



Full Length Article

Catalytic valorization of biomass derived glycerol under methane: Effect of catalyst synthesis method

Danielle Austin^a, Aiguo Wang^a, Peng He^a, Hui Qian^b, Hongbo Zeng^c, Hua Song^{a,*}^a Department of Chemical and Petroleum Engineering, University of Calgary, 2500 University Drive, NW, Calgary, Alberta T2N 1N4, Canada^b National Institute for Nanotechnology, National Research Council, Edmonton, Alberta T6G 2M9, Canada^c Department of Chemical and Materials Engineering, University of Alberta, 9211-116 Street NW, Edmonton, Alberta T6G 1H9, Canada

ARTICLE INFO

Keywords:

Glycerol

Catalyst

Aromatization

ZSM-5

ABSTRACT

The feasibility of upgrading glycerol using Zn, Cu and Ga modified ZSM-5 was investigated. Different catalyst synthesis techniques were compared for their performance on the aromatization of glycerol under a methane environment at 400 °C and initial pressure of 5 bar. GC–MS analysis showed that the catalyst synthesized using deposition precipitation (DP) resulted in the best performance in terms of the highest yield of monoaromatics in the liquid product when compared with the other synthesis techniques. XRD, NH₃-TPD, Pyridine DRIFT, TEM, CO Chemisorption and XAS were employed to better understand the influencing parameters. High crystallinity, high acidity with a higher proportion of medium acid sites and high metal dispersion were identified as the most important factors influencing aromatization performance. Evidently, the deposition precipitation synthesis technique is effective in obtaining each of these attributes. Additionally, a methane environment increased aromatic production when compared to an inert environment. Methane was found to not only maintain high metal dispersion throughout the reaction, but may participate in the reaction as well. The synthesis technique utilized for the upgrading of glycerol can influence the distribution of products, allowing for increased selectivity of the desired product. The demonstrated feasibility and excellent upgrading performance of the DP synthesized catalyst could make the production of biodiesel more economical and environmentally friendly.

1. Introduction

The world energy market is currently dominated by fossil fuels. With increasing concern surrounding climate change and dwindling resources that are associated with the use of fossil fuels, renewable energy sources are becoming increasingly desirable and are currently the fastest growing energy source [1]. Biodiesel, is an attractive option because it utilizes abundant, low cost carbon resources, which has resulted in a recent escalation in its production and consumption. In industry, biodiesel is widely obtained from the transesterification of natural oils such as waste vegetable oil or animal fats [2,3]. During this process, approximately 10% by weight of the feedstock is converted into glycerol [4–6]. Although glycerol is used in a wide range of applications, it is often only used in small quantities, creating a surplus of glycerol and negatively affecting the value of biodiesel [7]. Converting the glycerol by-product into higher value chemicals would increase the economic favourability of producing biodiesel.

The conversion of glycerol has been studied for the production of syngas, olefins, acrolein, lactic acid, diols, alkyl aromatics and more [8–12]. Due to the many uses of aromatics, including fuels,

pharmaceuticals, chemical applications and dyes, the effective aromatization of glycerol would have a positive economical effect on the production of biodiesel [13]. HZSM-5 has shown promise in the aromatization of glycerol in an alcohol or aqueous solution [14] as well as in a continuous flow reactor [15], however, in both cases oxygenates were found to be the dominant products. Oxygenates in fuels cause quality, transportation and compatibility issues, making removal of oxygen from the liquid product an important consideration [16,17].

Zinc and copper oxides have been successfully utilized for the hydrogenolysis of glycerol to remove hydroxyl groups to form diols [18–20]. By using Zn and Cu on a ZSM-5 support, more oxygen can be removed and maximum aromatics can be obtained in the liquid product. Due to the high cost associated with hydrogen gas, it would be preferable to use an alternative hydrogen source such as methane, which is low cost and abundant. However, methane is currently difficult to utilize as it is a highly stable molecule with a C–H bond activation energy of 413 kJ/mol [21]. From our previous work, it was found that Ga may be useful in activating CH₄ at around 400 °C through a non-oxidative pathway and promoting aromatization [22,23]. Previously, methane has been successfully employed for the deoxygenation

* Corresponding author.

E-mail address: sonh@ucalgary.ca (H. Song).

of glucose, meaning it should be technically feasible to use methane for the removal of oxygen in glycerol [24]. Thermodynamically, assuming xylene is the major product for the aromatization of glycerol in a methane environment ($\text{CH}_4 + \text{C}_3\text{H}_8\text{O}_3 \rightarrow \text{C}_8\text{H}_{10} + \text{H}_2\text{O}$), the reaction is feasible based on the negative calculated Gibbs free energy ($\Delta_r G$) of -103 kcal/mol at 400°C .

Preliminary experiments showed positive results for high selectivity of aromatics in the liquid product utilizing Zn, Cu and Ga on a HZSM-5 support in a methane environment. In the present work, five different catalyst synthesis methods were compared for their glycerol aromatization performance to explore the effective metal active sites and its role played in the reaction. Deposition precipitation (DP), incipient wetness impregnation (IWI), ion exchange (IE), a physical mixture of 1%Ga/ZSM-5 and CuO/ZnO and hydrothermal synthesis (HS) were the synthesis methods employed. The information gained from this study can lead to the optimization of a catalyst for the valorization of glycerol thus making biodiesel more cost effective. Having more economical options for renewable energy can reduce the world's dependency on fossil fuels by replacing them with cleaner energy options.

2. Experimental

2.1. Catalyst preparation

The ammonium ZSM-5 zeolite with Si/Al = 23 and specific surface area of $425\text{ m}^2\text{g}^{-1}$ was purchased from Zeolyst and calcined at 600°C for 3 h in air to attain H-type ZSM-5 for further use. Five different techniques were used to prepare the catalysts, while maintaining a formula of 5%Zn-1%Cu-1%Ga/ZSM-5. For each of the techniques, Zn ($\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (99%, Alfa Aesar), $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (98%, Alfa Aesar) and $\text{Ga}(\text{NO}_3)_3$ (99.9%, Alfa Aesar) were used as metal precursors. Incipient wetness impregnation (IWI) was performed with an aqueous solution of the above precursors, followed by drying in the oven at 88°C overnight and calcining at 600°C for 3 h in ambient air, this catalyst is marked as Zn-Cu-Ga/ZSM5-IWI. A second catalyst was prepared by deposition precipitation (DP). HZSM-5 was deposited into an aqueous solution of the metal precursors, which was maintained at a pH of 8 using sodium carbonate and allowed to stir for 1 h. The catalyst was recovered by vacuum filtration, washed and filtered again three times, dried at 88°C overnight and calcined at 600°C for 3 h in ambient air, this catalyst is marked as Zn-Cu-Ga/ZSM5-DP. A third catalyst was prepared using IWI to prepare 1%Ga/ZSM-5 and coprecipitation to synthesize CuO/ZnO. The two catalysts were physically mixed, this catalyst is marked as Ga/ZSM5-CuO/ZnO. A fourth catalyst was prepared by ion exchange (IE). Ammonium ZSM-5 zeolite was added to four 1.0 M solutions in sequence. The first two containing zinc nitrate, the third containing copper nitrate and the fourth containing gallium nitrate. These solutions were each stirred for 50 h at 80°C after which the catalyst was recovered by vacuum filtration, dried overnight at 88°C and calcined at 600°C for 3 h in ambient air, this catalyst is marked as Zn-Cu-Ga/ZSM5-IE. Lastly, hydrothermal synthesis was used to incorporate Zn, Cu and Ga into the MFI framework. TEOS (98%, Sigma Aldrich) was used as the source of Si with $\text{Al}(\text{NO}_3)_3$ (98%, Alfa Aesar), NaOH (98%, Alfa Aesar), TPAOH (0.1 M, Sigma Aldrich) and DI H_2O used in molar ratios to Si of 23:1, 0.2:1, 0.1:1 and 45:1 respectively. The metal nitrates were added to obtain the desired weight percent. The solution was placed in an autoclave and held at 180°C for 5 days. The catalyst was recovered by centrifuge, dried and calcined. IE was used to remove the sodium with a 1.0 M solution of ammonium nitrate (99%, Sigma Aldrich), stirred for 18 h at 400 rpm and 80°C . The catalyst was then calcined at 600°C for 3 h in ambient air to obtain the H type zeolite, this catalyst is marked as Zn-Cu-Ga/ZSM5-HS.

2.2. Performance evaluation

The glycerol aromatization reaction was conducted using a 300 mL

Parr® batch reactor. In a typical run, 1.0 g of catalyst and a glass vial filled with 3.0 g glycerol were loaded into the reactor. The air was purged out of the reactor using nitrogen and after passing a leak test, it was pressurized to 5 bar with methane or nitrogen. The reactor temperature was then ramped up with a rate of $20^\circ\text{C}/\text{min}$ to the target temperature of 400°C and held for 40 min. Upon reaction completion, the reactor was allowed to cool down to room temperature before product collection. The formed liquid product embedded into the charged solid catalyst was extracted using 10 mL CS_2 (GC grade, EMD Chemicals) as the solvent. Each experiment was repeated twice to ensure repeatability, with the average values of the two runs being reported.

The liquid yield, coke yield, and substitution index reported in this paper are given by the following equations:

$$\text{Liquid Yield} = \frac{\text{weight of liquid collected in the reactor}}{\text{weight of fed glycerol}} \times 100\%$$

$$\text{Coke Yield} = \frac{\text{weigh to coke formed}}{\text{weigh to fed glycerol}} \times 100\%$$

$$\text{Substitution Index} = \sum \left(\frac{n_i}{m_i} \times y_i \right)$$

where n is the number of substitution groups, m is the number of carbon atoms in the aromatic ring and y is molar fraction for each component, i.

2.3. Characterization

The composition of the liquid products was determined by pre-calibrated Gas Chromatography-Mass Spectrometer (GC-MS: PerkinElmer GC Claus 680 and MS Clarus SQ 8T) equipped with a Paraffins-Olefins-Naphthenes-Aromatics (PONA) column (Agilent HP-PONA). The oven temperature of the GC was programmed to hold at 35°C for 15 min, ramp to 70°C at $1.5^\circ\text{C}/\text{min}$, rise to 150°C at $3^\circ\text{C}/\text{min}$ and hold for 30 min, then ramp to 250°C at $3^\circ\text{C}/\text{min}$ and hold for 2 min.

The gas products were analyzed by a four-channel Micro-GC (490, Agilent). Upon reaction completion, the reactor was allowed to cool down to room temperature before product collection. The reactor was connected to the Micro GC, the gas product was analyzed by the connected micro-GC equipped with thermal conductivity detectors, which can precisely analyze H_2 , O_2 , N_2 , CH_4 , and CO in the first channel equipped with a 10 m molecular sieve 5A column; CO_2 , C_2H_2 , C_2H_4 , and C_2H_6 in the second channel installed with a 10 m PPU column; and $\text{C}_3\text{-C}_6$ and $\text{C}_3\text{-C}_5$ (“=” denotes alkenes) in the third and fourth channels charged with a 10 m alumina column and one 8 m CP-Sil 5CB column, respectively. Ar and He were the carrier gases for the first and other three channels, respectively. The composition of the gas products was used to calculate the moles of each species assuming the ideal gas law. The moles of methane in the feedstock were calculated in a similar manner to determine the methane conversion.

The transmission electron microscopy (TEM) images were performed on a JEOL 2100 Transmission Electron Microscope operated at 200 kV equipped with an X-ray analyzer for Energy-Dispersive X-ray (EDX) for elemental analysis using Oxford INCA Energy under STEM mode with 1 nm probe. The sample was first dispersed in ethanol and sonicated for about 2 min. A $10\ \mu\text{L}$ droplet was placed on a Ni grid before the TEM images were recorded.

The powder X-ray Diffraction (XRD) analysis of the catalysts was carried out on a Rigaku ULTIMA III X-ray diffractometer with a Cu K α irradiation source at a voltage of 40 kV and current of 44 mA. All powder diffraction data were acquired between a 2θ of $3\text{-}90^\circ$, using 2° step/min.

Acidity measurements were performed by ammonia temperature programmed desorption (NH_3 -TPD) using ~ 200 mg samples in a Finesorb-3010 Chemisorption Analyzer. Ammonia was selected due to

Download English Version:

<https://daneshyari.com/en/article/6632140>

Download Persian Version:

<https://daneshyari.com/article/6632140>

[Daneshyari.com](https://daneshyari.com)