



Liquid fuel production by aqueous phase catalytic transformation of biomass for aviation



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HIGHLIGHTS

- Biomass sugar/polyol was converted to aromatics by one-pot aqueous phase catalysis.
- Liquid fuel yield of 32 wt% with 84.3% aromatics was obtained over Ni-based catalyst.
- One economic route was proposed for bio-aromatic production as bio-based jet fuel.

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ABSTRACT

The commercial jet fuels usually contain about 40% aromatics and naphthene. However, conventional technologies on bio-jet fuels production by hydrodeoxygenation of plant oil and biomass gasification/Fischer–Tropsch synthesis can't produce renewable aromatics. In this paper, the liquid fuels with high aromatics content were produced by aqueous phase catalytic conversion of biomass sugar/polyol over Ni@HZSM-5/MCM-41 catalysts. Liquid fuel yield of 32 wt% with aromatics content of 84.3% was obtained under the conditions of 300 °C, WHSV of 1.25 h⁻¹, GHSV of 2500 h⁻¹ and 4.0 MPa of hydrogen pressure with mixed polyol (60% sorbitol + 40% xylitol) as feedstocks. The produced bio-aromatics are substituted benzenes, naphthalenes, and aromatic olefins, which is a wonderful crude oil to be used as jet fuels after it was hydrogenated to improve quality (deep deoxygenation/chemical bond saturation).

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1. Introduction

Renewable energy, especially the advanced liquid fuels from biomass resources, has the potential to be a substitute of traditional fossil fuels. Exploitation and utilization of high-quality liquid fuels will be beneficial to the rapid development of relative industries, the guarantee of the national energy security, the alleviation of energy crisis, the improvement of social environment and sustainable development [1,2]. It is speculated that about 8 wt% of total petroleum-derived products are jet fuels. Large jet fuel consumption leads to large CO₂ emission and significant environment impacts. For this sake, renewable and sustainable jet fuel produced from biomass attracts increasing attention [3,4].

The conventional technologies on jet fuel production from biomass include hydrodeoxygenation of plant oil and biomass gasification following with Fischer–Tropsch (F–T) synthesis. However,

aromatics and naphthalene can't be produced by these two kinds of technologies [5]. Novel technologies should be invented to overcome these challenges.

A great deal of efforts has been concentrated on the aspect by pyrolysis of biomass, especially by catalytic fast pyrolysis (CFP) at high temperature of above 600 °C [6,7]. In this process, zeolites such as ZSM-5, Beta and Y were usually used as the catalyst for aromatization, wherein ZSM-5 catalyst was confirmed to exhibit the highest catalytic activity for aromatics production due to its unique microporous structure and shape selectivity [8–10]. High yield of aromatics (23.2 wt%) from solid pinewood was achieved over a bi-functional Ga/ZSM-5 catalyst. Ga species promoted the rate of decarbonylation and olefin aromatization reaction. ZSM-5 catalyzed oligomerization reaction to form aromatic compounds. However, large amount of coke was inevitably formed and resulted in the rapid deactivation of the catalyst.

Recently, a promising technology (aqueous phase catalytic conversion of biomass) has been developed for direct conversion of biomass based sugar/polyol to liquid fuels [11]. Lignocellulosic biomass is generally converted into carbohydrates or sugar monomers

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(e.g., xylose and glucose) by acid or enzymatic hydrolysis, and further transformed to liquid fuels by aqueous phase catalytic processing [12]. Since the reaction occurs in aqueous phase, the alkane products are hydrophobic and can be automatically separated from the aqueous phase, which exhibits the great advantage of energy saving without additional distillation. Dumesic and co-workers developed a two-steps process for selective conversion of glucose and sorbitol to monofunctional hydrocarbons, which was further transferred to aromatics over HZSM-5 catalyst [11]. This two-stepped approach is as following: (1) Aqueous phase catalytic conversion of 60 wt% polyol solution to monofunctional compounds including furan, alcohol, ketone, and organic acids over 10 wt% Pt–Re/C (Pt: Re = 1:1, atom ratio) catalyst. (2) Reforming of this monofunctional compounds to aromatics and iso-paraffin over HZSM-5 catalyst at 400 °C. However, obtaining 60 wt% polyol solution is difficult because biomass hydrolysis usually produces low concentration of sugar solution. Especially, in this two-stepped process, large amount of gaseous byproducts such as C₁–C₄ alkanes were formed, which resulted in the decrease of liquid fuels yields.

We have recently prepared a bi-functional Ni/HZSM-5 catalyst modified by pure silica MCM-41 for one-pot aqueous phase catalytic conversion of dilute polyol solution to liquid fuels [13]. The resultant Ni@HZSM-5/MCM-41 catalyst exhibited excellent catalytic performance for the conversion of biomass-derived polyol to C₅–C₆ alkanes [14]. Preliminary results showed that high yield of aromatics could be obtained by one-pot aqueous phase catalytic conversion of sugar/polyol solution over Ni@HZSM-5/MCM-41 catalyst.

In this regard, the Ni@HZSM-5/MCM-41 composite catalyst was adopted to generate aromatic compound by one-pot aqueous phase catalytic conversion of sugar/polyol solution. The effects of the catalyst preparation, reaction temperature and feedstocks on the aromatics production were investigated in detail. The potential feasibility of the jet fuels substitution by the produced bioaromatics was discussed.

2. Experimental

2.1. Catalyst preparation and characterization

The Ni@HZSM-5/MCM-41 catalyst was prepared by the incipient wetness impregnation. HZSM-5 and pure silica MCM-41 were supplied by Nankai University catalyst Co., Ltd. (Tianjin, China). Ni(NO₃)₂·6H₂O (AR, 99.9%) was bought from Tianjin Fucheng Reagents (Tianjin, China). Prior to the preparation, the weight ratio of HZSM-5 (80–100 mesh, Si/Al atomic ratio of 38) and MCM-41 (100–120 mesh) was fixed with 1.5 in deionized water at room temperature for 3 h at the stirring speed of 300 rpm, followed by drying in air at 110 °C for 12 h. The dried samples were calcined at 500 °C for 6 h. Then the resulted sample was impregnated with an aqueous solution of nickel nitrate at room temperature for 12 h, followed by drying in air at 110 °C for 12 h. The dried sample was calcined at 500 °C for 6 h. The Ni loading was 0–20 wt%, and thus the resulted catalysts was denoted as x%Ni@HZSM-5/MCM-41 (x means Ni loading amount).

The crystalline structure of the catalysts were characterized by X-ray diffraction (XRD) (X Pert Pro MPD with Cu K α (λ = 0.154 nm) radiation, Philip) operated at 40 kV and 100 mA. Scanning angle (2 θ) ranged from 5° to 80°. Small angle X-ray diffraction was also performed in the range of 2 θ from 0.5° to 10°.

The BET surface area, external surface area and pore volume of catalysts were determined by nitrogen adsorption at 77 K using a QUADRASORB SI analyzer equipped with QuadraWin software system. All samples were degassed at 573 K for 8 h before adsorption measurements. The surface area was calculated by

the Brunauer–Emmett–Teller (BET) method. The mesoporous pore volume was calculated with the Barret–Joyner–Halenda (BJH) model and the micropore volume was calculated with the T-plot method.

The thermal behavior of the catalysts before and after reaction for 20 h were examined by non-isothermal thermogravimetric analysis (TGA) using a Mettler Toledo instrument (TGA/SDTA851e), the thermogravimetric (TG) and differential thermogravimetric (DTG) curves were recorded from 50 °C to 800 °C at a heating rate of 20 °C/min, under an air atmosphere.

Infrared spectra of pyridine adsorption (Py-IR) were recorded on a Thermo Nicolet Nexus FT-IR spectrometer equipped with a liquid nitrogen cooled MCT detector. The samples were pressed into a self-supported wafer and treated at 400 °C in an in situ IR cell for 0.5 h followed by cooling to 50 °C under vacuum to record the background spectra of the cell and the catalyst wafer. Subsequently, the samples were exposed to pyridine vapor for 10 min and then evacuated at the same temperature in order to remove physical adsorbed pyridine. The spectra were recorded in the range of 1700–1400 cm⁻¹ with 32 scans and a resolution of 4 cm⁻¹.

2.2. Aqueous-phase catalytic reaction and products analysis

The aqueous-phase catalytic reaction was carried out in a stainless steel tube reactor (0.8 cm inner diameter and 50 cm in length). 4 g of x%Ni@HZSM-5/MCM-41 catalyst was filled in the reactor per run. Prior to reaction, the catalyst was reduced in situ by a flow of H₂ (30 ml min⁻¹) at 500 °C for 3 h and then cooled down to reaction temperature. Meanwhile, H₂ and reactant of sugar or polyol were co-fed into the reactor in a down flow direction under a designed pressure. The liquid products were accumulated in a gas–liquid separator and drained periodically into a collecting container. The effluent gas was cooled to room temperature and sampled for analysis.

The gaseous products were measured via a wet flow meter and analyzed by an Agilent GC-7890A gas chromatograph (GS-GasPro capillary column, 60 m \times 0.32 mm) equipped with a thermal conduct detector (TCD) and a flame ionization detector (FID). The aqueous phase species were analyzed by Waters Alliance e2695 HPLC with UV–Vis (Waters 2489) and Refractometer (Waters 2414) detector by using a Shodex SH1011 column (8 \times 300 mm). 0.005 M H₂SO₄ as mobile phase flowed at a rate of 0.5 ml min⁻¹. The analysis of the oil products were performed on an Agilent GC-7890A gas chromatograph (HP innowax capillary column 19091 N-133 N, 30 m \times 250 μ m \times 0.25 μ m) equipped with a mass spectrometer (5975C) by using 99.995% of He as the carrier gas. The total carbon content (TOC) and C/H weight ratio in the liquid samples were measured by a Vario EL III elemental analyzer (\pm 0.2%).

2.3. Heating value of synthesized liquid fuel

Heating value of synthesized fuel was detected by bomb calorimeter (WZR-1T-CII&IKA C2000, \pm 0.2%). The combustion of a stoichiometric mixture of fuel and oxidizer in a steel container at 25 °C is initiated by an ignition device. When hydrogen and oxygen react during combustion, water vapor is produced. The vessel and its content are then cooled to the original 25 °C.

3. Results and discussion

3.1. Characterization of catalysts

The XRD patterns of composite catalysts with different Ni loadings are shown in Fig. 1a. The peaks at 2 θ of 37.5°, 43.4° and 63.2° are attributed to the (111), (200) and (220) crystal facets of NiO

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