

Application of Core-Shell Modeled Composite Catalysts for Biofuel Production from Nonedible Vegetable Oils†

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In the present study we report the synthesis, characterization and catalytic activities of microporous HZSM-5, mesoporous AIMCM-41 and composite AIMCM-41/ZSM-5 catalysts. All the catalysts were synthesized by hydrothermal method. The formation of composite catalyst was confirmed by XRD, N₂ sorption studies and SEM techniques. The catalytic activities were studied towards the cracking of jatropha and castor oils and the results are discussed.

Key Words: Composite catalyst, Jatropha, Castor, Cracking, Biofuel, Gasoline.

INTRODUCTION

The indiscriminate extraction, lavish consumption of fossil fuels and rapid growth in motor vehicle activity have led to reduction in underground-based carbon resources and contributed to high levels of urban air pollution. An alternative fuel with low toxic content and in correlation with sustainable development, energy conservation, efficiency and environmental preservation is the most sought after and hence new research has been focused in this area¹. Vegetable oils are the right alternative sources as the fuel produced from them are sustainable, economic and do not emit toxic pollutants. In addition the fuel has shorter CO₂ cycle.

Several methods have been reported for the production of biofuel such as transesterification, pyrolysis and catalytic cracking. The biodiesel derived through transesterification method cannot be used in the present day's engine as such. Biodiesel has to be blended either with gasoline or with diesel and hence is not cost effective. Although biodiesel is a biodegradable and environmental friendly fuel, it is not economical and not engine friendly². Fuel obtained through pyrolysis is not attractive as the operational temperature of pyrolysis is very high (> 1000 °C) and it yields only straight chain hydrocarbons. However catalytic cracking of vegetable oils yields the fuel of superior characteristics. Earlier reports on catalytic cracking of vegetable oils show that fuel obtained through this process can be used as such without engine modifications³.

Microporous materials have been widely used as cracking catalysts due to their excellent properties such as acidity and shape selectivity⁴. Though it produced fuel with high octane rating, the yield of gaseous products was found to be high. In addition, the micropores of these catalysts limit the access of bulky triglyceride molecules to the acid sites located inside the pores of zeolite catalysts. Thus triglycerides can react only at the external acid sites of catalyst leading to less conversion. This has led to the search of catalyst with large pores. Mobil coworkers discovered hexagonal unidimensional mesoporous MCM-41 catalyst (M41S family) with a pore size of 2-50 nm⁵. These materials have been employed in many acid catalyzed reactions such as alkylation, cracking *etc.* Its large pore makes it a potential catalyst for cracking reaction involving large triglyceride molecules. But they suffer from hydrothermal stability and low acidity. In order to enhance their acidity aluminium ions are introduced into silicon framework which resulted in finding of new AIMCM-41 materials. However the combination of large pore and less acidic AIMCM-41 and small pore and highly acidic ZSM-5 will have synergistic effect.

In the present study we report the synthesis of microporous (HZSM-5, Si/Al = 15), mesoporous (AIMCM-41, Si/Al = 25) and composite catalyst (AIMCM-41/ZSM-5) with various coating ratios using hydrothermal method, characterization using XRD, BET N₂ sorption studies, TPD and SEM techniques and catalytic activities of all the catalysts towards the cracking of jatropha and castor oils using fixed bed reactor. The conversion of vegetable oils, % composition of different products

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such as BLF, gas, water and coke, the selectivities towards green gasoline, green kerosene and green diesel (GD) obtained in the cracking of non edible oils are compared and discussed.

EXPERIMENTAL

Vegetable oils: The jatropha oil was kindly supplied by DIBER (Defence Institute of Bio-Energy Research, Nainital, India). Castor oil was obtained from local market. The oils was filtered to remove the solid particles if any present in it.

CDH, India supplied the precursors such as sodium *meta* silicate, sodium aluminate and aluminium sulphate required for the synthesis of various solid acid catalysts such as HZSM-5, AIMCM-41 and AIMCM-41/ZSM-5 (25, 15, 10). Sulphuric acid was purchased from Merck. Tetra propyl ammonium bromide (TPABr) and cetyl trimethyl ammonium bromide (CTAB) were procured from SRL, India.

Synthesis of HZSM-5: Sodium silicate and aluminium sulphate were used as sources of silicon and aluminium respectively. TPABr surfactant was used as structure directing agent. ZSM-5 with Si/Al = 15 was synthesized using the reported methods⁶.

Synthesis of AIMCM-41: Cetyl trimethyl ammonium bromide (CTAB) was used as structure directing agent and sodium meta silicate and aluminium sulphate were used as the sources for silicon and aluminium respectively. Sodium silicate (42 g) was dissolved in 160 mL of water. Aluminium sulphate solution (1.13 g in 10 mL of water) was added and stirred for 1 h. The pH of the mixture was adjusted to 11.6 using 4 N H₂SO₄ and was stirred for 1.5 h. The CTAB (14.58 g) dissolved in 48 mL of water was added drop wise to the obtained gel and stirred for 2 h. The gel was autoclaved at 160 °C for 17 h in an air oven. The product obtained was washed, filtered, dried and calcined at 550 °C for 1 h in the flow of N₂ and 5 h in the flow of air.

Synthesis of composite materials: Composite catalysts were synthesized by taking 10 g of ZSM-5 (Si/Al = 15) and overgrowing AIMCM-41 so as to get 10 % of AIMCM-41 over HZSM-5. The different catalysts obtained are coded as AIMCM-41/ZSM-5 (A, B, C) where A refers to Si/Al ratio of AIMCM-41, B refers to Si/Al ratio of HZSM-5 and C refers to the % coating of AIMCM-41 over HZSM-5.

Catalyst characterization: X-ray diffraction was done using seifert X-ray diffractometer JSO 2002 using Nickel filtered CuK_α radiation ($\lambda = 1.514 \text{ \AA}$) at 2θ values of 1°-5° and 1°-70° for AIMCM-41 and AIMCM-41/ZSM-5. The BET surface area of the catalysts was measured by using BET surface area analyser (Micromeritics Pulse Chemisorb 2700) at liquid N₂ temperature by using 30:70 ratio (N₂: He). Temperature programmed desorption study was carried out for acidity determination (ChemiSoft TPx 2750 V1. 02 Unit 1, Micromeritics, USA). The morphology of catalysts was studied by scanning electron microscope (FEI Quanta 200 ESEM FEG, USA).

Catalytic activity: The catalytic activities of the synthesized catalysts were evaluated using a fixed bed flow reactor (2 cm width, 40 cm height) made up of quartz. The catalytic cracking reactions were carried out over 0.5 g of catalyst at the temperature of 400 °C, WHSV of 4.6 h⁻¹ for 2 h. At the end

of every 1 h, N₂ gas was flushed for 10 min to remove any remaining products in the catalytic reactor. The products obtained in the cracking reaction were cooled by a Leibig condenser and collected in a receiver. The liquid products collected for every 1 h was analysed by gas chromatograph (Shimadzu GC 17A) equipped with a flame ionization detector (FID) and using Apeizon L packed column (2 m length, 1/8" diameter). The gaseous products were analysed with a thermal conductivity detector (TCD) using Poropak Q column (2 m length, 1/8" diameter). The percentage conversion of oil, percentage yield of BLP and gaseous products and percentage selectivity towards green gasoline, green kerosene and green diesel were calculated.

RESULTS AND DISCUSSION

Characterization of AIMCM-41: The XRD pattern of mesoporous catalyst AIMCM-41 (25) is shown in Fig. 1. The corresponding HKL values of 100, 110, 200 and 210 planes confirm the formation⁷ of MCM-41. The interplanar distance and unit cell size were calculated using the following equations. ($d = n\lambda / 2 \sin\theta$ and $a_0 = 2d_{100}/\sqrt{3}$).

The XRD pattern of composite catalyst matched with the reports earlier (Fig. 2). The presence of both mesoporous and microporous nature of composite catalysts are identified from the peaks⁸ at 2.2° and 22°-25°. The interplanar distance and unit cell size of both mesoporous and composite catalyst were calculated and they are given in Table-1.

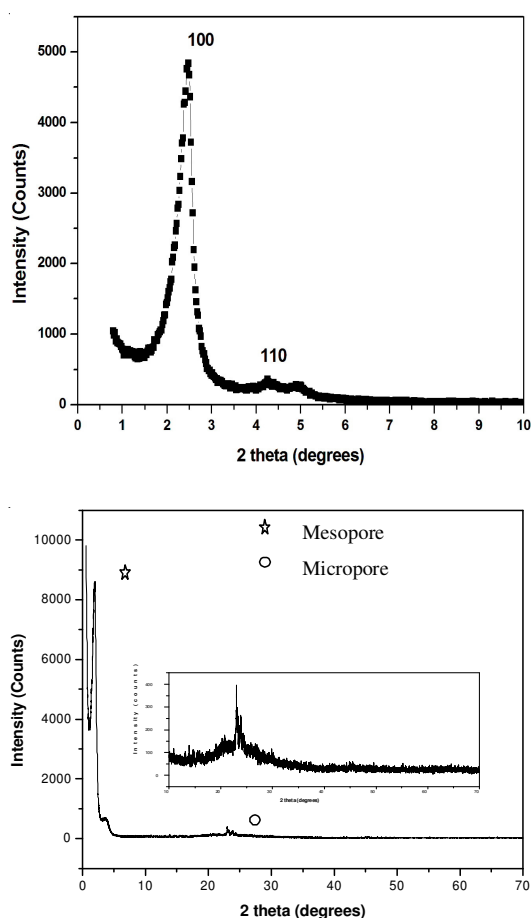


Fig. 1. and 2. XRD pattern of AIMCM-41 (25) and AIMCM-41/ZSM-5 (25, 15, 10)

It was observed from the above table that as the particle diameter increased a_0 also increased. The number and the strength of acidic sites of the synthesized catalysts are determined by TPD studies and is given in Table-1. Among the catalysts the microporous HZSM-5 was found to be highly acidic in nature (4.67 mL/g of NH_3). Both mesoporous (AlMCM-41) and composite (AlMCM-41/ZSM-5) catalysts possessed slightly weaker acidic sites (3.80 mL/g of NH_3). The BET surface area of the synthesized catalyst is given in Table-1. Among the catalysts synthesized, AlMCM-41 was found to have the highest surface area followed by composite and microporous materials. The decrease in the surface area of composite catalysts may be attributed to the very low % coating of high surface area material (AlMCM-41) over low surface area material (HZSM-5).

Catalysts	d_{100} (nm)	Unit cell a_0 (nm)	Total acidity (mL/g)	Surface area (m^2/g)
HZSM-5	3.58	-	4.67	483
AlMCM-41	3.85	4.13	3.80	951
AlMCM-41/ZSM-5 (25, 15, 10)	4.47	5.16	3.80	510

The adsorption isotherms of AlMCM-41 (25) and AlMCM-41/ZSM-5 (25, 25, 10) are shown in Fig. 3a and b respectively. Fig. 3a and b depict a typical type IV isotherm corresponding to mesoporous materials. A steep increase at P/P_0 0.3-0.4 is due to the N_2 uptake and capillary condensation and it confirms the presence of mesoporosity of the material⁹. Hysteresis in the isotherm curve shows pores are tubular in shape and open at both ends.

The adsorption desorption isotherm of and AlMCM-41/ZSM-5 (25, 15, 10) shows two steps of increase in uptake of N_2 . The first rise at 0 - 0.1 corresponds to microporous HZSM-5 and the second increase at 0.2-0.4 is due to the presence of mesoporous AlMCM-41 present in composite material.

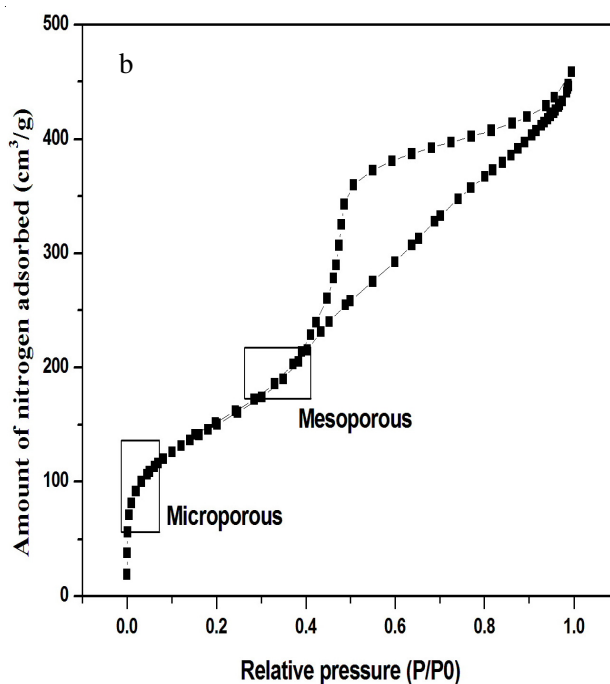
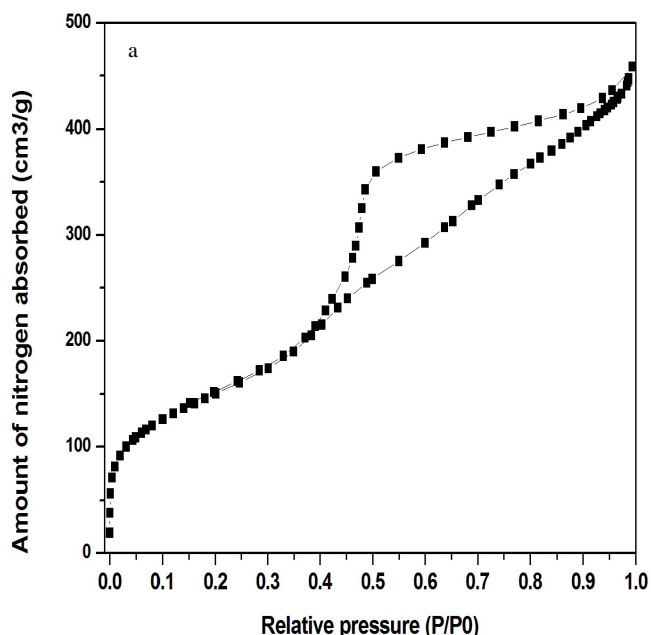


Fig. 3. a and b. N_2 adsorption desorption isotherms of AlMCM-41 (25) and AlMCM-41/ZSM-5 (25, 15, 10)

The SEM picture of composite catalyst is shown in Fig. 4. Figure clearly shows the fibrous layers of MCM-41 forming sponge like structures. A random distribution of silica fibres around ZSM-5 core was seen surrounding the pore.

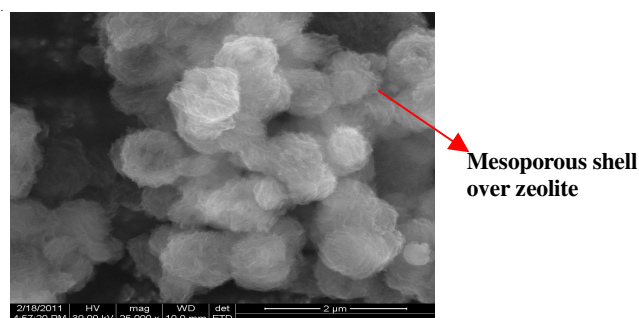


Fig. SEM photograph of AlMCM-41/ZSM-5 (25, 15, 10)

Catalytic activity: The catalytic activity, product distribution and selectivity towards various fractions such as green gasoline, green kerosene and green diesel in cracking of jatropha and castor oils over HZSM-5 (15), AlMCM-41 (25) and AlMCM-41/ZSM-5 (25, 15, 10) are given in Table-2. The cracking reaction was carried out for 3 h at the optimized reaction conditions (Reaction temperature - 400°C and WHSV- 4.6 h^{-1}) reported by us earlier. The samples collected at the first hour were subjected to chromatographic analysis. In the cracking of jatropha oil, the mesoporous catalyst AlMCM-41 ($\text{Si}/\text{Al} = 25$) was found to convert 65 % with 39 % selectivity towards green gasoline. Composite catalyst synthesized by coating 10 % of mesoporous catalyst AlMCM-41 ($\text{Si}/\text{Al} = 25$) over ZSM-5 [AlMCM-41/ZSM-5 (25, 15, 10)] was found to be the best active catalyst for the cracking of all the oils.

Composite catalyst showed remarkable performance in cracking of jatropha (conversion -99 %) and castor oil (92 %).

TABLE-2
CATALYTIC ACTIVITY TOWARDS CRACKING OF VEGETABLE OILS

Oils	Catalysts	Conv. (%)	Yield of BLF (%)	Yield of gas (%)	Yield of coke (%)	Yield of water (%)	Selectivity towards (%)		
							GG	GK	GD
Jatropha	HZSM-5	62	29	23	1	9	50.0	30.0	20.0
	AlMCM-41 (25)	65	39	18	5	3	37.0	47.0	16.0
	AlMCM-41/ZSM-5 (25, 15, 10)	99	70	19	7	3	61.2	20.8	18.2
Castor	HZSM-5	82	38	34	1	8	31.6	58.6	9.8
	AlMCM-41 (25)	88	68	15	3	2	22.4	40.5	36.4
	AlMCM-41/ZSM-5 (25, 15, 10)	92	66	19	4	2	47.5	22.9	29.6

(Reaction conditions: Temperature-400 °C, WHSV-4.6 h⁻¹ and Reaction time-1h)

HZSM-5 converted jatropha and castor oil into 62 % and 82 % respectively whereas AlMCM-41 converted jatropha and castor into 65 % and 88 % respectively. Composite catalysts not only showed very high conversion of oils but also a very high % yields of the desired product i.e. bioliquid fuel (BLF). AlMCM-41/ZSM-5 (25, 15, 10) yielded 70 % and 66 % of useful BLF. In all the cases composite catalyst has shown significant selectivity towards green gasoline. 61 % and 47 % selectivities towards green gasoline fraction were obtained in the cracking of jatropha and castor oils respectively. The difference in catalytic activities of the same composite catalyst in the cracking of jatropha and castor may be due to difference in the physico-chemical properties of the oil such as alkyl chain length and degree of unsaturation of vegetable oils.

Conclusion

Microporous, mesoporous and composite materials were synthesized by hydrothermal method and characterized. The presence of mesoporosity and microporosity in composite catalyst was confirmed by XRD, N₂ sorption studies and SEM analysis. Among the synthesized catalysts CMZ (25, 15, 10)

showed excellent activity towards the cracking of jatropha and castor oils (92 % and 99 % respectively) with very high selectivity towards green gasoline (61 % and 48 %).

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