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Hydroprocessing of Crude Jatropha Oil Using Hierarchical Structured TiO_2 Nanocatalysts

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Abstract

Hydroprocessing of crude jatropha oil (CJO) has been studied over different hierarchical structured titania (TiO_2) nanomaterial supports doped with Ni and Ce metals. Three different hierarchical structured TiO_2 suport material were used including commercial TiO_2 nanopowder, titania nanotubes (TNT) and titania nanosheets (TNS). The TNT and TNS support nanomaterials were synthesized using hydrothermal chemical route. However, the catalyst loading was performed using wet impregnation method. All the catalysts were characterized using Field Emission Scanning Electron Microscopy (FE-SEM), Transmission Electron Microscopic (TEM) and Accelerated Surface Area and Porosimetry (ASAP) analysis. NiCe/TNT catalysts exhibited highest conversion of triglycerides to hydrocarbon products as compared to NiCe/TiO_2 and NiCe/TNS. The main products involved in the HC reaction are straight chain hydrocarbons ranging n-C15 to n-C18. However, the reaction pathways observed are: hydrodeoxygenation (HDO) and decarboxylation/decarbonylation (DCO/DCN). DCO/DCN was found to be the major reaction route under the studied conditions.

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Keywords: Hydroprocessing; TiO_2 nanotubes; TiO_2 nanosheets; Crude Jatropha oil; Hierarchical structured nanomaterials

1. Introduction

Depleting world's energy resources and increasing greenhouse gasses are emphasizing towards the search of

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renewable energy sources. Biofuels obtained from vegetable oils are considered as sustainable and environmental friendly alternate for fossil fuels due to sulfur and nitrogen free emissions [1, 2]. Hydroconversion (HC) of triglycerides from vegetable oils have attracted immense focus of researchers as the hydrocarbon products obtained from the reaction are similar to fossil diesel fuels, therefore commonly known as 'green diesel' [3, 4].

Hydroprocessing of triglyceride yields straight chain hydrocarbons of 15-20 carbon range. The process involves reaction of triglyceride molecules with H_2 gas at high pressure usually above 30 bar and temperature in the range 250-350 ^{0}C in the presence of suitable active catalyst [5]. The reaction of triglycerides follows three main reaction routes: hydrodeoxygenation (HDO), decarboxylation (DCO) and decarbonylation reactions (DCN). HDO reaction pathway yields the hydrocarbon products with the same carbon number as in the parent glyceride molecule but DCO/DCN gives the product with 1 carbon less than the parent molecule. Therefore, various research works have been done tailoring the selectivity towards a specific route of reaction to get desired product. It has been proved that the catalyst is the key factor not only for controlling reaction but also for selectivity towards a certain route of reaction [1, 6].

For HC reactions, the most extensively used catalysts are sulfided metal catalysts and noble metal catalysts [7, 8]. Transition metal catalysts requires sulfiding the catalyst with sulfur containing compounds such as CS_2 or H_2S, in order to activate the catalyst [8, 9]. However, prolonged reactions using these catalysts can cause sulfur contamination of the products which in turn effects the quality of the biofuel obtained. On the other hand, noble metals are also not suitable for large scale usage because of their high costs. Commonly used metal oxide supports include zeolites, carbon, mesoporous silica, TiO_2, Al_2O_3, SiO_2, MCM-41 and SAPO-11, while active metals include the combination of NiCo, NiMo, CoMo and NiW etc. [10]. Though, very less research work has been done using rare earth metals like Lanthanides and Actinides. It has been reported that rare earth metals when combined with transition metals proved to be very active catalysts due to their tremendous properties like, thermal stability, less carbon deposition, high catalytic activity and good dispersion capability [11-13]. It has been stated that cerium metal greatly enhance the activity of Ni/Al_2O_3 catalyst for hydrogenation reaction [14]. Thus, the main objective of this work is to synthesize the hierarchical structured TiO_2 nanomaterials doped with Ni and Ce metals in order to utilize for the hydroprocessing of crude jatropha oil.

Nomenclature

HC	Hydroconversion
TNT	Titania nanotubes
TNS	Titania nanosheets
CJO	Crude jatropha oil

2. Methodology

2.1. Catalyst synthesis

2.1.1. Synthesis of TiO_2 nanosheets (TNS)

Titania nanosheets (TNS) were prepared using the following procedure. Initially, hydrofluoric acid (HF) (37% solution), and ethanol were added to commercially available titania nanopowder (Degussa P25) with 99.7% purity (Sigma-Aldrich), in a Teflon-lined stainless steel autoclave. The autoclave was kept at a temperature of 150 ^{0}C for 24 h and then allowed to cool until room temperature. The white precipitates obtained after the hydrothermal treatment were vacuum-filtered and washed with ethanol and deionized water alternately. The sample was then dried at 90 ^{0}C overnight to obtain titania nanosheets denoted as TNS.