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ORIGINAL ARTICLE

MCM-41 SYNTHESIZED FROM COAL FLY ASH AS A CATALYST IN THE PRODUCTION OF BIODIESEL USING PALM OIL.

M.R. DESHPANDE , N. V. KALYANKAR AND U.D. JOSHI

Netaji Subhash Chandra Bose College,
Yeshwant Mahavidyalaya, Nanded .
Netaji Subhash Chandra Bose College,

Abstract:

Coal fly ash was used to synthesize MCM-41 by alkali fusion followed by hydro-thermal treatment and was characterized using various techniques viz. XRD, SEM, FTIR, BET method for surface area measurement etc. The synthesis conditions were optimized to obtain highly crystalline MCM-41 with utmost BET surface area 1102m2/g with high purity. The crystalline nature of the prepared MCM-41 was found to change with fusion temperature and a maximum value was obtained at 5500 C. The cost of synthesized MCM-41 was projected to be very few as compared to that of commercial MCM-41.This work presents the results of transesterification reaction using palm oil as feedstock with methanol and coal fly ash (CFA) catalyst derived to produce methyl esters (biodiesel).The fly ash based catalyst was prepared using the wet impregnation procedure with different loadings of potassium. This was characterized by powder X-ray diffraction (XRD), SEM etc.

KEYWORDS:

Fly ash, palm oil, Transesterification, Methyl ester, MCM-41,XRD,SEM.

INTRODUCTION

The quantity of coal fly ash (CFA) generated by coal-based thermal power plants has been escalating at a shocking rate throughout the world. In India, more than 100 million tons of CFA is being generated annually with more than 75,000 acres of land being occupied by ash ponds. The disposal of such a huge amount of ash has become a pressing issue. Several approaches have been made for the proper utilization of CFA, one of them is the conversion of CFA into mesoporous MCM-41, which have wide applications in ion exchange, as molecular sieves, catalysts, and adsorbents. In recent times, a significant concentration is given on the mesoporous catalytic materials for ensuring fast synthesis of multipurpose organic compounds owing to their high surface area, large pore size and volume. Mesoporous materials have become an alternative source to make chemical process green and environmentally benevolent. Mesoporous molecular sieves designated as M41S have attracted much attention of many researchers, since their discovery at Mobile Oil Corporation in 1992. Mesoporous MCM-41 material can be synthesized using various silica precursors.

The present study is concerned with the synthesis of MCM-41 from CFA and its characterization using various techniques. CFA is mainly composed of some oxides resulting from inorganic compounds, which remain even after the combustion of the coal.SiO_2 and Al_2O_3, are the significant contents of CFA and show few variations with the type of coal.MCM-41 synthesis processes engross the addition of Sodium

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Hydroxide (NaOH) to the CFA slurry at higher temperatures. Blend of the NaOH–CFA mixture facilitates the formation of highly active Sodium-aluminate and silicates, which are eagerly soluble in water and enhance formation of MCM-41.The synthesis of MCM-41 was also studied with CFA of varying chemical composition. Investigated effects of the hydrothermal reaction parameters such as temperatures, Molarity of NaOH and reaction time on the properties of the treated CFA and also optimized the reaction parameters to obtain best quality product. Higher pH of the solution also showed better synthesis efficiency of MCM-41.It was thought desirable to collect CFA from thermal power plant at Parali TPS Maharashtra, India and renovate it into value added mesoporous material MCM-41 which could be used as catalysts for some industrially important reactions. The utilization of fly ash as a suitable feedstock for use as heterogeneous catalyst for the transesterification would allow beneficiation of fly ash in an environmentally friendly way which would make the process more economically viable. Biofuels are derived from renewable sources such as naturally occurring fats and oils, which may be obtained from variety of plants and animals. Since, diesel-fuel figures as an essential function in the industrial economy, biodiesel-synthesis has constituted the essence of current research in the field of biofuels. Biodiesel, a green fuel, is comprised of mono-alkyl esters of long chain fatty acids which are derived from fatty acid glycerides, and are major components of an oil or fat. Transesterification is the key and foremost important process to convert vegetable oil or animal fat into a diesel-like fuel .This is illustrated in Figure 1.

Fig. 1 Transesterification of triglyceride with alkyl alcohol

In transesterification, triglycerides in vegetable oil react with alcohol to form a mixture of glycerol and fatty acid alkyl esters. Among, alkali and acid-catalyzed transesterification; reaction is much slower with acid catalysts. Moreover, the corrosive acid-catalyzed transesterification needs extreme temperature and pressure conditions.Though, the catalytic activity of a base is higher than that of an acid, use of homogeneous base catalyst is non-practical because of the various issues such as catalyst removal after the reaction, substantial low ester yield and difficulty in product separation. These problems have provided a momentum for the search of steady, more environmental gracious, cost-effective and ecofriendly solid base catalysts MCM-41 for manufacturing of biodiesel. Development of environmentally safe applications for the utilization of coal fly ash is very important. Consequently, attempt was made to develop an efficient, inexpensive and environmental friendly fly ash-based heterogeneous catalyst for the esterification and/or transesterification reactions. In view of above, solid fly ash-based base catalysts were prepared and their catalytic performance in transesterification of palm oil was studied. In this study, fly ash loaded with NaOH was assessed for the transesterification of palm oil with methanol to methyl esters.

2.EXPERIMENTAL:

A) Materials:

The CFA sample was collected from Parali TPS, Sodium hydroxide and cetyl–tri-methyl-ammonium-bromide was procured from Sigma Aldrich Laboratories (India).Table:1 presents the physico-chemical properties of the CFA samples used in the present investigation resembles that SiO2, Al2O3 and Fe2O3 are the major constituents.

Table-1 : Chemical Composition Of As Collected CFA

Sr.No.	Compound	CFA Parali TPS (wt%)
1	SiO_2	65.12
2	Al_2O_3	19.87
3.	Fe_2O_3	6.01
4.	CaO	3.08
5.	K_2O	1.12
6.	TiO_2	1.71
7.	Na_2O	0.39
8.	MgO	0.81
9.	Surface area	1.48(m^2/g)

B) Synthesis of MCM-41

Initially, CFA was screened through a BSS Tyler sieve of 80-mesh size to eradicate the larger particles. The unburnt carbon along with other volatile materials present in CFA were removed by calcination at 800°C for 3Hr.CFA was then treated with hydrochloric acid for dealumination to remove iron to a certain extent, thereby increasing the activity, thermal stability and acidity of the synthesized material all aiming for better catalytic applications.An amorphous SiO_2 component in the CFA was used as Si-source for the synthesis of MCM-41.The synthesis was carried out as follows:

30gm CFA fused with 2M NaOH solution at 1000C for 4 hrs under stirring condition (300 rpm) in stirred autoclave. The mixture was filtered after cooling. Further 90ml of obtained supernatant solution was mixed with 1.1 gm of cetyl trimethylammoniumbromide (CTAB) and kept under stirring (300 rpm) at 850C. After 30min,3ml Ethyl acetate as a mild acid hydrolyser was vigorously mixed and the solution kept under stirring at 600 rpm for next 30min.The obtained solution was then allowed to cool to room temperature by natural convection and was adjusted to the selected pH by adding 5.25N H_2SO_4 solution under slow stirring. Precipitate obtained during pH adjustment was kept at room temperature for 18 hrs. The solid obtained after filtration was frequently washed by deionized water and dried at 100^0C for 2 hrs. This dried material was calcined under air from 500^0C to 800^0C at the interval of 50^0C at a heating rate of 1^0C/min.

3) CHARACTERIZATION:

pH values were measured with a digital pH meter. X-ray diffraction patterns of the collected CFA and synthesized materials were recorded on a Cu/30 kV/15 mA MiniFlex2 goniometer with a wave length of 1.540 A0. Infrared (FT-IR) spectra of collected CFA and synthesized materials were recorded on a FT-IR spectrometer (ATR eco ZnSe) using dry KBr as standard reference in the range of 500-4000 cm-1. Specific BET surface area was calculated using Surface area Analyzer Model SAA-2000 for all synthesized samples.

A)X-ray diffraction:

X-ray diffraction patterns of the collected CFA and synthesized materials were recorded on a Cu/30 kV/15 mA MiniFlex2 goniometer with a wave length of 1.540 A0.The samples were scanned from 2–10° (2, where is the angle of diffraction).

B) Morphological analysis by scanning electron microscope (SEM):

The morphological structure of the raw CFA, treated CFA and synthesized MCM-41 mesoporous materials were obtained by using scanning electron micrograph. The bulk elemental composition was also estimated from SEM by indirect method, and from these data the percentages of oxides were calculated.

D) Fourier transform infrared (FT- IR) spectra:

Infrared spectroscopic analysis of different materials was carried out to study their structural features and acidity. Infrared spectroscopic analysis of the prepared MCM-41 samples was performed with by a FT-IR spectrometer (ATR eco ZnSe) using dry KBr as standard reference in the range of 500-4000 cm$^{-1.}$

4. RESULTS AND DISCUSSION:

A) Mineralogical properties

The CFA mainly contains SiO_2, Al_2O_3, traces of Fe_2O_3 and the oxides of Mg, Ca,P,Ti etc. The percentage of chemical composition of CFA sample used in the current study is given in table 1.The X-ray diffraction patterns of treated CFA (using instrument Cu/30 kV/15 mA MiniFlex2 goniometer with a wave length of 1.540 A0) is shown in figure 2.

The XRD pattern of original fly ash mainly represents the presence of crystalline quartz and mullite and also amorphous material. CFA after treatment gives several sharp diffraction peaks, which are different from those present in the untreated CFA. The diffractograms shows that the original crystalline phases of CFA, quartz and mullite, are mostly absent in the treated materials.

B) Study Of Synthesized Material :

The X-ray pattern of the synthesized mesoporous silica material is an highly periodic silica phases which is normally reflected by the distinct XRD signatures at low 2 angles from 20 to 100 as shown in Fig.3 Sharp signal in XRD spectra indicates the presence of long range order of uniform hexagonal phase in the mesoporous materials. The well defined reflections from [100] plane are a prime characteristics of the hexagonal lattice symmetry of the MCM-41 structure.

Fig2. X-RD Pattern of treated CFA:

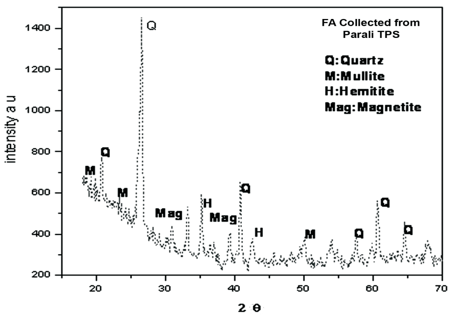
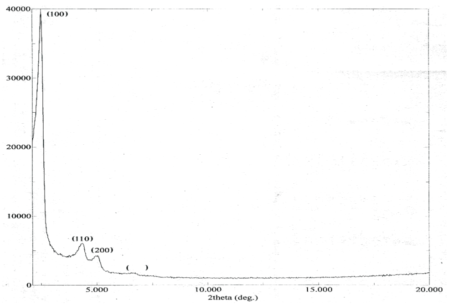


Fig3.XRD pattern of synthesized material



d_{100} value =35.3099, 2   =2.500, Intensity :14163 cps

$$I/I_o = 100. \text{ Unit cell parameter } a_0 \quad \frac{2}{\sqrt{3}} d_{100} \; a_0 \quad 40.8$$

The observation of three higher angle reflections other than d100 indicates that the product is likely to possess the symmetrical hexagonal pore structure typical of MCM-41. X-ray diffraction data therefore indicates that the supernatant of the CFA can be successfully used in the synthesis gel to prepare mesoporous materials.

C) STRUCTURAL FEATURES FROM INFRARED SPECTROSCOPY:

Infrared (IR) spectroscopy can capitulate information concerning structural details of the material. The IR spectra of treated fly ash is shown in figure 4. The two most intense bands for micro-mesoporous materials usually occur at 860–1230 cm–1 and 420–500 cm–1, are shown.The first is assigned to an asymmetric stretching mode and the second one to a bending mode of the T–O bond. All these bands are more or less dependent on the crystal structure. The mid infrared region of the spectrum contains the fundamental framework vibration of $Si(Al)O_4$ groupings. The IR spectral data for the absorbance band in between the wave numbers 980–1320cm^{-1} in the IR spectrum of CFA and treated CFA represents the presence of substituted Al atoms in the tetrahedral forms of silica frameworks. All these observations confirm the formation of MCM-41 on alkali and hydrothermal treatments of CFA.

Fig.4 FT-IR of calcined CFA

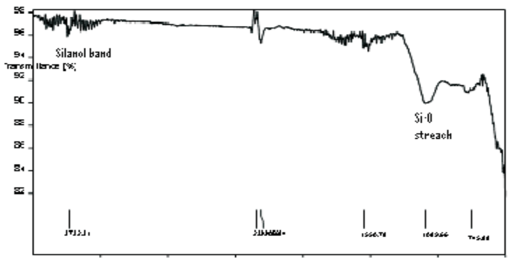
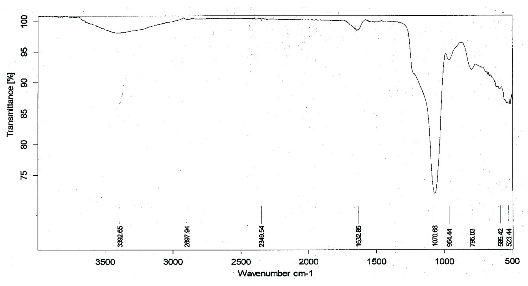


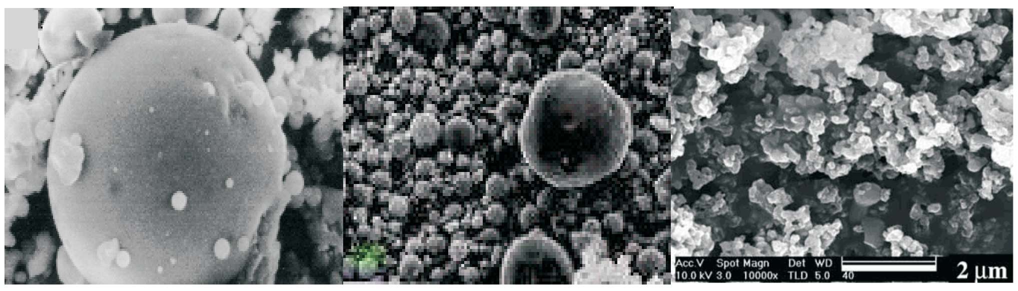
Fig.5 FT-IR of synthesized material



The FT-IR spectra of as synthesized Si-MCM-41 from coal fly ash are shown in Fig.5 From FT-IR spectra, the absorption bands around 2921 and 2851 cm^{-1} correspond to n-C-H and d-C-H vibrations of the surfactant molecules, such bands disappeared in the calcined sample indicating the total removal of organic material during calcinations. The broad band around 3392.65 cm^{-1}as observed due to surface silanols and O-H stretching frequency of adsorbed water molecule. Moreover the peaks in the range of 1500-1600cm-1 are because of the deformation mode of surface hydroxyl group. A peak at 1070.63 cm-1 and 964.44 cm-1 corresponds to the asymmetric and symmetric Si-O groups, respectively. The peaks in the range 1010-1079 cm-1 are assigned to M-O-M bonding, the bands from 960 to 990 cm-1 appeared due to Si-O-M (M=metal ions) vibrations in metal incorporated silanols.D) Scanning Electron Micrograph Study

The scanning electron micrographs (SEM) of the original CFA, treated CFA and synthesized Si-MCM-41are shown are shown in fig.6. The absence of the spherical particles in treated CFA indicates its high conversion into crystalline Si-MCM-41 on hydrothermal treatment. The crystal structure of the synthesized material was determined to be well ordered regular hexagonal.

Fig:6 The SEM micrographs of the(a) original CFA (b) treated CFA (c) synthesized Si-MCM-41



(a) (b) (c)

E) Transesterification reaction

All the reactions were carried out at atmospheric pressure, and the influence of several variables in its conversion was studied using the following ranges:

Temperature (100-180^{o}C),
Reaction time (3-20Hrs),
Various amounts of catalyst (5-15wt %)
Methanol/oil molar ratio (6 – 15)

were taken in a two neck round-bottom glass batch reactor placed in an oil bath under reflux with a stirring speed of 500 rpm. The reaction mixture was heated up to 150ºC with continuous stirring until the completion of the reaction, then centrifuged. The solid catalyst was recovered and the residual methanol was separated via rotary evaporation. The glycerol was separated and recovered after petroleum ether treatment, samples were withdrawn from the separated mixture with a glass capillary and diluted with hexane to perform TLC studies. The completion of the reaction and primary characterization of the product was analyzed by silica gel TLC technique to check the conversion of the triglyceride into methyl esters. A mixture of using hexane/ethyl acetate/acetic acid (80:20:2 v/v/v) was used as the mobile phase and silica gel as the stationary phase. Biodiesel shows a higher mobility than vegetable oil with the selected solvent system and complete conversion of vegetable oil to biodiesel was supported by the disappearance of the vegetable oil spot on the TLC plate.

F) Influence of process parameters

So as to recognize the catalytic activity of the loaded catalyst and maximizing the conversion of the palm oil to biodiesel, an optimization of the transesterification reaction were carried out, they include % catalyst loading, methanol to oil molar ratio, reaction time, temperature

a) Effect of catalyst loading

The effect of the amount of catalyst used in the conversion of the triglyceride to methyl esters was studied as the % loading of catalyst with respect to oil was varied from 5 to 15%wt /wt keeping all other reaction parameters identical. As shown in Fig.7, it was observed that the oil conversion increased with an increase in catalyst loading. The highest conversion of 81.89% was obtained at a catalyst loading of 15% wt/wt which was comparative with the conversion value of 76.81% at 10%wt/wt. From the view-point of the reaction kinetics, a larger amount of catalyst leads to a higher yield of methyl esters in a shorter reaction time.

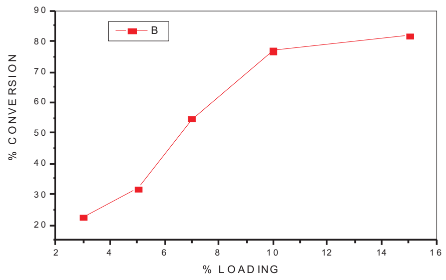


Fig.7: Influence of catalyst loading on oil conversion under the reaction conditions of 160ºC, reaction time of 5hrs and a methanol: oil ratio of 15:1

b) Effect of reaction time

In order to study the influence of the reaction time on the oil conversion using the NaOH/CFA catalyst, a set of experiments were carried out at 3, 5, 9, 15 and 20 hours. The results are shown in Fig.8. It can be observed that the oil conversion was not greatly affected by an increase in the reaction time. This implied that, the reaction equilibrium had been reached after 5hrs when the reaction temperature was 160ºC.

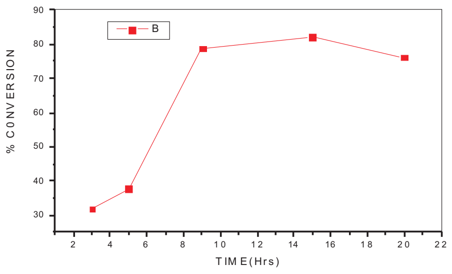


Fig.8: Influence of reaction time on oil conversion under reaction conditions of 160ºC, 15% catalyst loading and a methanol: oil ratio of 15:1

c) Effect of reaction temperature

Transesterification can occur at different temperatures depending on the oil used and temperature is a crucial parameter as it influences the reaction rate and yield of the methyl esters and in order to determine the effect of reaction temperature on the oil conversion, experiments were conducted at 100, 120, 140, 160 and 180°C. The results are shown in Fig.9, it was observed that as reaction temperature increased, there was a corresponding increase in the conversion of the triglycerides to methyl esters, showing peaks at temperatures ≥ 160°C. The highest conversion was 89.34% at a reaction temperature of 200°C which compares to the conversion value of 87.12% at the reaction temperature of 160°C.

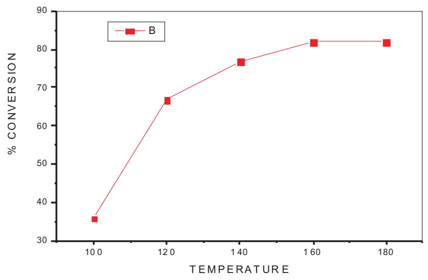


Fig. 9: Influence of reaction temperature onoil conversion under reaction time of 5hrs, a catalyst loading of 15%wt/wt and a methanol:oil ratio of 15:1.

d) Effect of molar ratio of methanol:oil

One of the most important factors that affect the yield of ester is the molar ratio of alcohol to triglyceride. It is of important for screening catalyst performance. Specifically, it has also been proven that that the use of excess alcohol is a good option in improving the rate of the transesterification reaction where heterogeneous catalysts are considered. The effect of the molar ratio was of methanol to oil on the conversion of the methyl ester was examined by varying the amount of methanol with a fixed amount of sunflower oil (20g) in the reactions at 160°C. amounts of methanol were set and amounts corresponding to the methanol: oil molar ratios of 6:1, 9:1, 12:1, 15:1 were used. The result is illustrated in Figure 10. Fig. 9. Influence of reaction temperature on oil conversion under reaction time of 5hrs, a catalyst loading of 15%wt/wt and a methanol: oil ratio of 15:1.Fig.10. Influence of methanol: oil ratio on oil conversion under reaction temperature of 160°C reaction time of 5hrs and a catalyst loading of 15%wt/wt. From the Figure, it can be seen that the highest methyl ester conversion of 86.1% was observed at a methanol: oil molar ratio of 15:1. It can be also be observed from the activity profile that as the molar ratio increased from 6:1 to 15:1, the conversion was found to increase from 56.23 to 86.1%. Further addition of methanol into the reaction phase did not show any significant increase in the conversion. Moreover, a limitation to the use of a greater amount of methanol needed to propel the forward reaction is that an occurrence of flooding of the active sites by the methanol molecules rather than triglyceride molecules which might hinder the completion of the triglyceride conversion to methyl esters as conversion at methanol oil ratios higher than 15 appeared to decline.Also, feeding too much alcohol adversely affects the transesterification process by rendering the product separation difficult as glycerol; co-product specie of methyl ester is highly soluble in methanol, which reverses the transesterification progress according to Le Chatelier's principle. Another important variable affecting the yield of methyl ester is the type of alcohol to triglyceride. In general, short chain alcohols such as methanol, ethanol, propanol, and butanol can be used in the transesterification reaction to obtain high methyl ester yields. This was not considered in this study.

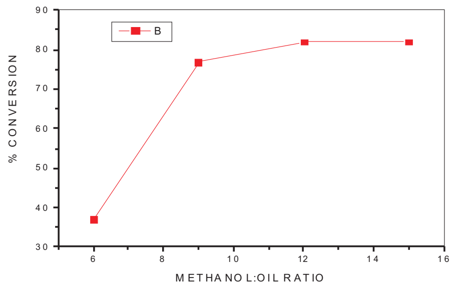


Fig.10: Influence of methanol: oil ratio on oil conversion under reaction temperature of 160°C reaction time of 5hrs and a catalyst loading of 15%wt/wt.

Table 3: Maximum Allowed Quantities in Biodiesel.

Property	Biodiesel	Biodiesel(in this work)
Viscosity at 35^{o}C, mPa.	3.25-3.99	3.79
Viscosity at 35^{o}C, mm^2/s	1.7-5.28	4.12
Specific gravity, g/ml	0.73	0.74
Flash point, , CC, ^{o}C	100-150	130

CONCLUSION

A study of heterogeneous acid catalysts for biodiesel production based on methanol transesterification is presented in this article. The use of fly ash loaded with NaOH has been found suitable for the conversion of palm oil to methyl esters and glycerol. The fly ash based catalyst loaded with 5% wt NaOH at a reaction temperature of 140ºC exhibits maximum oil conversion (83.89%). The oil conversion increases with increased catalyst loading. The highest conversion of oil was obtained at a catalyst loading of 15 %wt/wt. Influence of process parameters such as reaction time, reaction temperature and molar ratio of methanol to oil were also carried out. The oil conversion was not greatly affected by an increase in the reaction time. However, reaction time between 5 to 8 hours will lead to better oil conversion. The highest conversion was observed at a temperature of 150oC. The activity profile shows that increase in the methanol to oil ratio from 6:1 to 15:1 resulted in increased conversion from 41.11% to 83.89%. A decline in the oil conversion was observed when the recovered catalyst was recycled for use. Heterogeneous catalysts are the key to new developments in the production of biodiesel.

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