Aviation Fuel Production from Lipids by a Single-Step Route using Hierarchical Mesoporous Zeolites

Deepak Verma, Rohit Kumar, Bharat S. Rana, Anil K. Sinha*

CSIR-Indian Institute of Petroleum, Dehradun-248005, INDIA

*Email: asinha@iip.res.in, Ph: 91-1352525842

Supplementary Information

Experimental Details:

In our approach to the synthesis of hierarchical mesoporous ZSM-5, octadecyldimethyl(3-trimethoxysilylpropyl)ammonium chloride (ODAC) was added to a conventional alkaline mixture for zeolite ZSM-5 synthesis taking tetrapropylammonium bromide (TPABr) as the micropore template. The molar composition of the mixture was 1 Al2O3/10 TPABr/10 Na2O/38 SiO2/1.4-4.2 ODAC /7,200 H2O. In a typical synthesis, 2.0 g sodium aluminate, 28.0 g TPABr and 8.0 g NaOH were first dissolved in 1,350 g H2O. To the resultant solution, a mixture of 85.7 g tetraethylorthosilicate, 11.7g and 37.5g of ODAC (60% methanol solution) for LSAC (low surface area crystalline) and HSASC (high surface area semi-crystalline) sample respectively was added under vigorous stirring. Si/Al ratio was 19 for all samples. The final mixture was further stirred for 2 h at room temperature to obtain a homogeneous mixture. This mixture was heated hydrothermally at 140^0C for 2 days, in an autoclave. The precipitated product was filtered and washed with distilled water. The product was dried in an oven at 100^0C and subsequently calcined in air at 550^0C.

Hydroconversion reactions are carried out in fixed bed trickle reactor with sulfided catalysts listed in table 1. The catalysts were prepared by conventional impregnation of the support using an aqueous solutions of $(NH_4)_6Mo_7O_{24}$ (Sigma Aldrich), $Pt(NH_3)_4Cl_2$(Sigma Aldrich), and $Ni(NO_3)_2$ (Sigma Aldrich). The support was mixed with the impregnation solution and after stirring for 1 h it was dried at 100 ºC and calcined in an air stream at 400 ºC for 1 h. N_2 adsorption-desorption using a Belsorp instrument of samples evacuated at 350°C for 3 h was used to determine specific BET surface area (S_{BET}) and pore volume. Pore size was calculated from the desorption branch of the adsorption-desorption isotherms by the Barrett-Joyner-Halenda

(BJH) method. Ammonia adsopriton microcalorimetry was used to determine the acidity. TEM images were recorded using a JEM-2000EX II microscope (JEOL) operated at 200 kV.

The catalysts (2.5 ml) diluted with SiC (2.5 ml) to ensure sufficient catalyst-bed length and to improve the reaction-heat transfer, were loaded into a stainless steel tubular reactor (1.3– cm I.D and 30 cm in length) and the experiments for hydroprocessing of pure jatropha oil were carried in a commercial bench-top micro-reactor (Autoclave Engineers' BTRS – Jr®) with single-zone tubular furnace, for vapor phase catalyst evaluation in continuous down-flow mode. Hydrogen pressure was controlled by a back pressure regulator, gas flow was controlled by a mass flow controller, catalyst bed temperatures were controlled by temperature controllers and registered by two thermocouples. A high pressure liquid metering pump was used to maintain desired liquid flow. The gas-liquid reaction mixture passed through the pressure gas-liquid separator to separate gaseous fraction (containing hydrogen with small quantitities of CO, CO_2, propane and other lighter hydrocarbons) from hydroprocessed effluent. Gaseous products were released to atmosphere by a gas-meter and analyzed. Liquid product was drained to the atmospheric separator in order to remove trace amounts of gases.

The catalysts were presulfided using a mixture of dimethyl disulfide and gas oil at atmospheric pressure and 350˚C for 9h. The reaction condition for all the catalytic hydrotreating experiments were varied as follows: temperature 330-450˚C, pressure 10-80 bar, LHSV 1-2 h^{-1} and H_2 to feed ratio of 1500 ml/ml. Jatropha oil (1.7% FFA, 19.5%C16:0, 7.9%C18:0, 45.4%C18:1, 27.3%C18:2, Bhushan Oil, India) and algal oil (1.6% FFA, 51%C16:0, 2%C18:0, 39%C18:1, 7%C18:2, Soley Institute, Turkey) were use as feed. The liquid products were withdrawn after stabilization of reaction conditions (12 h) in two-hour intervals (at each temperature) and analyzed by off-line gas chromatography after separation of the water phase.

We analyzed the liquid products thrice during stabilization period by GC to monitor constant activity, stabilization of process parameters were also confirmed in terms of reactor hydrogen pressure, temperature as well as hydrogen and liquid flow. Two samples were collected at each reaction condition and analyzed by GC for constant activity to ensure that there was no observable catalyst deactivation during an experiment. The reaction gases were analyzed using a Varian 3800-GC equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). Liquid feed compositions and product samples were analyzed by GC-MS and with Varian 3800-GC using CP-Sil Pona CB column for detailed hydrocarbon analysis (ASTM D5134-9), vf-5ms column for hydrocarbons, free fatty acids, triglycerides and Varian Select TM Biodiesel column for free fatty acids, triglycerides (results reported as vol%).

The concentration of sulfur in the feed and liquid products was determined by XRF analysis (OXFORD Lab X model 3000 sulfur analyzer) following ASTM D-4294 method. Total acidity number (TAN) was determined following ASTM D974 method. Product density (@15 °C) was determined according to ASTM D4052 method.

Supporting Table 1: Physiochemical properties of mesoporous and microporous catalyst supports.

| Catalyst	$^{a}S_{BET}/m^2g^{-1}$	$^{b}V/cm^3g^{-1}$	$^{c}D_p/nm$
Mesoporous Al$_2$O$_3$	262	1.03	6
Mesoporous SAPO-11	312	0.61	2.7
Microporous SAPO-11	189	0.69	<1nm
Microporous Beta	386	1.10	<1nm
Mesoporous SiO$_2$-Al$_2$O$_3$	250	0.29	8.1
Mesoporous H-ZSM-5(LSAC)	486	0.40	4.25
Mesoporous H-ZSM-5(HSASC)	753	0.68	4.4

^{a}surface area, ^{b}pore volume, ^{c}Pore size (mesopore sizes calculated from adsorption branch of isotherm using BJH method)

Supporting Fig. 1

Nitrogen sorption isotherm and BJH pore size distribution of mesoporous supported catalysts: (a) Ni-W/SiO$_2$-Al$_2$O$_3$ and (b) Ni-Mo/Al$_2$O$_3$.
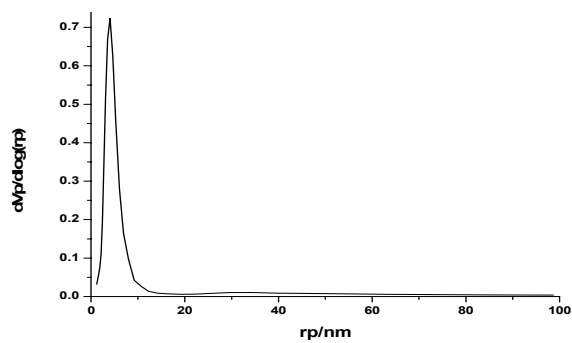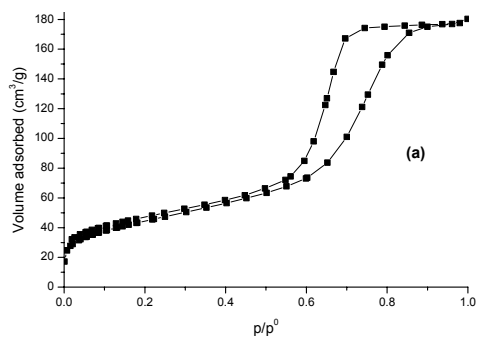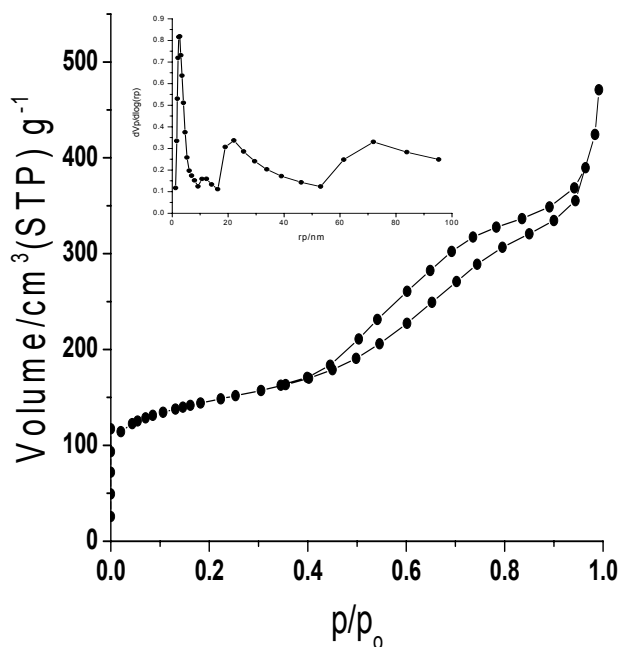

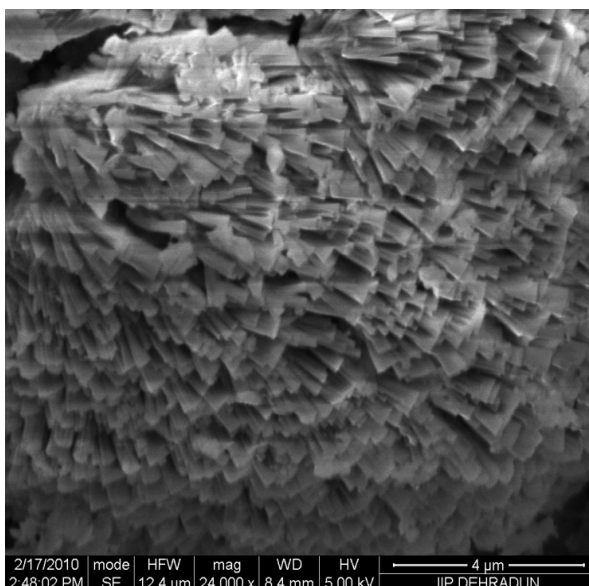(a) Ni-W on mesoporous SiO$_2$-Al$_2$O$_3$
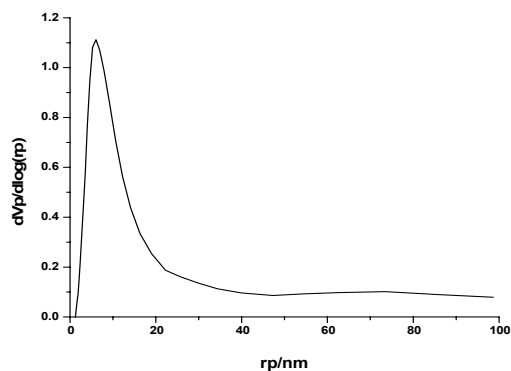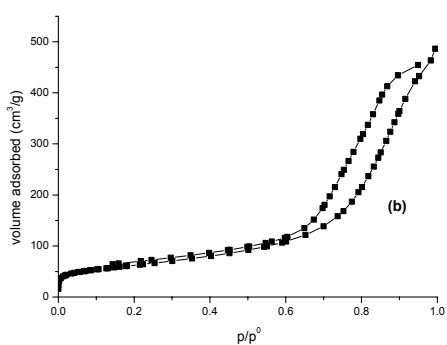
(b) Ni-Mo on Al$_2$O$_3$

Supporting Fig. 2

a: Nitrogen sorption isotherm of hierarchical mesoporous SAPO-11 (inset: BJH pore size distribution plot)

b: SEM image of hierarchical mesoporous SAPO-11

Supporting Fig. 3
27Al MAS-NMR spectra of LSAC (top) and HSASC (bottom) samples.

The spectra show peaks corresponding to both tetrahedral and octahedral coordination of Al, at about 50 and 0 ppm, respectively. The peak intensity ratios of tetrahedrally and octahedrally coordinated Al in the samples shows that HSASC sample contains much more octahedral Al (the extraframework Al) than the LSAC sample.