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Selective production of green gasoline by catalytic conversion of *Jatropha* oil

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ABSTRACT

A catalytic process for value addition of bio-oil derived from the *Jatropha curcas* plant through the production of green gasoline has been described. Four zeolite based catalysts possessing different porosity and acidity have been prepared by using Ultrastable Y (HY), Beta (BEA), micro-crystalline ZSM-5 (MZ) and nano-crystalline ZSM-5(NZ) zeolites. The textural properties of the samples have been characterized by XRD, SEM, BET surface area, pore volume, pore size distribution and micro-calorimetric ammonia adsorption studies. These catalysts have been exploited for the production of green fuel suitable for gasoline applications. Among the various catalysts, the nano-crystalline ZSM-5 synthesized in the laboratory exhibited excellent catalytic properties such as moderate acidity and stacking order of mesoporosity (which is absent in microcrystalline ZSM-5) responsible for the production of gasoline with as high as 77.4% selectivity and 95 research octane number (RON). The catalyst also exhibited enhanced time-on-stream stability supported by coke resistance ability (derived from TGA analysis of spent catalyst) when compared with the other zeolites within the studied period of 20 h. The present study provides a new catalytic process for production of gasoline from *J. curcas* oil for biorefinery.

1. Introduction

Fuel production from renewable feedstocks is continuously gaining importance and zeolite catalyzed processes are emerging as practical solutions for the effective conversion of these feedstocks through the production of hydrocarbons that belong to a wide range of fuels and chemicals [1,2]. The oils extracted from non-edible sources such as *Jatropha curcas* is one of the major feed sources for the economical way of production of fuels [3]. The ease in cultivation of the plant and its growth capacity in variety of dry and wastelands on one hand and its high oil content on the other hand qualify the plant as major alternative to the fossil fuel sources [4,5].

Among the various fuel types, the production of bio-diesel is widely studied by adopting trans-esterification reaction. However, the process requires long reaction times and consumes high quantity of methanol to produce mono-alkyl esters of long chain fatty acids [6,7]. The huge amount of glycerol (about 10%) obtained as unavoidable by-product during bio-diesel production also affects the product yields and process economics [8]. The bio-diesel obtained by this method also has some limitations to use alone for its practical applications of the fuel. In spite of its lower toxic emissions, the increased emissions of nitrogen oxides limit the use of pure biodiesel (B100) and not economical [9]. Therefore biodiesel requires fossil fuel as a blending-stock so as to make it suitable for use in diesel engine [10–12]. The blending of biodiesel is also limited by several factors, such as energy density, cold flow and stability. The higher the percentage of biodiesel blended (above 20%) the lower the energy content of diesel per gallon. High-level biodiesel blends can also impact engine warranties and formation of gel at cold temperatures and suffer from microbial contamination in tanks [9].

In addition, the pyrolysis process used for the bio-oil conversion needs high energy for facilitating high temperature reactions and produces mostly gaseous products along with diesel range straight chain hydrocarbons [13]. In search of efficient ways for value addition of *J. curcas* oil, production of relatively low boiling range hydrocarbon fuels such as gasoline through cracking based catalysis is gaining importance recently. The low temperature operation, controllable cracking reaction through tailored acid properties of the catalysts, low cost of production and ready to use quality of the gasoline product make this method practical for value addition of feedstock for industrial applications [14].

Zeolites possessing wide variation in porosity and tunable acidity have potential catalytic applications for a wide variety of molecular transformations, especially in hydrocarbon production not only from petroleum but also from the various types of renewable feedstocks such as *Jatropha* oil [15]. Among these, the ZSM-5 zeolite of pentasil family has advantage of shape selectivity suitable for formation of short range aromatics (benzene, toluene and xylenes) while avoiding the bulky molecular transformation leading to coke formation within the constraint space of pores advantageous for the life of the catalyst

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[16,17]. While the medium pore of ZSM-5 is suitable for the production of aromatics, the molecular size of triglycerides in the *Jatropha* oil suggests the need of larger pores for the effective transformation of the feed [18–20]. Acidity is another important property of the catalyst that influences the catalytic activity and the nature of the product.

Liu et al. produced C_{15}–C_{20} range hydrocarbon product from hydrotreatment of *Jatropha* oil over $NiMoLa/Al_2O_3$ catalyst [21]. While, Gong et al. applied $NiMoP/Al_2O_3$ catalysts for the production of high quality diesel blending stock (C_{15}–C_{18} range hydrocarbons) through hydro-treating of *Jatropha* oil [22]. Junming et al. have successfully produced high quality diesel range product from various woody oils (including *Jatropha* oil) using a variety of catalysts such as Al_2O_3, MCM-41 and CaO. Among these, the CaO catalyst is reported to exhibit the highest yield of (76 wt.%) organic liquid product along with 10 wt.% coke when using *J. Curcus* oil as feedstock [23]. Studies of Deng et al. indicated a superior performance of nanosized solid basic catalyst for the production of bio-diesel from *Jatropha* oil [24]. While most of these studies are concerned with bio-diesel production, very little is reported for the possible production of other carbon range products such as gasoline. The studies of Sharma et al. indicated the suitability of ZSM-5 catalyst for the conversion of *Jatropha* oil to produce gasoline along with kerosene and diesel range products [25]. Further studies by the same authors on micro-meso composite catalyst envision the need of additional mesoporosity for effective conversion of the *Jatropha* oil [26].

All the above-mentioned studies indicate the scope in catalyst development for the selective production of the desired hydrocarbon component. Since olefins are the intermediate species in the formation of aromatics and gasoline, the acidity of zeolites is expected to play vital role in the quality and yield of gasoline range product as in the case of fossil fuel processing. However, one cannot expect the similar product pattern in processing of fossil fuel and bio-oil (e.g. *Jatropha* oil) due to the difference in composition and complexity of the latter feed and thus initiates the need for studying the influence of such catalytic properties on the *Jatropha* oil conversion.

The oils extracted from non-edible sources such as *J. curcas* is one of the major feed sources for the economical way of production of fuels. The ease in cultivation of the plant and its growth capacity in variety of dry and wastelands on one hand and its high oil content on the other hand qualify the plant as major alternative to the fossil fuel sources. The value upgradation of such feedstocks viz. *Jatropha* oil through cracking is recently gaining importance due to its low temperature operation, controllable cracking reaction through tailored acid properties of the catalysts, low cost of production and ready to use quality of the gasoline product.

In an attempt to address the subject of selective production of gasoline from *J. curcas* oil and the influence of acidity and porosity properties of catalysts on the catalyst performance, we have conducted systematic studies on various catalysts that belong to micro-crystalline ZSM-5 (medium pore) (MZ), Beta (BEA) and Ultrastable Y (HY) (large pore) zeolites. In addition to this, a nano-crystalline ZSM-5 (NZ) exhibiting additional mesopores was also studied to understand the role of extra-porosity.

2. Experimental

2.1. Catalyst preparation

Micro-crystalline ZSM-5 (MZ) and nano-crystalline ZSM-5 (NZ) having Si/Al atomic ratio of 30 have been synthesized to understand the effect of acidity and porosity on *J. curcas* oil conversion. Another micro-crystalline zeolite sample HY (Si/Al atomic ratio 5) and BEA (Si/Al atomic ratio 25) are also used in the present studies. The properties of NZ exhibiting stacking order of mesoporosity is compared with the sample MZ.

2.1.1. Synthesis of micro-ZSM-5 (MZ) sample

In this synthesis, sodium silicate (Merck) was used as silica source and sodium hydroxide was slowly added to this solution, followed by the addition of aluminum nitrate and tetrapropyl ammonium hydroxide (TPAOH, Merck). The components were mixed with constant stirring at room temperature (25 °C). The pH of the resulting gel was then adjusted to 10.5 by adding 1:1 H_2SO_4 solution before charging it in Teflon lined autoclave for hydrothermal synthesis at 180 °C for 3 days (72 h) [27,28].

2.1.2. Synthesis of nano-ZSM-5(NZ) sample

In this synthesis tetraethyl orthosilicate (TEOS, Merck) was used as silica source. TEOS being an organic silica source was expected to come in the aqueous phase slowly. Al source was added slowly to precooled tetrapropyl ammonium hydroxide (TPAOH, Merck) solution and after that TEOS was added drop wise. The components were mixed with constant stirring. After adding all the ingredients, the solution was left to hydrolyze at room temperature (25 °C) for 41 h. The gel obtained was thus heated at 80 °C to evaporate water and ethanol formed during the hydrolysis of TEOS and to obtain a concentrated gel. The concentrated gel was charged in a Teflon lined autoclave for hydrothermal synthesis as in the case of MZ zeolite sample. The synthesis was performed at 170 °C for duration of 48 h [29].

All the synthesized samples were filtered and washed with deionized water, followed by drying at 100 °C and calcination at 500 °C for 4 h under vacuum. The powder forms of zeolites are converted into extrudates by mixing with 40 wt.% of pseudoboehmite powder followed by drying at 100 °C and calcination at 500 °C before using them for reaction [30,31].

2.1.3. Micro-crystalline BEA and HY catalysts

BEA zeolite with Si/Al atomic ratio 25 and HY zeolite with Si/Al atomic ratio 5 were obtained from Sud-Chemie India Ltd., in powder forms. These zeolite powders, MZ and NZ powders are shaped to extrudate form by mixing an inert alumina binder, pseudoboehmite with zeolite: binder ratio of 3:2 by weight, followed by adding sufficient amount of 3 vol.% glacial acetic acid for peptization. Wet extrusion of the resultant paste was carried out through a 2 mm in diameter size metallic syringe for the formation of wet extrudates. The extrudates were allowed to dry at room temperature overnight and further dried at 100 °C for 7 h followed by calcination at 500 °C for 4 h.

2.2. Physico-chemical characterization

The morphology and crystal structures of zeolties were characterized by the SEM (Quanta 200F instrument, Netherlands) and XRD (Rigaku Dmax III B, Japan). The N_2 adsorption–desorption isotherms were measured at 77 K on ASAP (Model 2010) Micrometrics USA instrument. Before measurement the samples were evacuated overnight at 250 °C. The BET surface area was calculated from linear part of plot according to IUPAC recommendations [32]. The micro-calorimetric measurement of ammonia adsorption was carried out at 175 °C. Differential heat of ammonia adsorption was determined by introducing small quantities of ammonia onto the outgassed sample, till the neutralization of all acid sites occurred on the catalyst surface. The heat of adsorption evolved for each dose was calculated from the resulting thermo-grams and the amount of ammonia adsorbed was calculated from the pressure change. Acidity of zeolite samples (extrudates) were measured from heats of adsorption of ammonia by micro-calorimetry. The amount of ammonia adsorbed per gram of catalyst was considered as the total acidity. The acidity is arbitrarily classified into (a) strong acidity (heat of adsorption $>$ 100 kJ/mol), (b) medium acidity (heat of adsorption from 100 kJ/mol to 75 kJ/mol) and (c) weak acidity (heat of adsorption $<$ 75 kJ/mol). The coke formed on the spent catalysts is evaluated by Thermogravimetric analysis (TGA, PerkinElmer Diamond). The thermograms of the samples are recorded