

SYNTHESIS AND CHARACTERIZATION OF MODIFIED MESOPOROUS SILICA-IMOBILIZED Cu(II)-ACETONITRILE COMPLEX AND ITS APPLICATION IN TRANSESTERIFICATION OF FRYING OIL

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ABSTRACT

Mesoporous silica has attracted rapidly growing attention in catalysis. In this work, mesoporous silica was synthesized by using CTAB surfactant and then modified by AlCl_3 . Such material was used as support for Cu(II)-acetonitrile complex and applied in transesterification of frying oil. The XRD pattern of the obtained silica confirms the availability of characteristic peak on silica surface while its TEM exhibits the uniformity of nanochannel of the mesoporous silica. The particle size of silica support has become smaller after grafting process showed by SEM images. FT-IR spectra of the materials indicated that the Cu(II) grafted on the mesoporous silica was in the form of its acetonitrile complex. Surprisingly, the Cu loading the grafted catalyst was found to be very high. That was 21%, when the catalyst applied on transesterification of the examined frying oil the amount of total methyl ester yielded were of 65%.

Keywords: mesoporous silica, AlCl_3 , Cu(II)-acetonitrile complex, transesterification

INTRODUCTION

Highly ordered mesoporous silica in 1992 attracts rapidly growing attention in its application. MCM-41 as one member of M41s family from Mobil Corporation has been synthesized using CTAB as structure directing agent and confirm the uniform pore size (2-50 nm), tunable pore size, large surface area, high pore volume, and high thermal stability^[1]. Their advantages have great interesting and promising field and potential to apply in catalysis, support^[2], and adsorbent^[3].

The important limitation of mesoporous silica is the lack of active site in its framework. Many researches have been reported to increase the potential application by incorporated other metals such as $\text{Al}^{[4]}$, $\text{B}^{[5-7]}$, $\text{Ti}^{[8]}$, $\text{Pd-Au}^{[9]}$ to its framework and modification of silica surface with weakly coordinated anion $\text{BF}_4^{-[10]}$, $\text{B}(\text{C}_6\text{F}_5)_4^{-[11]}$,

$\text{B}\{\text{C}_6\text{H}_5(\text{m-CF}_3)_2\}_4^-$, $\{(\text{C}_6\text{F}_5)_3\text{B-C}_3\text{H}_3\text{N}_2\text{-B}(\text{C}_6\text{F}_5)_3\}$, $\text{Al}\{\text{OC}(\text{CF}_3)_3\}_4^{-[12]}$ and $\text{AlCl}_3^{[13]}$. These ways attributed to improve thermal stability and active site in mesoporous silica.

Cu(II)-acetonitrile complex has employed in catalytic process. Syukri et al reported Cu(II)-acetonitrile complex potential to enhance in cyclopropanation reaction^[2,14]. Its complex confirm poor efficiency for economic and environmental due to recyclability, reuse, and regeneration of homogeneous catalysts isn't applicable. And the great attempt have been done a immobilization of homogeneous catalyst in support material. In our previous work, modified silica was synthesized with AlCl_3 in surface silica via electronic interaction and potential to applied in transesterification reaction^[13]. In this work, mesoporous silica as supported material was modified by AlCl_3 and then was immobilized by complex of Cu(II)-acetonitrile. Mesoporous silica and the

grafted catalyst was characterized by FT-IR, XRD, SEM, TEM, and AAS. This catalyst obtained was then applied in transesterification of frying oil. Frying oil confirm the pure oil that contains low free fatty acid.

EXPERIMENTAL SECTION

Materials

The following materials, Sodium silicate (Na_2SiO_3 ; MERCK), CTAB ($\text{C}_{19}\text{H}_{42}\text{BrN}$; MERCK), acetic acid glacial (CH_3COOH ; MERCK), hydrochloric acid 37% (HCl; MERCK), aniline ($\text{C}_6\text{H}_5\text{NH}_2$; MERCK), toluene ($\text{C}_6\text{H}_5\text{CH}_3$; MERCK), aluminium trichloride (AlCl_3), copper sulphate (CuSO_4), aquadest, methanol, frying oil were used without purification for the synthesis of the grafted catalyst.

Instrumentation

Mesoporous silica and the obtained catalyst were characterized by XRD, FTIR, SEM, TEM, and BET. Copper contain in grafted catalyst was analysed by AAS and methyl ester formation as a product of reaction was followed by GC-MS.

Procedure

Synthesis of mesoporous silica

We have prepared mesoporous silica with follow the molar ratio 1 SiO_2 : 0.27 CTAB : 60 H_2O [14]. In a typical synthesis, 49.20075 g CTAB was dissolved in 270 mL H_2O . 45.2088 mL Na_2SiO_3 in H_2O was added dropwise under stirring, pH adjusted at 11 by adding CH_3COOH , stirred for 24 hs and aged for 16 hs. The resulting gel is transferred into polyethylene bottle and followed hydrothermal treatment at 373 K for 3 days. The obtained solid was washed with aquadest and dried at 373 K for 24 hs. The powder was extracted with acidified methanol for 3 hs to remove surfactant in mesoporous silica. The

obtained solid product was washed by aquadest/methanol and dried at 373 K for 24 hs and white powder formed.

Synthesis of modified mesoporous silica

Mesoporous silica was mixed with aniline (toluene) and stirred for 24 hs. Anhydrous aluminium trichloride was added into the mixture. The resulting suspension was filtered, washed with toluene, and dried at room temperature. Solid obtained was grayish colours.

Synthesis of grafted catalysts

Modified silica, anhydrous CuCl_2 , and acetonitrile were starting materials for synthesis of the catalyst. Starting materials were mixed and stirred for 24 hs and washed with acetonitrile, and dried at room temperature. The catalyst obtained were characterized by FTIR, XRD, SEM, BET, and TEM.

Catalytic activity test of grafted catalyst on frying oil transesterification

The amount of 1 weight % of catalyst was respectively added to methanol and stirred (300 rpm, 60 °C) for 15 minutes. Afterward, frying oil was put into catalysts-methanol solution and stirred for 3 hs. The solution was analyzed by GC-MS. Yield of methyl ester product was accounted as in equation 1.

RESULTS AND DISCUSSION

XRD Analysis

Figure 1 displays the wide angle XRD pattern of silica which observed at 22.35°. Its observed the main characteristic of silica (ICDS #75303). Grafting of complex Cu(II)-acetonitrile in silica shows the decreasing intensity of peak, broadening, and shift to higher 2θ and attribute the grafting metal complexes in inside the channels of mesoporous silica and also indicate the disorder of framework of silica.

$$\text{yield of products} = \frac{\text{peak area} \times \text{volumes of methyl ester produced} \times 100\%}{\text{volumes of oil taken for the reaction}} \quad (1)$$

FT-IR Analysis of The Grafted Catalyst

The IR technique was employed to identify the formation of grafted catalyst on the bands characteristic.

FTIR spectra in Figure 2 showed bands at 1085 cm^{-1} and 794 cm^{-1} observed stretching vibrations of Si-O-Si framework. The stretching band at 3434 cm^{-1} characteristic –OH groups from adsorbed water and silanol groups in mesoporous silica and additional bands at 461 cm^{-1} due to their deformation of Si-O bonding from SiO_4 . Band at 797 cm^{-1} revealed that –O-H bending from Si-OH. Present band at 2927 cm^{-1} prove that the methyl groups from surfactant. Modification of surface mesoporous silica with AlCl_3

attributed stretching vibrations of Si-O-Si at 960 cm^{-1} [15].

Morphology Surface Analysis

The morphology for mesoporous silica are detected by scanning electron microscopy. Images of mesoporous silica and grafted sample are shown in Figure 3.

Mesoporous silica samples exhibit smooth surface silica and the TEM images in Figure 4 showed the uniform morphology of mesoporous silica and found the nanometer scale of particle. While grafted catalyst showed the irregular shape particle. Irregular particle revealed with XRD in figure 1 that lower crystallinity and disorder of particle will be occur after grafting complex.

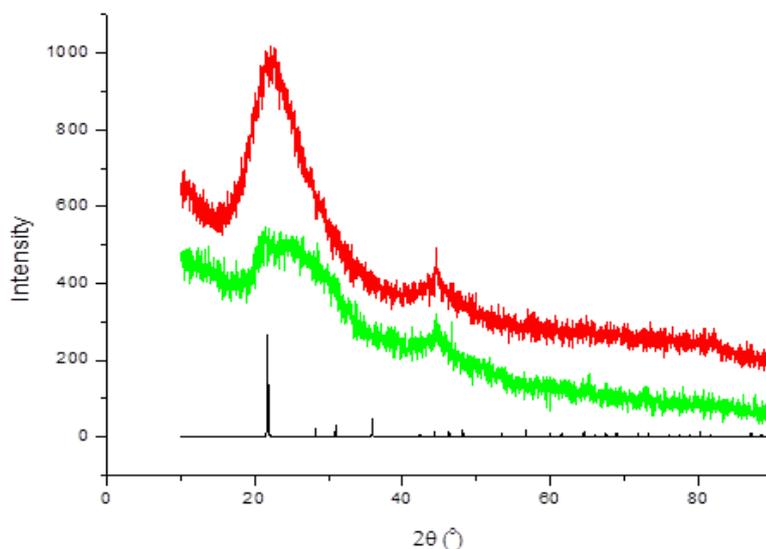


Figure 1. XRD pattern of (a) mesoporous silica (b) grafted catalyst.

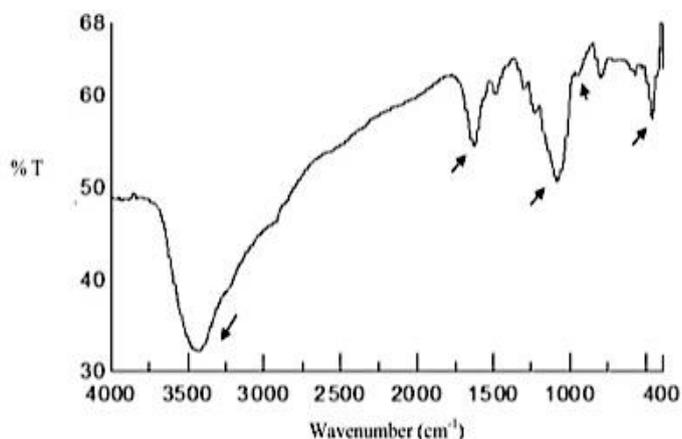


Figure 2 Spectra of grafted catalyst.

BET

Mesoporous silica exhibits isotherm type IV (IUPAC) that it confirm the hysteresis loop of mesoporous silica in figure 5. Monolayer adsorption in pore wall was followed capillar condensation at P/P^0 0,7-0,85. Pore diameter of mesoporous silica obtained was 7.05 nm. Its confirm the mesoporous silica was obtained using CTAB as molecular templating agent.

AAS Analysis

Copper metal loading in grafted catalyst was analyzed by AAS and found 21,32% Cu content in catalyst. In our previous work, using modified silica gel as support which have micrometer size only found 6.19% Cu in catalyst [13]. Higher content of metal loading was influenced by the amount of silanol groups in surface. Mesoporous silica has larger surface area than silica amorphous and surely, the amount of silanol groups can be increased.

Catalytic Activity of Grafted Catalyst

Yield of methyl ester in grafted catalyst found 65,24% of product that it contain hexadecanoic acid methyl ester (31.16%), octadecanoic acid methyl ester (3.18%), 9-octadecenoic acid methyl ester (32.40%), and 9,12-octadecadienoic acid methyl ester

(3.62%) in Figure 6. The increasing of metal loading can increase the yield of product due to the active site of catalyst and larger surface area.

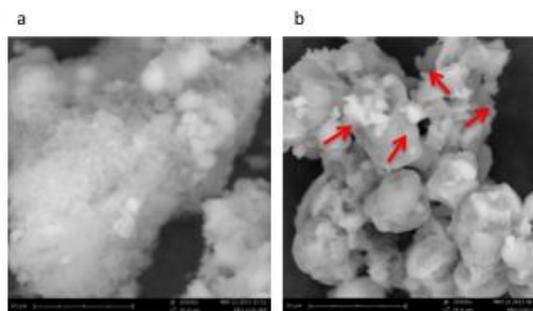


Figure 3 SEM images of (a) mesoporous silica (b) grafted catalyst.

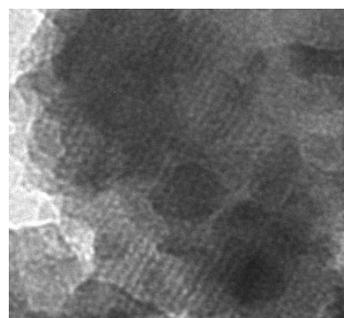


Figure 4 TEM images of mesoporous silica.

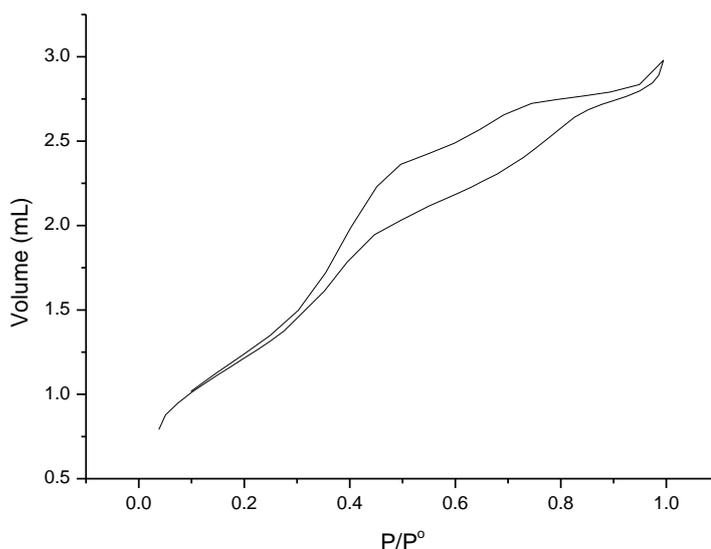


Figure 5. N₂ adsorption-desorption of mesoporous silica.

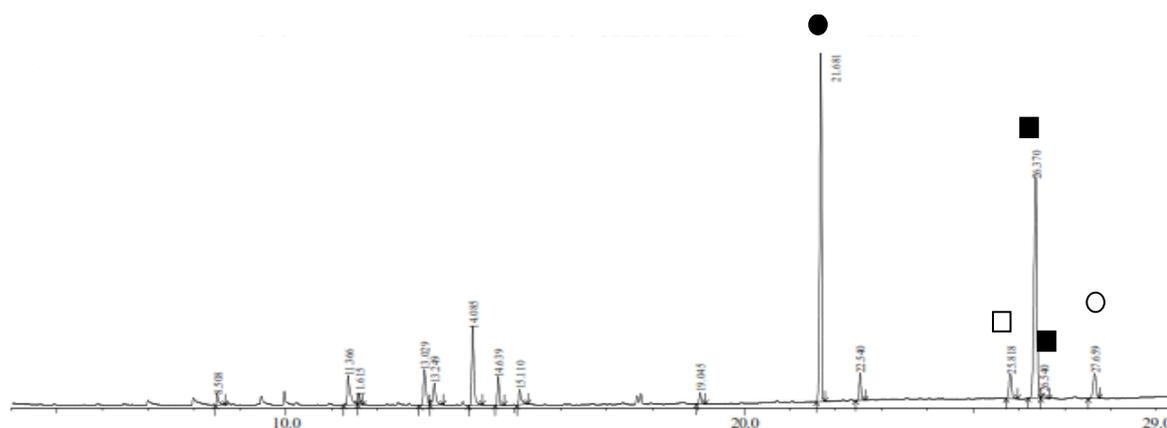


Figure 6. Chromatogram of product acatalytic activity grafted catalyst.

CONCLUSION

The mesoporous silica is the one of candidate a support material in catalyst. Mesoporous silica obtained has the pore diameter about 7 nm. Using mesoporous silica as support can increase the metal loading content and catalytic activity. The catalyst obtained exhibit good catalytic activity which 21% Cu contain was found 65% of product.

ACKNOWLEDGEMENTS

Authors thank specially to LLPM of Andalas University for financial support by SIM-LITABMAS project. All colleagues are also appreciated for their assistance on this work.

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