6]. To combine advantages of both catalysts might be done by heterogenization of homogeneous catalysts into support material [1-4]. Silica, mesoporous silica (MCM-41, MCM-48, and SBA-15) are examples of inorganic supports while polymer P4VP as organic support which are used to employe for that purpose [9-11].

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Activity of heterogeneous catalyst was affected by active site such as metal, metal oxide, and complex compounds. Complex compounds based on transition metals used to be catalysts [12]. Success synthesis of acetonitrile ligated Cu(II) complexes and applied in many reactions such as cyclopropanation reactions, olefination reactions, isobutene polymerization in homogeneous and heterogeneous phase.

Unlike reported previously [2] where modified support was prepared by introducing organoboron into the surface of silica, in this work the boron compound is replaced by cheaper modifier, aluminium trichloride, which can be promising candidate to be used industrially. Furthermore, the aim of silica modification is to maintain the Lewis acidity of metal center of complex catalyst grafted on it without losing any ligand or counter anion. Acetonitrile coordinated transition metal complexes are very important because their weakly coordinating to metal center can perform easily to be replaced by strongly coordinating ligands (e.g. substrates) to initiated catalytic process.

This paper described a cationic complex $[Cu(NCCH_3)_6]^{2+}$ which was connected to the surface of aluminum trichloride modified silica via electrostatic interaction. The obtained grafted materials were characterized by FTIR, NL-PSA, and AAS. This newly synthesis of catalyst was then applied for transesterification reaction. The resulting products were analyzed by GC-MS. The product desired from this reaction is called biodiesel and may promisingly be alternatively energy source [13-15].

EXPERIMENTAL SECTION

Materials

The following materials, silica gel (SiO_2), aniline ($C_6H_5NH_2$), aluminium trichloride ($AlCl_3$), anhydrous copper sulphate ($CuSO_4$), acetonitrile (CH_3CN), toluene ($C_6H_5CH_3$) and aquadest, distillated methanol, frying oil were used without purification for the synthesis of the immobilized catalyst. Distillated methanol and frying oil were used for the catalytic test.

Instrumentation

The obtained catalyst was characterized by FTIR (Spectrophotometer Infrared FT-IR Perkin Elmer 1600 series) and Nano Laser Particle Size Analyzer (Fritsch Analysette 22 Wet Dispersion Unit, Nano Tec Plus). Copper metal loading on modified silica was measured by AAS (Younglin AAS 8020 Atomic Absorption Spectrophotometer). Methyl ester yielded from transesterification was then analyzed by GC-MS (Shimadzu GCMS-QP2010).

Procedure

Synthesis of catalyst

Silica gel was firstly heated at 200 °C for 1 h then mixed with aniline (>Si-OH : N = 1:1.2) in 50 mL toluene and stirred for 24 h. Anhydrous aluminium trichloride addition into the mixture was the next step and stirred was continued for another 24 h. The resulting suspension was filtered, washed with toluene, and dried at room temperature. Solid obtained was grayish colors and called modified silica.

Modified silica, anhydrous copper sulphate, and acetonitrile were starting materials for synthesis of the catalyst. Starting materials were mixed and stirred for 24 h, washed with acetonitrile, and dried at room temperature. The catalyst obtained was characterized by FTIR and Nano Laser-Particle Size Analyzer.

Leaching test

1 g of the solid catalyst was suspended in acetonitrile and stirred for 24 h. Afterward, the solution part was separated by filtration and analyzed by AAS (Younglin AAS 8020 Atomic Absorption Spectrophotometer) to determine its Cu content.

Optimalization of the immobilized Cu(II) catalyst on transesterification of frying oil

Catalytic activity of catalysts applied in transesterification of frying oil with a variation of catalyst concentration, stirring rate, and duration of reaction. The amount of 0; 0.25; 0.50; 0.80; 1.10; 1.30; and 1.50 weight % of catalyst was respectively added to methanol and stirred (200 rpm, 60 °C) for 15 min. Afterward, frying oil was put into catalysts-methanol solution and stirred for 1 h. The above solution was analyzed by GC-MS (Shimadzu GCMS-QP2010). Yield of methyl ester product was accounted as following equation:

$$\text{yield of product} = \frac{\text{peak area x vol. of methyl ester produced x 100\%}}{\text{vol. of oil taken for the reaction}}$$

Variations of stirring rate were run at 200 rpm, 300 rpm, 400 rpm, and 500 rpm. Meanwhile for duration of reactions was investigated for 30 min, 60 min, 90 min, 120 min, 6 h, 9 h, and 10 h.

RESULT AND DISCUSSION

FTIR Analysis of the Catalyst

Fig. 1 showed the FTIR spectra of parent silica, modified silica, anhydrous copper sulphate, and catalyst obtained. Silica gel has specific adsorption at 3467 cm^{-1} which was assigned for O-H stretching of silica surface [16]. Based on this fact, the silica posses both of Si-OH bonding (silanol groups) and hydroxyl

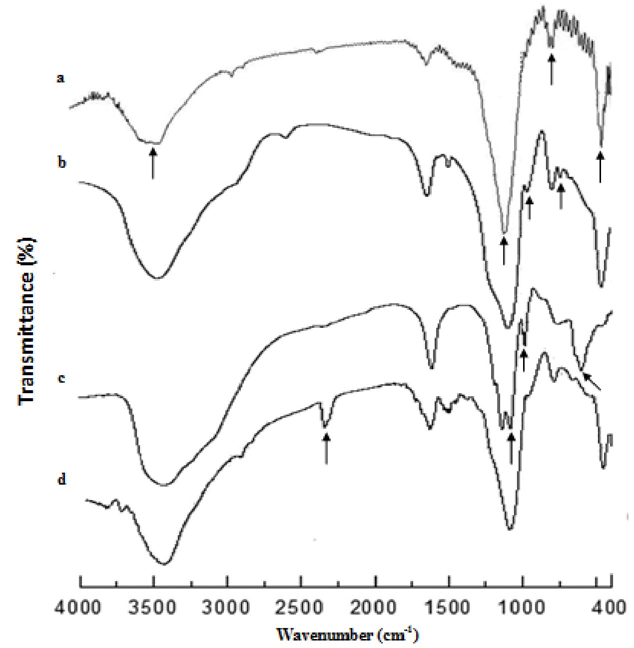

Fig 1. FTIR spectra (a) parent silica, (b) modified silica, (c) anhydrous copper sulphate, and (d) catalyst obtained

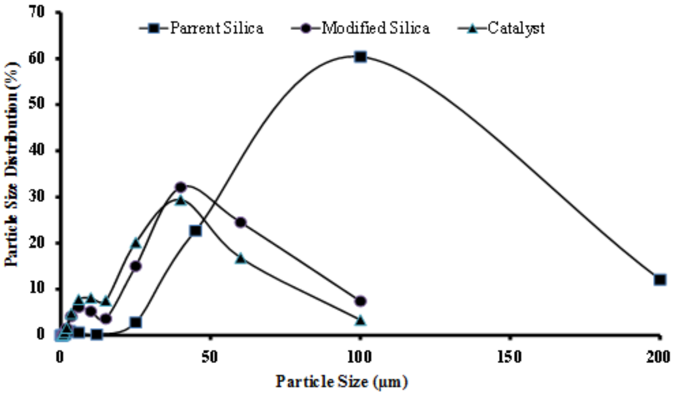

Fig 2. Distribution and particle size of parent silica gel, modified silica, and catalyst obtained

groups from adsorbed water [17]. The second's band at 1094 cm^{-1} was assigned for siloxane groups, Si-O-Si. Additional bands appear at 469 cm^{-1} and 798 cm^{-1} due to their deformation of Si-O bonding from SiO_4.

Band of modified silica appeared with weak intensity at 966 cm^{-1}. It indicated the appearance of Si-O with metals bonding, Si-O-Al. Band at 740 cm^{-1} was assigned to H-N-H wagging of anilinium cation. Bands of catalysts obtained appear at 2363 cm^{-1} could be assigned to nitrile (C≡N) group vibrations of the grafted compounds. The υ(CN) vibration of free $NCCH_3$ would be expected at 2253 and 2293 cm^{-1} [1-4]. In catalyst spectra, disappearance of bands at 740 cm^{-1}, 611 cm^{-1} and 1092 cm^{-1} from $C_6H_5NH_3^+$ ion. Furthermore, bands intensity at 798 cm^{-1} from Si-OH bending in such catalyst weaker than the one in parent silica caused by interaction between silanol groups with Cu(II) metal center. The availability of shifted CN stretching vibration also could be argued as a successful grafted of Cu(II) acetonitrile complex on the modified silica [1].

NL-PSA Analysis

NL-PSA gave information about size and distribution of particle. It can be seen from Fig. 2 a broadening of parent silica distribution in 1.5-200 µm range with dominated by 100 µm particle size. A broadening distribution of this material indicated that the silica was amorphous.

Modified silica has narrow distribution and smaller particle size than its parent silica which seemingly as a consequence of the interaction between $AlCl_3$ as modifier with silica surface. When grafted Cu(II) complex on modified silica, the particle size and distribution slightly decreased that can be favorable for its catalytic activity due to larger specific surface area.

Atomic Absorption Spectroscopy (AAS)

AAS analysis provided the amount of metal loading and metal leaching rate. It was found that the metal loading of Cu in the catalyst were 6.19% (by mass) and only undergoes 0.16% loss into the solvent after 24 h leaching test. This small value indicated that the Cu(II) metal center was strongly bounded on the modified silica through electrostatic interaction.

Catalytic Application at Optimal Conditions

Catalyst concentrations

The product of catalyst concentration was analyzed by GC-MS. In Fig. 3, by adding 0–1.5% catalyst into the mixture of methanol and frying oil the yield of methyl ester collected increases until about to 0.8% which contain 7.49% product. The product obtained were methyl ester which found 3.10% methyl palmitate (at 11.946 min retention time), and 4.39% methyl oleate (at 16.626 min retention time). At this point higher of yield of methyl ester due to the most populated formation of methoxide anion which is very important to initiate the transesterification of frying oil containing triglyceride at that point will also be assumed as a key factor [13]. Increased of catalyst concentration make yield of methyl ester obtained dramatically step down to almost zero.

Stirring rate

Yield of methyl ester in stirring rate variations as depicted in Fig. 4. The yield amount of methyl ester at 300 rpm is the best condition due to higher product

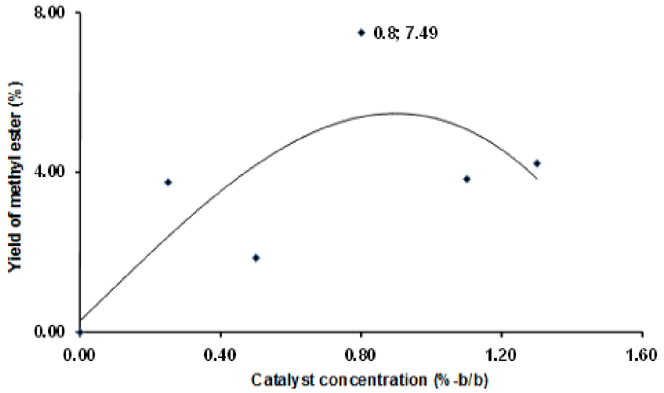

Fig 3. Catalyst concentration Vs totally methyl ester obtained in this work

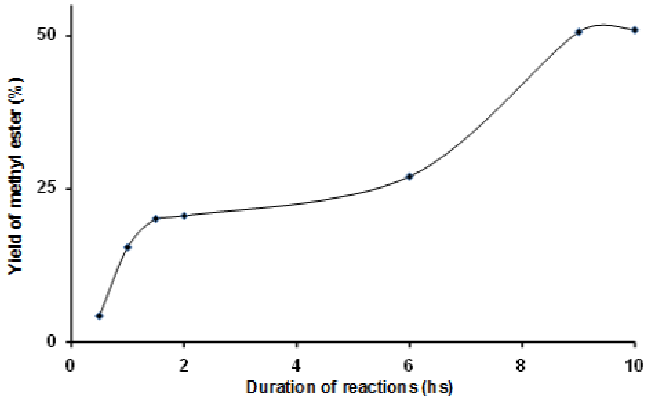

Fig 5. Curve of methyl ester product total from reaction times variations

obtained. At 300 rpm was found 26.45% of product that contain 5.16% of methyl palmitate, 13.45% methyl oleate, and 3.84% methyl stearate (at 11.468 min retention time). This phenomenon can be argued that at this rate the adsorption-desorption of substrates on catalyst surface reaches its equilibrium that allows the catalyst to work optimally.

The duration of the reaction

As can be observed in Fig. 5, the longer of duration of reaction was run into higher product obtained. In this paper, the longer of duration time of reaction were 6, 9 and 10 h. It was founded 26.99, 50.60, and 51.00% of product. This fact showed a significant effect of the duration of transesterification reaction to allow more substrate to interact with the surface of such immobilized Cu catalyst.

CONCLUSION

Immobilization of Cu(II)-acetonitrile complex on modified silica can be performed and promisingly can be applied in transesterification of frying oil. The catalyst shows its optimal conditions at 0.80% catalyst concentration, and 300 rpm stirring rate. However its dependence on the duration of reaction time still to be solve in the next research.

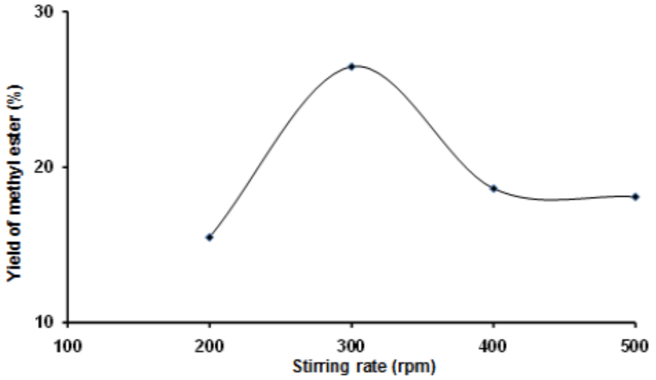

Fig 4. Stirring velocity gives significant impact on catalytic activity of the catalyst used in this reaction

ACKNOWLEDGEMENT

We would like thanks to Material Chemistry Laboratory staff for their help in the FTIR and NL-PSA measurement. Then our thanks go to Central Unand Laboratory and LABKES Padang Laboratory for their help in AAS and GC-MS measurement, respectively.

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