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Research Article

The Effect of Mesoporous H-ZSM-5 Crystallinity as a CaO Support on the Transesterification of Used Cooking Oil

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Abstract

Transesterification of used cooking oil was carried out over calcium oxide supported on mesoporous H-ZSM-5 prepared from kaolin as solid base catalysts. Solid basic catalysts investigated in this study were characterized by XRD, FTIR spectroscopy, and N_2 adsorption-desorption techniques. The XRD pattern showed peaks corresponding to the CaO and mesoporous ZSM-5 in the sample. The peak intensity of the CaO increased as the CaO loading in ZSM-5 was increased. The characterization based on FTIR spectroscopy revealed that CaO/H-ZSM-5 solids have functional groups characteristics of both CaO and mesoporous H-ZSM-5 which appeared in the band at around 550 cm^{-1} and 480 cm^{-1}. The isotherm of N_2 adsorption-desorption of CaO/H-ZSM-5 indicated the type IV isotherm with the presence of hysteresis loop. For the catalytic activity, the biodiesel yield using catalyst of 10 % CaO/HZSM-5 (100 %), 30 % CaO/HZSM-5 (100 %), 50 % CaO/HZSM-5 (100 %) were 24.34, 27.37, and 29.73 %, respectively. It also related with the basic active site, when loading CaO increased, the basic active site also increased.

Keywords: CaO/H-ZSM-5; Zeolite; Mesoporous; Cooking Oil; Transesterification

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1. Introduction

The fuel consumption constantly rising from year to year. This is obvious because lately in Indonesia often scarcity of fuel oil, and even Indonesia has become the importer of petroleum. Therefore, it is necessary to develop alternative fuel sources. Biodiesel is a liquid fuel that recently studied as an alternative fuel because it has several advantages compared with diesel.

It is mainly produced through the transesterification reaction of vegetable oils, which is a natural source of renewable and sustainable [1,2]. In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol [3]. Transesterification reaction can take place without using a catalyst, but it requires special conditions such that relatively long reaction time, high temperatures and pressures. Catalysts which have been used in the transesterification reaction is homogeneous and heterogeneous catalysts. However, the use of heterogeneous

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catalysts is more favorable than the homogeneous catalyst, because it is more environmentally friendly and easily separated from the product. Heterogeneous catalysts have been studied have a relatively high catalytic activity, but requires phase synthesis is complex and time-consuming. Thus, for further research to look for heterogeneous catalysts are an ideal, inexpensive, environmentally friendly in nature, and is effective for the transesterification reaction [4].

Among the heterogeneous catalysts studied, CaO has been considered a promising heterogeneous base catalyst for biodiesel production [5-9]. Alkali oxides CaO not only has a high alkalinity and activity, but also not soluble in methanol solvent medium in which the transesterification reaction [6]. To increase the catalytic activity, some research on supporting CaO material with a large surface area such as silica, alumina, and zeolite. Material support sustain good dispersion of the metal oxide so as to increase the surface area of the active site. Researcher [7] have done synthesis catalyst of CaO/mesoporous silica by impregnation method. Mesoporous silica has a surface area and large pore volume and has a uniform pore size. Calcium acetate, which has been impregnated in the mesoporous silica solids, distributed evenly on the surface of silica and filled the pores.

Referring to the previous studies, in this research, we have prepared CaO/H-ZSM-5 mesoporous using impregnation method with a variety of support (crystallinity of 64.41; 74.40; and 100 %) and CaO loading (10 %, 30 %, and 50 %w/w). Then, the catalysts were characterized and tested for the activity in the transesterification reaction.

2. Materials and Methods

2.1 Materials

The materials used in this study were mesoporous ZSM-5 (crystallinity of 64.41; 74.40; and 100 %) prepared from Indonesian kaolin based on our previous results with some modification [10], calcium acetate ($Ca(CH_3COO)_2.H_2O$, Merck, 93-95 %), ammonium acetate (CH_3COONH_4, Merck, >98 %), methanol (CH_3OH, Merck 99.9 %), ethanol (C_2H_6O, Merck, 99.9 %), sodium hydroxide (NaOH), toluena (C_7H_8, Merck, 99.9 %), phenolphthalein (Merck), neutral red (Merck), 2,4-dinitroaniline (Merck), 4-nitroaniline (Merck), nitrogen gas, and used cooking oil.

2.2 Ion exchange

Na-ZSM-5 solid was neutralized, dried, and calcined at a temperature of 550 °C (2 °C/min) with N_2 flow for 1 hour followed by the flow of air for 6 hours to remove of the organic template. For cation exchange, 1 gram solid was refluxed with 50 mL of ammonium acetate 1 M for 3 hours at 80 °C. Then the solids was filtered and dried at 100 °C for 24 hours. The dried solid was continued for calcinations process at temperature of 550 °C for 5 hours in a tubular furnace (2 °C/min).

2.3 Preparation of catalyst CaO/H-ZSM-5

Three different kinds of support used in this study was the H-ZSM-5 with the crystallinity 64.41; 74.40; and 100 %. The catalyst of CaO/H-ZSM-5 was synthesized by wet impregnation method and obtained through thermal decomposition. An amount of calcium acetate dissolved in distilled water was added to the solid H-ZSM-5. The CaO was dispersed on the support of H-ZSM-5 with a variation of the mass ratio CaO:H-ZSM-5, i.e. 10:100, 30:100 and 50:100 [5]. The mixture was stirred at 80 °C for 40 minutes using a magnetic stirrer. After the mixture was dried at 105 °C for 12 hours, the solid was then calcined at a temperature of 800 °C for 2 hours [11]. The activities of the CaO/H-ZSM-5 catalyst was compared to the three support. Determining the effect of crystallinity support and the optimum loading were also conducted.

2.4 Catalyst characterization

Powder X-ray diffraction (XRD) patterns of the solids samples were collected on Philips X'pert XRD instrument with Cu Kα radiation with a step size of 0.04° and counting time of 10 s. The samples were grinded in agate mortar before analysis. The data were recorded in the 2θ range of 5-70°. Fourier transform infrared (FTIR) spectra of the samples were recorded on a Shimadzu spectrophotometer using the KBr pellet technique, in the range of 400-4000 cm^{-1}. Nitrogen adsorption-desorption were recorded on Adsorption-Desorption Nitrogen Quantachrome Instruments with measured at 77 K after pretreatment at 673 K for 4 h under vacuum. The total surface area was determined by the BET method, the total pore volume was obtained as the amount of nitrogen adsorbed at P/P_0 of 0.99, and the *t*-pot method was used to distinguish micropores from mesopores.

2.5 Catalytic activity

Transesterification reaction was carried out with reflux method. Three-neck-round-bottom-flask was placed on an oil bath equipped with temperature controller, magnetic stirrer and reflux condenser. The reaction temperature in this system was 65 °C with methanol to oil molar ratio of 12:1 and 2 % w/w catalyst.

The catalyst of CaO/H-ZSM-5 was mixed with methanol in a round bottom flask connected to a condenser which is placed in the bath with the reaction temperature of 65 °C. The oil has also been heated at a temperature of 65 °C. The mixture was stirred using a magnetic stirrer at constant speed for 2 hours. To stop the reaction, the mixture was immersed in a container of water at room temperature and the catalyst was separated from the product using a centrifuge at 6000 rpm for 30 minutes.

Transesterification product was transferred to a separating funnel and allowed to stand overnight to completely phase separates glycerol and biodiesel. Glycerol phase (bottom layer) separated in advance, after the biodiesel phase (top layer) was washed with warm distilled water to remove residual glycerol. Then, the remaining water and methanol were evaporated at 105 °C for 2 hours to obtain biodiesel with high purity [11].

2.6 Determination of FAME (Fatty Acid Methyl Ester) content

Biodiesel synthesis product was characterized by Gas Chromatography (GC) to determine the extent of the area so that it can be calculated methyl ester concentration. Then the value of these concentrations can be used to calculate the yield of biodiesel as stated in Equation (1) [3].

$$Yield = \frac{W_B / C_I}{W_A} x C_{Tot} x 100\% \qquad (1)$$

where, W_B denotes mass of biodiesel (g), C_I is biodiesel concentration (ppm), W_A symbolizes mass of oil (g), and C_{tot} is concentration of methyl ester (ppm).

3. Results and Discussion

3.1 Characterization of catalyst

X-ray diffraction technique was used for phase identification of samples ZSM-5, CaO, and CaO/H-ZSM-5 with different of loading CaO and crystallinity of ZSM-5 itself. The results of the XRD diffractogram 2θ (°) of 5-70 samples are shown in Figures (1)-(3). The XRD patterns of mesoporous ZSM-5 samples showed peaks at 2θ (°) of 7.99; 8.86; 23.14; 23.98; and 24.48, corresponding to the MFI structure of the crystal, as reported by Goncalves *et al.* [12]. Meanwhile, the XRD patterns of CaO samples showed peaks at 2θ (°) of 32.21; 37.38; 53.87; 64.15; and 67.37, which are characteristic of crystalline peaks of CaO from thermal decomposition of calcium acetate. The XRD pattern of CaO was similar to the results reported [13]. The peaks of the XRD patterns of mesoporous ZSM-5 and CaO samples were appeared on all CaO/H-ZSM-5 samples, indicated that the samples contains CaO crystals and ZSM-5.

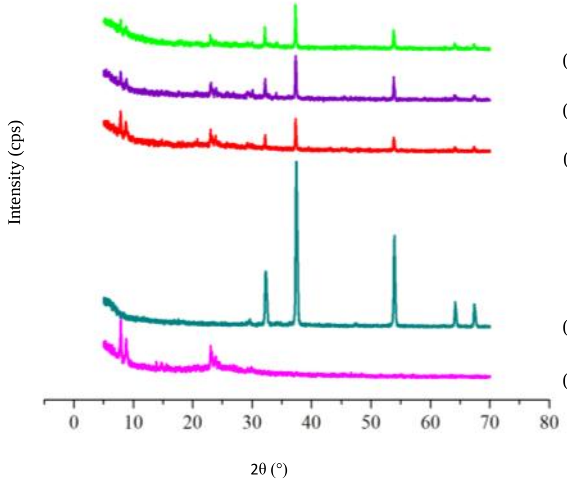

Figure 1. XRD patterns of catalyst samples: (a) ZSM-5 (64.41 %), (b) CaO, (c) 10 % CaO/H-ZSM-5, (d) 30 % CaO/H-ZSM-5, (e) 50 % CaO/H-ZSM-5

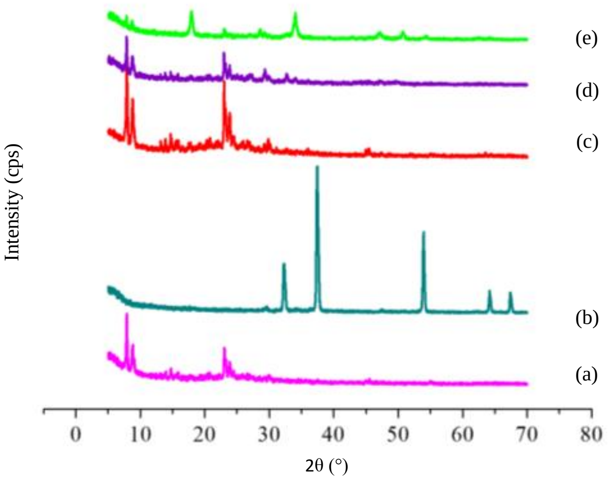

Figure 2. XRD patterns of catalyst samples: (a) ZSM-5 (74.40 %), (b) CaO, (c) 10 % CaO/H-ZSM-5, (d) 30 % CaO/H-ZSM-5, (e) 50 % CaO/H-ZSM-5

However, the sample of 10 % CaO/H-ZSM-5, 30 % CaO/H-ZSM-5 and 50 % CaO/H-ZSM-5 shows the differences at peaks intensity. Overall, the XRD pattern shows that as loading of CaO in ZSM-5 increased, CaO peaks intensity becomes higher than the peaks intensity of ZSM-5. XRD peak intensity related to the concentration of CaO and mesoporous ZSM-5 in the sample. High concentrations have resulted in high peak intensity in the diffraction lines. Similar finding has been reported by Pasupulety *et al.* [13] that the increased of Ca loading on Al_2O_3, the peak intensity of CaO will also be increased.

Characterization by FTIR spectroscopy was aimed to the identification of functional groups on the samples. Figure 4 shows the infrared spectra of the samples, i.e. 10, 30, and 50 % of the CaO/H-ZSM-5 (100 %). Peak at 917 cm^{-1} is Al–OH vibration, while the peaks at 1107 cm^{-1} is the vibration of in plane Si–O stretching. The appearance of the peaks at 1090, 796, and 450 cm^{-1} were characteristic of the silica-based materials framework. The shoulder peaks at ~ 1220 cm^{-1} was assigned to the external asymmetry stretching of Si–O–Si bond and the peak at 960 cm^{-1} was attributed to the terminal silanol groups (Si–OH) on the wall surface of the mesopores. The absorption band at 548 cm^{-1} was the characteristics of the five ring unit in pentasil structure such as ZSM-5 zeolite. The CaO samples showed OH band at wavenumber of about 3600 cm^{-1}, CH band at 2300-2900 cm^{-1}, CO band in the wavenumber around 1400, 1700, and 875 cm^{-1}, as well as on the absorption band of CaO on the wavenumber around 400 cm^{-1} [14]. Meanwhile, samples with impregnation method showed a specific absorption band which is a combination of an absorption band samples of ZSM-5 and CaO, but with different intensities depending on the loading of CaO. At the higher CaO loading , the intensity of the absorption band CaO in the CaO/H-ZSM-5 sample also increased. These intensity of the bands are related to the concentration of CaO and ZSM-5 in the sample. The result of FTIR analysis supported of the XRD data.

The N_2 adsorption-desorption of the solid products have been carried out to determine specific surface area, the pore size distribution, the total pore volume, and the pore structure of the materials [12]. The N_2 adsorption-desorption isotherms of CaO impregnated ZSM-5 with a variation of Ca loading of 10, 30, and 50 % (w/w) are shown in Figure 5. The N_2 adsorption-desorption isotherm of the CaO/H-ZSM-5 indicates the type IV isotherm with the presence of hysteresis loop (P/P_0 of 0.3-1.0) due to the capillary condensation processes, which is a characteristic of mesoporous material. The micropore and mesopore surface area calculated from the isotherms data are given in Table 1. The BET surface area of 10 % CaO/H-ZSM-5 (100 %) is 159.737 m^2/g, while *t*-plot micropore and mesopore surface area are 102.787 m^2/g and 56.950 m^2/g, respectively. Table 1 summarized the physical characteriza-

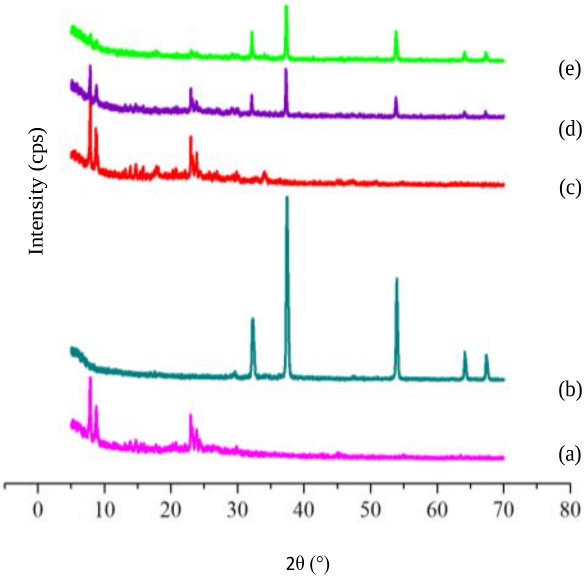

Figure 3. XRD pattern of samples: (a) ZSM-5 (100 %), (b) CaO, (c) 10 % CaO/H-ZSM-5, (d) 30 % CaO/H-ZSM-5, (e) 50 % CaO/H-ZSM-5

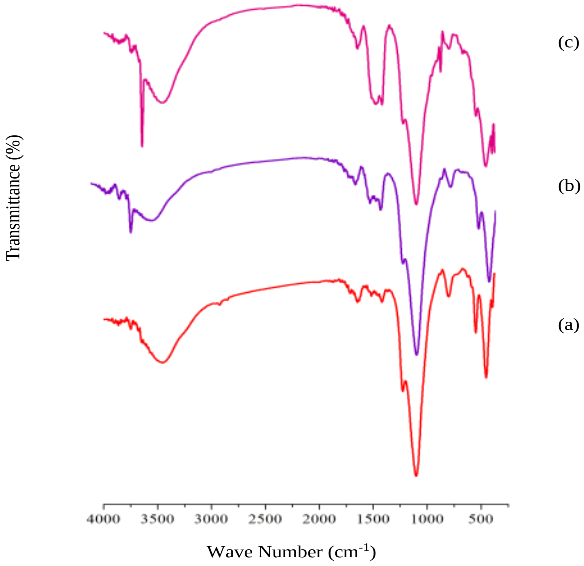

Figure 4. Infrared spectra of samples: (a) 10 % CaO/H-ZSM-5 (100 %), (b) 30 % CaO/H-ZSM-5 (100 %), (c) 50 % CaO/H-ZSM-5 (100 %)

tion of the CaO/H-ZSM-5 catalyst calculated from the analysis of N_2 adsorption-desorption data. The specific surface area of the CaO/HZSM-5 catalyst decreases significantly when the loading Ca extended from 30 % to 50 %. This results are consistent with the previous results [15] that CaO was uniformly dispersed in SBA-15, as therefore, the higher loading of Ca causes a drastic decreased in surface area.

3.2 Catalytic activity

All CaO/H-ZSM-5 samples were examined as catalyst in the transesterification of waste cooking oil with methanol. Based on calculations yield of biodiesel, it is known that the yield of biodiesel produced increased in accordance with the increase of the CaO catalyst loading. The CaO were dispersed on the support of crystalline H-ZSM-5, i.e. the 10 % CaO/H-ZSM-5 (100 %) catalyst produced biodiesel with the yield of 24.34 %. The biodiesel yield showed a slight increase with the use of a catalyst of 30 % CaO/H-ZSM-5 (100 %) with the yield of 27.37 %. Meanwhile, the catalyst of 50 % CaO/H-ZSM-5 (100 %) produced biodiesel yield of 29.73 %. These finding related to the basic active site, in which at loading CaO increases, the basic active site increased. The correlation between loading CaO with the yield is shown in Figure 6.

Loading CaO also affect the pore volume of the catalyst. The higher loading CaO, the pores full filled by the basic active site. In the reaction between oil and methanol, the catalyst provides sufficient adsorption sites for methanol, so that O–H bond of methanol broke out

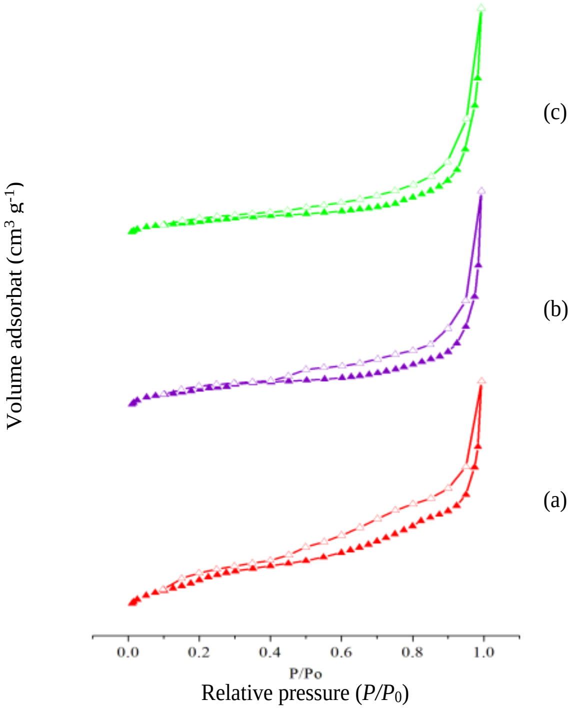

Figure 5. N_2 adsorption-desorption isotherms: (a) 10 % CaO/H-ZSM-5(100 %), (b) 30 % CaO/H-ZSM-5(100 %), (c) 50 % CaO/H-ZSM-5(100 %)

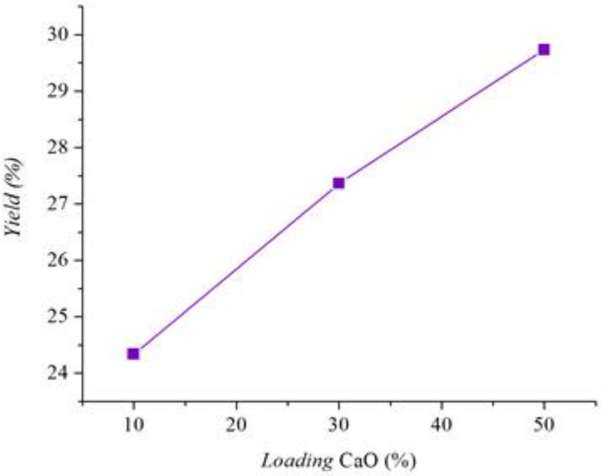

Figure 6. Correlation between CaO loading (CaO/H-ZSM-5 100 %) with yield

Table 1. Surface area, pore volume and pore diameter of sample CaO/H-ZSM-5

Sample	S_{BET} ^{a} (m^2/g)	S_{meso} ^{d} (m^2/g)	S_{micro} ^{b} (m^2/g)	V_{meso} ^{b} (cm^3g^{-1})	V_{micro} ^{b} (cm^3g^{-1})	$V_{total\ pore}$ ^{c} (cm^3g^{-1})	D_{meso} (nm)^d	D_{micro} (nm)^e
10 % CaO (100 %)	159.737	56.950	102.787	0.166	0.058	0.224	3.82	0.35
30 % CaO (100 %)	105.487	34.268	71.219	0.152	0.043	0.195	3.82	0.45
50 % CaO (100 %)	57.016	24.814	32.202	0.147	0.022	0.169	3.82	0.45

$^a S_{BET}$ (Total Surface Area) by BET method.
$^b S_{micro}$ (micropore surface areas), Vmeso (mesopore volume), V_{micro} (micropore volume) by *t*-plot method
^{c}Adsorbate volume at P/P_0 0.99
$^d S_{meso}$ (mesopore surface areas), D_{meso} (mesopore diameter or distribution) by BJH method
$^e D_{micro}$ (micropore diameter or distribution) by SF method

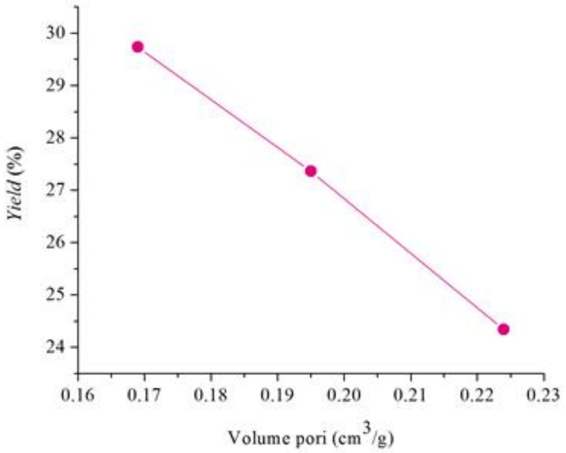

Figure 7. Correlation between loading CaO (CaO/H-ZSM-5 100 %) with biodiesel yield

forming CH_3O^- and H^+ ions. Then the CH_3O^- ions reacts with triglyceride molecule to form biodiesel. Thus, the more active site of the base catalyst, the more ions CH_3O^- formed, as therefore, the conversion of triglyceride is also increased. The catalyst resulted the highest biodiesel yield in this reaction is 50 % CaO/H-ZSM-5 (100%). The correlation between loading CaO, pore volume, and biodiesel yield are shown in Figure 7.

4. Conclusions

Preparation and characterization of CaO/H-ZSM-5 has been studied using XRD, FTIR, and N_2 adsorption-desorption techniques. On the basis of the results, as the addition of CaO increases, the intensity of CaO diffraction line was increased, while specific surface area and pore diameter were decreased. FTIR spectroscopy showed the characteristics peaks of CaO and mesoporous ZSM-5. Characterization by N_2 adsorption-desorption showed that the impregnation of CaO on mesoporous ZSM-5 did not only caused pore blocking and filling, but also decreasing of the surface area of mesoporous catalyst. For the catalytic activity of CaO/H-ZSM-5 in the transesterification reaction of used cooking oil, biodiesel was produced in higher yields with increased of CaO loading for catalyst CaO/H-ZSM-5 (100 %).

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