Synthesis of NH₂/MCM-41 Catalysts Using Silica of Sidoarjo Mud and Their Characterization for Palm Oil Transesterification

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Abstract: *Synthesis of NH₂/MCM-41 catalysts using silica from Sidoarjo mud and their characterization for palm oil transesterification have been carried out. The silica was separated from the mud by reflux method. The product was then analyzed by X-ray Flouresence (XRF) and used as silica source in the MCM-41 synthesis. The MCM-41 was synthesized by hydrothermal method at 100 °C for 24 h and calcined at 540 °C for 5 h. The MCM-41 was then modified using 3-Aminopropyltrimethoxysilane (3-APTMS) by grafting method under N/Si mol percent ratio of 1, 3, 5 and 10 to produce NH₂/MCM-41 catalysts. The MCM-41 was analyzed by XRD, FT-IR, Porosimeter and TEM, while that of the NH₂/MCM-41 was characterized by FT-IR and porosimeter. Transesterification of palm oil was carried out under methanol/oil mol ratio of 15 and 10 wt.% of catalyst toward the oil. The transesterification products were analyzed by GC and GC-MS.*
The result showed that the MCM-41 had pore diameter and surface area of 3.5 nm and 390.94 m²/g. The highest production (wt%) of ester was obtained by NH₂/MCM-41 5% catalyst i.e. 90.44 wt%. The catalyst have a life-time of about 4 h.
Keywords: *catalyst, palm oil, Sidoarjo mud, transesterification.*

I. Introduction

On may, 2006 an eruption of mud and fluid occured in drilling location of PT Lapindo Brantas, Porong, Sidoarjo, East Java. The eruption produce large amount of mud and covered more than 640 hectare area around it [1]. The Sidoarjo mud consist of Al_2O_3, SiO_2, CaO, TiO_2 and Fe_2O_3 of 21, 16, 50, 6.14 and 1.74 wt.% [2].

The Mobile Composition of Matter number 41 (MCM-41) is amorphous material consist of uniformly and highly ordered network of silica with hexagonally shaped. The pore size of the MCM-41 can be controlled from 2 to 10 nm by use of an appropriate surfactant as a template and adding of co-surfactant. The mesoporous MCM-41 has been proven very useful as a catalyst support and an adsorbent because of high surface area and thermal stability. The MCM-41 can be synthesized by hydrothermal method at 100-120 °C. Pure silica substance such as sodium silicate and TEOS (tetraethylorthosilicate) generally used as silica source in the MCM-41 synthesis. To reduce the production cost, silica from the Sidoarjo mud can be used as silica source. The previous research shown that the mesoporous MCM-41 can be synthesis from coal fly ash [3] as silica source by hydrotermal method. The Sidoarjo mud is highly composed of silica, thus it can be used as silica source. Based on the above explanation the authors undertaken synthesis of MCM-41 by hydrothermal method using silica source from Sidoarjo mud. The MCM-41 was then modified using 3-APTMS by grafting method to produce NH₂/MCM-41 catalysts. In this process the mol ratio of N/Si was controlled. The catayst was then applied in transesterification process of palm oil. The catalyst life time was also predicted.

II. Experimental

2.1 Materials

The materials used for the preparation of the NH₂/MCM-41 catalyst were: Sidoarjo mud from drilling location of PT Lapindo Brantas in Porong, Sidoarjo, hydrocloric acid (HCl, Merck), cetyltrimethyl ammonium bromide (CTAB, Merck), sodium hydroxyde (NaOH, Merck), methanol (CH_3OH), toluena ($C_6H_5CH_3$), 3-aminopropyltrimethoxysilane (3-APTMS, Aldrich), and palm oil.

2.2 Instrumentation

The equipments used in this research included chemical laboratory glassware, X-ray difraktometer (XRD, Shimadzu XRD-6000), X-ray flouresence (XRF, PANalytical MiniPal 4), fourier transform-infra red (FT-IR, Shimadzu Prestige-21), gas chromathography-mass spectroscopy (GC-MS, Shimadzu QP2010S), transmission electron moscophy (TEM, Pixel Spremeter-X 39173) and gas sorption analyzer (GSA, Quantachrome NovaWin2 1200e version 2.2).

2.3 Procedure
Extraction of silica from Sidoarjo mud

Extraction of silica from Sidoarjo mud was done by batch methode. The Sidoarjo mud was dried and sieved to 100 mesh. The mud was washed throughly with water overnight and dried. The mud was refluxed with HCl 6 M solution under stirring in a round-bottom flask at 90 °C for 3 h, then washed with water up to pH 7. The mud (80 g) and 400 mL of 6 M NaOH solution were refluxed under stirring in a round-bottom flask at 90 °C for 16 h. The filtrate was separated then titrated by HCl 3 M until pH 8. The formed precipitate was filtered, washed with destiled water and dried overnight at 80 °C. The dry precipitate was named as extracted silica and analyzed by XRF.

Synthesis of MCM-41

The MCM-41 was synthesized by hidrothermal methode. The CTAB (2.3 g) and 47 mL of destilled water were mixed at 40 °C. The silica solution was prepared by dissolve of 4,2 g silica at 140 mL of 1,5 M NaOH solution. The silica solution was added dropped wise to the surfactant solution under vigorous stirring. After 60 min, the pH was adjusment to 10 by dropwise addition of 3 M HCl solution and the resulting mixture was stirred for 3 h in a static condition. The silica-surfactant gel found was hydrothermally treatment at 100 °C in a teflon-lined stainless steel autoclave for 24 h. After cooling at the room temperature, the resulting solid product was washed with distilled water until it neutralized and dried in an oven at 80 ℃ overnight. The template was removed through calcination in air at 540 ℃ for 5 h with heating rate of 2 °C/min before further application. The samples then analyzed by XRD, FTIR, TEM and GSA.

Modification of MCM-41 by 3-APTMS

The NH₂/MCM-41 was synthesized by grafting method. The calcined MCM-41 (0.5 g) was refluxed in 20 mL of toluene containing different amount of 3-APTMS (N/Si=1, 3, 5 & 10 mol%) for 5 h. The powder of NH₂/MCM-41 was collected by sentrifugator, washed with toluene and methanol then dried overnight at 50 °C. The resulting product was NH₂/MCM-41x samples, where x = 1, 3, 5 and 10% is the theoretical proportion of the amino-organoalkoxysilane toward the Si source. The samples were then analyzed by XRD, FTIR and GSA.

Transesterification of palm oil

Transesterification of palm oil into biodiesel was carried out by refluxing the oil and methanol 1:15 molar ratio with 10 wt.% of the NH₂/MCM-41 as a catalyst at 65 °C for 2 h. At the end of the reaction, the reactor was cooled to room temperature and the catalyst was separated from the product mixture using sentrifugator. The biodisel product was separated from gliserol and then washed with warm destillated water. The product was then analyzed by GC-MS.

III. Result And Discussion
3.1 Extraction of silica from lapindo mud

Table 1 shown that SiO_2 content in the H_2O washed sample was 44.24 wt.%, that was proved that the silica content in the mud was already high. After refluxing with HCl and NaOH the concentration of SiO_2 in the sample increased to 53.8 and 94.87 wt.%.

Table 1. Composition of mud after washed with water and refluxed by HCl and NaOH

Compound	Concentration (%)		
	H₂O washed	HCl refluxed	NaOH refluxed
SiO₂	44,24	53,86	94,87
Al₂O₃	14,02	16,20	1,49
Fe₂O₃	27,93	13,34	0,18
CaO	6,53	5,19	0,15
Cl	-	0,66	1,90
Other	7,28	10,92	1,59
Total	100,00	100,00	100,00

3.2 Characterization of NH₂/MCM-41 catalyst
3.2.1 Powder X-ray Diffraction (XRD)

The low angle of XRD patterns of the uncalcined, calcined and modified mesoporous silica MCM-41 were shown in Fig. 1. For uncalcined MCM-41 (Fig. 1a), the XRD diffractograms displayed the typical reflections at 2θ values of 1.8 (100), 3.5 (110) and 4.0 (200) while that of the calcined MCM-41 (Fig. 1c) showed two characteristic diffraction peaks at 2θ values of 1.9 and 3.7 which correspond to the (100) and (110) planes. The main peak at 2-3° of 2θ assigned the ordered hexagonal structure of MCM-41, while the other weak peaks at 4-6° of 2θ attributed the highly ordered of the structure [4]. Upon calcination in the air at 813 K for 5 h with heating rate 2°/min., the intensity of the calcined MCM-41 XRD peaks increased by about 3 times

compared to the uncalcined MCM-41. These results reflect that the degree of ordering was dramatically improved by surfactant removal [5].

The calcined MCM-41 was then modified with APTMS by grafting method. The reaction between MCM-41 and 3-APTMS was showed in Fig. 2 [6]. The XRD pattern of NH₂/MCM-41 5% shown in Fig. 1b. The NH₂/MCM-41 5% showed characteristic diffraction peaks at 2θ values of 1.9 which correspond to the (100) planes. After modification of calcined MCM-41 the peak at 2θ values of 3.7 (110) from was dissapear. This behavior was caused by the scattering contrast between pores and walls, suggesting the inclusion of the functional groups inside the pores. The patterns had confirmed that the presence of the hexagonal structure of the pores and suggested that the modification process did not affect the framework integrity of the ordered MCM-41 [7]. The previous research related to the modification of mesoporous silicas have reported the similar behavior [7-9].
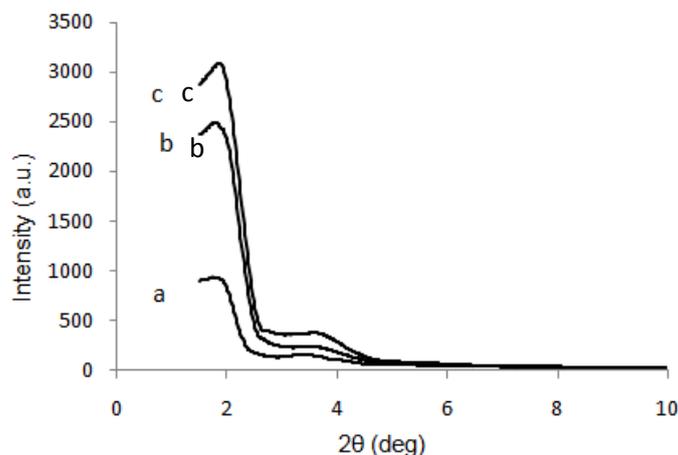

Fig 1. Diffractogram of (a) uncalcined MCM-41, (b) NH₂/MCM-41 5% and (c) calcined MCM-41
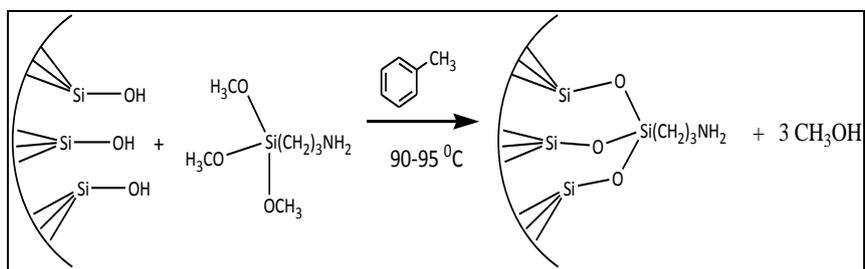

Fig 2. Reaction of MCM-41 and 3-APTMS [8]

3.2.2 Fourier Transform Infrared (FTIR) Spectroscopy

The FT-IR spectras of uncalcined and calcine MCM-41 were shown in Fig 3a and b. A description of FT-IR adsorptions bands of both spectra: the bands at 1080 cm^{-1} and 1221 cm^{-1} are from vibration of Si-O-Si; the band at 3,448 cm^{-1} is a characteristic band of Si-OH and water molecules adsorbed; the bands at 1635 cm^{-1} are from vibration of water molecule adsorbed [10]. The bands at 2924, 2854 and 1473 cm^{-1} that are from vibration of asymmetric and symmetric streching -CH₂- from surfactant molecul (template) dissappeared after calcined. Those bands indicated that the template had been removed and MCM-41 was succesfully synthesized.

The FTIR spectra of modified MCM-41 are shown in Fig. 4. The characteristic of aminoprophyl groups showed bands of streching vibrations of -CH₂- between 2990 and 2890 cm^{-1} and NH₂ scissor at 1560 cm^{-1} [8]. The NH₂/MCM-41 5% (Fig. 4b) showed bands at 2931 and 1527 cm^{-1} which characteristic of aminoprophyl groups. Those bands indicated that the 3-APTMS was succesfully grafted in to the MCM-41 produced NH₂/MCM-41 sample.
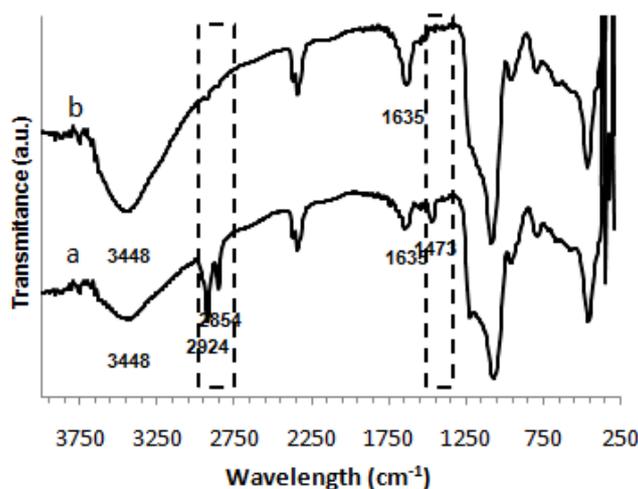
Fig. 3. FT-IR spectra of (a) uncalcined and (b) calcined MCM-41

3.2.3 BET surface area

The N_2 adsorption–desorption isotherms of the MCM-41 and NH₂/MCM-41 5% materials were shown in Fig. 5. The both samples shown the type IV isotherm typical of mesoporous materials. Adsorption/desorption step between 0.2 and 0.4 partial pressures (p/p_o) reveals the mesopores were filled. Comparison of the two curves in Fig. 5 shown that the BET surface area decreased from the MCM-41 to NH₂/MCM-41 5% sample. The MCM-41 presented an average pore diameter of 36 Å, total pore volume of 0.3827 cc/g and BET surface area of 424.579 m²/g. The NH₂/MCM-41 5% presented an average pore diameter of 35 Å, total pore volume of 0.3827 cc/g and BET surface area of 390.943 m²/g. The decrease of BET surface area, total pore volume and average pore diameter indicated the presence of aminoprophyl funcional group at the MCM-41 sample.

Tem

The structure of material sample was also characterized by high-resolution transmission electron microscopy (TEM) and the micrographs were shown in Fig. 6a and b. The TEM micrographs (Fig. 6) confirmed that the material have typical MCM-41 type, highly parallel channel-like porous structure packed in a hexagonal symmetry. Also, it can be seen from these figures that the pore structure was regular over the whole particle in both pictures (Fig. 6a and b).
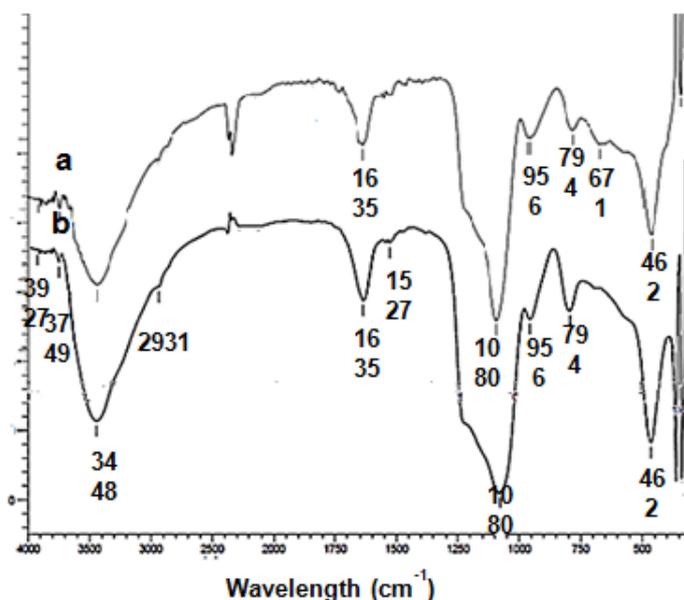

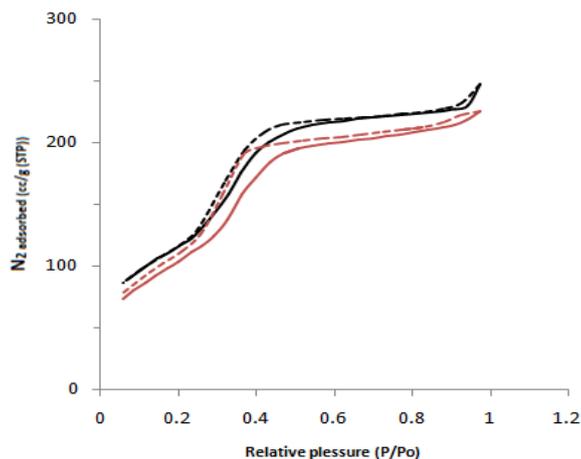**Fig. 4** FT-IR spectra of (a) calcined MCM-41 and (b) NH₂/MCM-41 5%

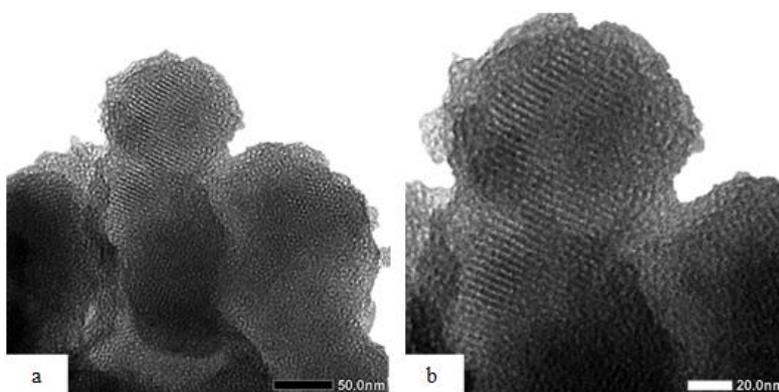**Fig. 5.** N_2 adsorption-desorption of MCM-41 (**--**) and NH₂/MCM-41 5% (**--**)

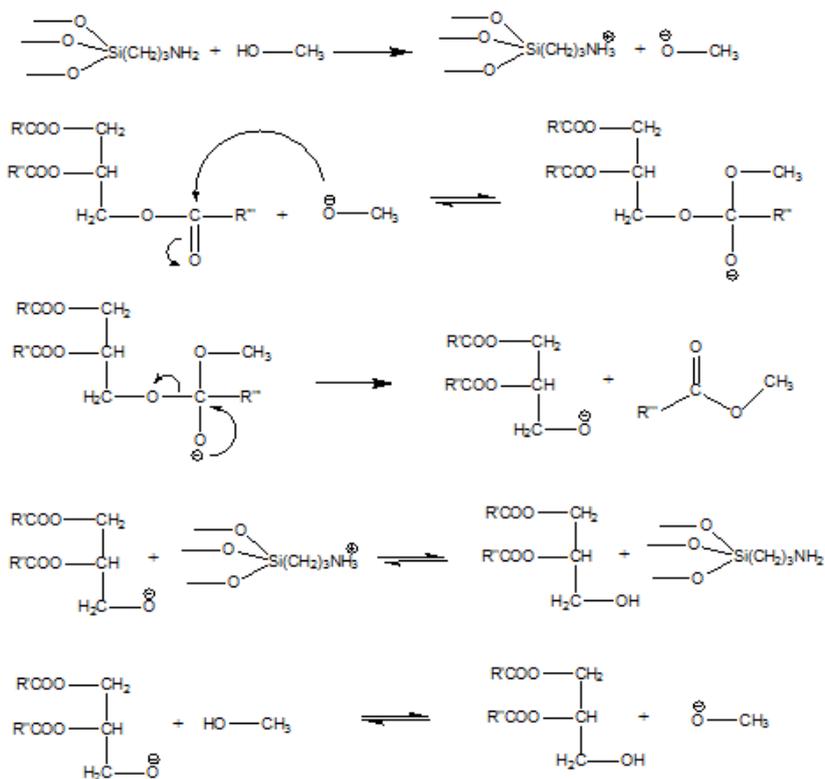**Fig. 6.** TEM micrograph of the MCM-41 sample: (a) 50 nm and (b) 20 nm

Fig. 7. Transesterification reaction between methanol and triglyceride from palm oil with NH₂/MCM-41 catalyst

3.3 Palm Oil Trasesterification

Palm oli transesterification has been done to test the activity of NH_2/MCM-41 x (x= 1, 3, 5 and 10% mol of N/Si) catalyst. The transesterification reaction was showed in Fig. 7. The result of transesterification process was shown in Fig. 8. From the Fig. 8 it was known that the increase in mole ratio of N/Si caused an increase in percent conversion of methyl ester. This phenomenon was comparable with the increase of the number of N or base sites contained in the MCM-41, thus the product obtained was also higher because the reaction was faster. In a case of the mole ratio of N/Si 10% the conversion was decreased. This is thought to occur because there are several possibilities. The first possibility is the saponification reaction due to the too many sites bases contained in the catalyst material. The second possibility is the reverse reaction of methyl esters to fatty acids, it happens because the reaction time is too long [11]. said that if the reaction time is too long, it will lead to product reduction because the transesterification reaction is a reversible reaction. This was evidenced from the GC-MS result that the two peaks of lauric and myristic acid were appeared in an area of 8.88 and 1.34 %. Thus, it can be stated that there was reversible reaction during the transesterification.
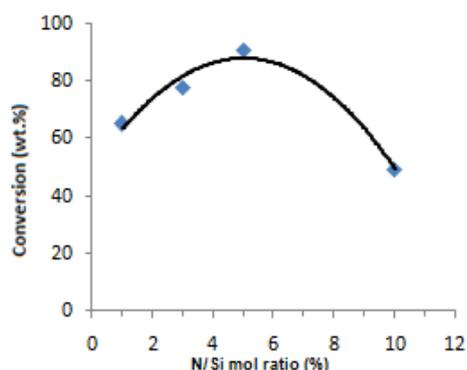

Fig. 8. Methyl ester conversion of palm oil transesterification.

The Methyl ester products of the catalysts have been shown in Table 2. Based on the Table. 2, it can be seen that the main composition of the ester was methyl palmitate (C16: 0) and methyl oleate (C18: 2). This result was obtained because the main content in palm oil is palmitic acid and oleic acid.

Determination of the catalyst life-time was performed using a NH_2/MCM-41 5% catalyst. The reaction was performed three times using the same catalyst for 2 h for each reaction process. The conversion of methyl ester obtained in this process was shown in Fig. 9. At the twice runs the catalysts still provide conversion of palm oil into methyl ester as indicated by the appearance of peaks in the chromatogram results of the GC-MS analysis (not shown). After the thrird runs of transesterification, the catalyst did not show activity. This result indicated that the catalyst has been deactivated. Deactivation of the catalyst due to the nature properties of the catalyst surface are hydrophilic covered by glycerol which is the other product from the previous transesterification (1st and 2nd runs). Glycerol attached to the catalyst causes the catalyst active sites and pores are covered, so the catalyst becomes deactivated. The existence of glycerol evidenced by the increased weight of the catalyst condition and still looks wet although it has been dried in an oven at 80 ° C for 24 h.

Table. 2 Distribution of ester produce by NH₂/MCM-41 catalyst

| Product	Content of ester products (%)			
	NH₂/MCM-41 10%	NH₂/MCM-41 5%	NH₂/MCM-41 3%	NH₂/MCM-41 1%
Lauric acid	8.88	-	-	-
Ethyl Palmitate (C16:0)	0.42	-	-	-
Methyl Miristate (C14:0)	1.08	0.88	1.20	-
Miristic acid	1.34	-	-	-
Methyl Palmitate (C16:0)	37.92	44.1	42.50	44.81
Methyl Palmitoleate (C16:1)	-	-	0,. 7	-
Dihepthyl ketone	2.89	-	-	-
Methyl Linoleate (C18:2)	5.36	6.95	-	-
Methyl Oleate (C18:1)	28.78	43.55	48.02	51.28
Methyl Stearate (C18:0)	3.11	4.50	0.44	3.91
10-nonadecanon	2.56	-	-	-
Methyl nonadecanoate	-	-	6.50	-
1,2-dodecanadiol	-	-	1.33	-
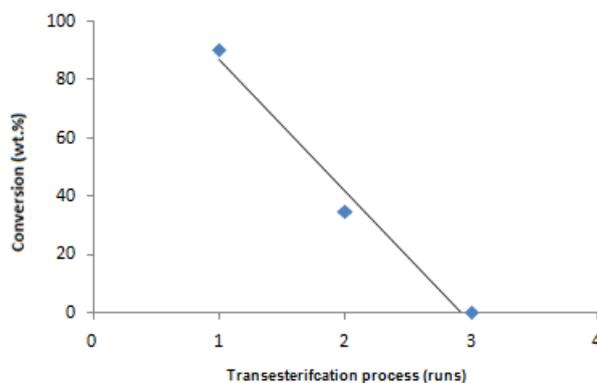
Fig. 9. Conversion of methyl ester in the determination of catalyst life-time

IV.   Conclusions

Silica extracted from Sidoarjo mud can be used as a silica source in the synthesis of MCM-41. The MCM-41 showed high ordered material, average pore diameter and BET survace area of 3.6 nm and 424.579 m^2/g. The NH$_2$/MCM-41 has average pore diameter and BET survace area of 3.5 nm and 390.94 m^2/g. The highest amount of methyl ester was produced by the NH$_2$/MCM-41 5% catalyst i.e. 90.44 wt.%. The catalyst have a life-time of about 4 h.

Acknowledgement

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