Effects of nano-structured CoMo catalysts on hydrodeoxygenation of fast pyrolysis oil in supercritical ethanol

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ABSTRACT

Effects of in-house prepared CoMo catalysts supported on various nano-structured materials (activated carbon, γ-alumina, HZSM-5, MCM-41 and SBA-15) and a commercial catalyst of Ru/C were compared for hydrodeoxygenation (HDO) of fast pyrolysis oil (PO) in supercritical ethanol at 300 and 350 °C. All catalysts proved to be effective for significantly reducing the molecular weight of the PO by HDO treatment at 350 °C. Although Ru/C catalyst produced the highest oil yield at both temperatures (66.6 wt% at 300 °C and 61.0 wt% at 350 °C) with the lowest and negligible coke formation (<1 wt%), the catalyst is very expensive and difficult for regeneration, so it is not a viable catalyst for bio-oil upgrading on a large scale. Among all the supported CoMo catalysts, CoMo/MCM-41 produced the highest yield of oil products (light oil (OL) + heavy oil (HO)) of the highest H/C molar ratio. With this catalyst, the oil yield attained 61.9 wt% at 300 °C and 57.8 wt% at 350 °C, and the spent catalyst after regeneration produced almost the same oil yields as the fresh one. In addition, CoMo catalysts supported on MCM-41 and SBA showed better resistance to coke/carbon deposition in the HDO process, compared with CoMo catalysts supported on HZSM-5 and Al_2O_3.

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1. Introduction

Biomass has drawn considerable attention as it has a great potential to be a sustainable, renewable and clean replacement for fossil fuels for the production of energy, fuels and chemicals [1,2]. Lignocellulosic biomass such as forestry/agricultural biomass and residues can be converted to solid, liquid and gaseous biofuel or chemicals through different technologies using biological, thermal or thermo-chemical methods [3].

Pyrolysis oil (PO) is usually obtained from fast pyrolysis of biomass is a complex mixture of various oxygen-containing organic compounds such as ketones, aldehydes, alcohols, carboxylic acids, phenols, sugar, etc. [4]. These oxygen-containing compounds bring about detrimental properties of bio-oil such as high oxygen content, high water content, high viscosity, low heating value, low pH value, poor ignition properties, chemical and thermal instability, and high acidity and corrosiveness [5,6].

Pyrolysis bio-oils have reactive organic compounds such as aldehydes and phenols, so they are chemically unstable over time. These compounds would react each other and produce macromolecules through polymerization. Since this process occurs with time, it is often called "aging". The main reactions which occur during aging are polymerization, etherification, esterification, and condensation which produce water [6–8]. The composition of bio-oil depends on different factors such as the production condition and raw materials [9]. Carboxylic acids such as acetic acid in bio-oil lead to corrosion of the vessels and lower stability [10]. Aldehydes and phenols in bio-oil with unsaturated carbon bond are prone for condensation and polymerization reactions; so large molecules would form especially in the presence of acids. Therefore, these reactions lead to rising of viscosity, instability, and difficulty in transportation and phase separation of bio-oil [11]. Thus, pyrolysis oils have many undesirable characteristics such as high viscosity, poor stability, high acidity and corrosiveness, due to their high molecular weights and high oxygen content it cannot be used directly as the engine fuel [12]. High oxygen content of bio-oil also results in a low heating value (LHV), being only half of the fossil fuels. In addition, bio-oil is immiscible and difficult for being co-processed with fossil fuels [13]. Therefore, upgrading of bio-oil is needed to overcome the undesirable properties in order to utilize the oil for fuels or chemicals.

Several methods such as thermal/catalytic cracking [14], esterification [15], emulsification [16] and hydro-de-oxygenation (HDO) [17] have been used to upgrade bio-oil. Compared with a catalytic cracking process which has severe coke/char deposition and fast catalyst deactivation problems, HDO is advantageous and a widely

used bio-oil upgrading process aiming to exclude oxygen from a bio-oil at moderate temperatures and high hydrogen pressure using heterogeneous catalysts (commonly NiMo or CoMo catalysts) [18]. Almost in all bio-oil upgrading methods, a common challenge is that bio-oil has macromolecular compounds that can block the pores of a catalyst and quickly deactivate the catalyst [10,19]. Mesoporous materials such as SBA-15 [20] and MCM-41 [19–22] are promising catalysts or support materials for various bio-oil upgrading processes, as these catalysts could considerably improve the composition of bio-oil, reducing the contents of oxygenated carbonyl and acid compounds, and maintain a longer catalyst lifetime [23]. By incorporating of metals of Mo and Co into the nanostructured mesoporous materials, the mesoporous material-supported catalysts proved to be very effective for HDO of bio-oils [19]. The large pore size with the strong acidity of SBA-15 or MCM-41 would lead to making promising catalysts for bio-oil upgrading to prevent the pore blocking by macromolecules [24]. The main advantage of using nanostructured catalysts for the bio-oil HDO process is given below: nanostructured catalysts generally have a higher specific surface area and large pore size and pore volume, which enhance the catalyst's activity and resistance to coke formation As such, in this study, nanostructured SBA-15 and MCM-41 mesoporous materials were chosen as the support for preparation of CoMo catalysts for pyrolysis oil HDO.

Recently, supercritical fluids have been demonstrated to be effective solvents for HDO upgrading of bio-oils [9]. Supercritical fluids (SCFs) have unique transport characteristics: gas-like low viscosity and high diffusivity and liquid-like density. They also can dissolve materials that are not usually soluble in a liquid or a gas phase [25,26]. Thus, the above unique transport characteristics of SCFs make them superior reaction media with faster mass and heat transfer rates [4]. The faster mass and heat transfer rates would eliminate the mass transfer resistance, reduce the reaction time (decreasing the formation of coke), and facilitate the gas-solid contact (promoting the hydrogen-processing reactions) [6,25,27,28]. Moreover, SCFs have superb solubility to dissolve the hydrogen gas, the bio-oil feed and the upgraded oil products or reaction intermediates, making one-phase reaction process, which would collectively promote the hydrogenation and HDO reactions in the hydro-processing process. Peng et al. [28,29] studied upgrading of bio-oil in subcritical and supercritical ethanol using $Al_2(SiO_3)_3$ or HZSM-5 catalyst. It was reported that supercritical condition improved the oil quality more effectively than subcritical condition. It also found that stronger acidic HZSM-5 (Si/Al = 22) catalyst can significantly improve cracking of heavy components of crude bio-oil in supercritical upgrading process. $Al_2(SiO_3)_3$ catalyst also can facilitate esterification reaction in supercritical condition and promote the acids conversion into different kinds of esters. Li et al. [30,31] investigated on upgrading of low boiling fraction of bio-oil over $Pt/Al_2(SiO_3)_3$, Pt/C and Pt/MgO catalysts and high boiling fraction over a series of supported mono and bimetallic catalysts in supercritical methanol. Tang et al. [10,24] studied the bio-oil upgrading process in supercritical ethanol under hydrogen atmosphere using $Pd/SO_4^{2-}/ZrO_2/SBA-15$ catalyst and also hydrocracking of pyrolytic lignin derived from rice husk at 260 °C over $Ru/ZrO_2/SBA-15$ or $Ru/SO_4^{2-}/ZrO_2/SBA-15$ catalyst in supercritical ethanol under hydrogen atmosphere. Zhang et al. [32] studied upgrading of bio-oil over $Pt/SO_4^{2-}/ZrO_2/SBA-15$ in supercritical methanol/ethanol under a hydrogen atmosphere, showing that supercritical ethanol performed better than supercritical methanol in the upgrading process since it had a longer alkyl chain that can dissolve higher molecular weight products and led to less coke formation. The critical pressure and temperature of ethanol are 6.148 MPa and 240.75 °C, which are lower than those of water and methanol. From the author's own research work, supercritical ethanol demonstrated to be very effective for HDO upgrading of

pyrolysis in terms of HDO efficiency. As such, supercritical ethanol was used as the HDO solvent in this study for pyrolysis oil upgrading.

In this research supercritical ethanol under hydrogen atmosphere was used for HDO upgrading of fast pyrolysis bio-oil into advanced drop-in bio-fuels over some nano-structured catalyst at two different temperatures, 300 and 350 °C.

The commercial Ru/C catalyst proved to be highly effective in bio-oil HDO though, it is very expensive and difficult for regeneration, so it is not a viable catalyst for bio-oil upgrading on a large scale. The main goal of this research was to explore inexpensive CoMo-based catalysts supported on nano-structured materials, e.g., SBA-15, MCM-41, Al_2O_3, activated carbon (pellet and powder form) and HZSM-5. Ru/C, a commercial catalyst, was tested as a bench mark in this work since it is known to be active in hydrogenation and HDO process [33,34]. All the CoMo-based catalysts were prepared using successive wetness impregnation method.

2. Experimental

2.1. Materials

Cobalt (II) nitrate hexahydrate, ammonium molybdate tetra-hydrate, Tetraethyl orthosilicate (TEOS), hexadecyltrimethylammonium bromide (CTAB), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG; Pluronic® (P-123) with an average molecular weight of ~5800), were all purchased from Sigma–Aldrich Inc., USA. In addition, a commercial catalyst for bio-oil HDO, i.e., ruthenium on carbon (Ru/C; Ru loading: 5 wt% Ru loading, BET surface area of 780.91 m^2/g, pore diameter of 33.92 Å) was also obtained from Sigma–Aldrich Inc. Activated carbon (0.8 mm pellets) and powder were purchased from Alfa Aesar, USA. HZSM-5 (SiO_2/Al_2O_3 = 38) was purchased from Pingxiang PangTai Industrial Co., Ltd. Pingxiang, Jiangxi, China. γ-Al_2O_3 was purchased from Inframat Advance Material, USA. Hardwood sawdust fast pyrolysis oil (PO; water content of 20.99 wt%, oxygen content of 36.40 wt%, and a heating value of 24.56 MJ/kg (on dry basis)) was obtained from Biomass Technology Group (BTG), Netherlands. All of the chemicals were used as received without further purification. Pure (anhydrous) ethanol was obtained from Commercial Alcohols (density 0.7885 g/mL, and water content <0.1 wt%). Acetone used was ACS reagent grade solvent, obtained from Sigma/Aldrich and used as received.

2.2. Preparation of mesoporous materials as supports and supported catalysts

The common method of synthesizing SBA-15 as described below was adopted [35,36]. A solution of 3 g pluronic surfactant (P123) and 200 mL of 2 M HCl was first prepared. This solution was stirred and heated for 3 h until the surfactant was dissolved in the solution and a homogenous solution was obtained. In the meantime, a solution of 22.5 mL of distilled water and 7.75 g of TEOS was made and added dropwise to the above-mentioned solution under continuous stirring for 2 h. Then, the final solution was transferred into a Teflon reactor and aged at 35 °C for 24 h. The temperature was then raised to 100 °C for 24 h to promote crystallization. Finally, the resulting product was filtered, washed with distilled water, dried and followed by calcination at 500 °C for 5 h.

MCM-41 was synthesized following the procedure detailed in by Cai et al. [37], as briefly described below: a solution of NH_4OH 25 wt% and deionized water was made firstly, then a specific amount of CTAB was added to the solution. The solution was stirred and heated until a homogenous solution was obtained. TEOS was then added dropwise to the final solution under continuous stirring