HYDRODEOXYGENATION OF BIO-OIL MODEL COMPOUNDS USING ZEOLITE-SUPPORTED TRANSITION METALS

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Abstract

The objective of this work is to investigate the effects of transition metal species on the catalytic hydrodeoxygenation (HDO) of three bio-oil model compounds. Ni, Pd and Ru were impregnated on ultra-stable Y (USY) zeolite, and each was used for anisole, 4-ethylphenol and benzofuran HDO. Electron microscopy and H_2 chemisorption indicated that each metal was well-dispersed through the zeolite, and reduction in H_2 was effective. We found that HDO of anisole was most easily-accomplished, while conversion of 4-ethylphenol occurred at the slowest pace. Pd-USY was the most effective catalyst for HDO of all three model compounds. Kinetic modeling of reaction intermediates and products was also performed to determine the effect of transition metal species on reaction pathway. Finally, USY support mesoporosity was investigated as a means to improve catalyst activity.

Introduction

High demand for liquid hydrocarbon fuels, coupled with the potentially disastrous effects of climate change, has rendered the conversion of biomass to fuels a desirable and sustainable alternative. Biomass is currently the only renewable and accessible carbon source on the planet, and biomass conversion to fuels is potentially carbon-neutral.

Biomass pyrolysis, the thermochemical conversion of biomass under inert atmosphere, can produce up to 70 wt.% of liquid bio-oil (Czernik and Bridgwater, 2004). Unfortunately, this bio-oil is unstable, acidic, viscous, and has a very poor heating value, making it an unsuitable combustion fuel. These properties arise from the presence of atomic oxygen in the bio-oil, which must be efficiently removed prior to application. Furans, phenols and methoxy compounds are all common bio-oil oxygenates (Mu et al., 2013). HDO is an effective way to remove this oxygen as water, maintaining valuable carbon in the oil.

HDO has been widely investigated as a bio-oil upgrading process. Inspired by refinery hydroconversion processes, NiMo and CoMo supported on Al_2O_3 are common HDO catalysts. However, these catalysts require sulfidation prior to reaction, introducing sulfur to the system and reducing a potential benefit of sulfur-deficient biomass. Moreover, these materials suffer deactivation in the presence of water. Other common catalysts are Pt group metals supported on SiO_2 and Al_2O_3, but these catalysts are expensive.

The focus of this work is the application of Pd, Ru and Ni supported on USY zeolite as potential HDO catalysts. USY is an attractive support due to high surface area, excellent hydrothermal stability, and a shape selective pore structure. Characteristic zeolite acid sites will aid in adsorption of reactants and removal of oxygen through dehydration pathways. Meanwhile, Pd is a common HDO metal species, whereas Ru has been shown to remove oxygen heteroatoms without excessive hydrogenation. Ni is abundant, inexpensive and an excellent hydrogenation catalyst. Each catalyst has been characterized to determine surface area, metal dispersion and active area, reduction effectiveness, morphology and location within the zeolite

support. Additionally, due to the microporous nature of the zeolite, there may be a transport limitation between the reactant oxygenates and zeolite and metal active sites. Hierarchical pore structure will be incorporated into the USY zeolite to determine how this affects impregnated metal species and reaction kinetics. The ultimate objective is to determine the efficacy of zeolite-supported transition metals on HDO of a variety of oxygenated bio-oil compounds.

Methods and Materials

Commercial USY zeolite was impregnated with Pd, Ru and Ni precursor solutions, dried, calcined and then reduced. Metal phases of the final material were identified using X-ray diffraction (XRD). Metal location and topology was determined using high resolution scanning transmission electron microscopy (STEM) with elemental mapping. Inductively coupled plasma (ICP) was performed to determine total metal loading. Metal dispersion and crystal size were determined using H_2 chemisorption. Finally, reduction characteristics of each material were found using temperature programmed reduction (TPR).

HDO experiments were performed in a stirred autoclave reactor at 200 °C and 750 psi. Anisole, 4-ethylphenol and benzofuran were selected as bio-oil model compounds, representing three common bio-oil functional groups. Samples were collected at timed intervals to determine reactant and product concentration with time. Initial reaction rate was determined assuming a first-order reaction, and kinetic rate constants for hydrogenation and deoxygenation were determined using a least-squares fit of a mechanism determined from the product distribution. A similar procedure was followed for HDO of anisole using Ni impregnated on mesoporous USY.

Catalytic Hydropyrolysis with ZSM-5 and Ni-ZSM-5

Figure 1 shows STEM images of (A) Ni-USY, (B) Ru-USY and (C) Pd-USY. All three images show that metal was present both in large particles on the surface of the zeolite, and in smaller particles within the zeolite crystal. Elemental mapping confirmed that each metal existed in the reduced state, with very low levels of oxygen detected within the metal particles. From Figure 1, it appears that the metal species are well dispersed within the zeolite. Metal dispersion was confirmed by H_2 chemisorption to be around 10 %.
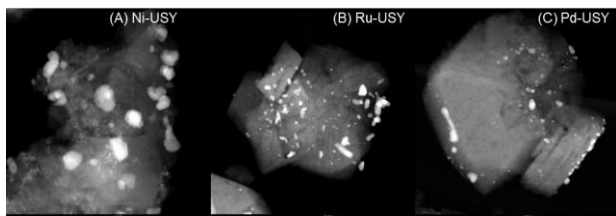

Figure 1. Dark field STEM images of (A) Ni-USY, (B) Ru-USY and (C) Pd-USY.

Figure 2 shows the conversion of (A) anisole, (B) 4-ethylphenol and (C) benzofuran as a function of time over Ni-USY, Ru-USY and Pd-USY. Conversion was greatest over Pd-USY for all three model compounds. Ru-USY outperformed Ni-USY for HDO of anisole and 4-ethylphenol, but not for benzofuran. Anisole and benzofuran conversion reached 100 mol% using Pd-USY, but 4-ethylphenol conversion reached a maximum of only 90 mol%. The primary product for anisole conversion over all three catalysts was cyclohexane, whereas ethylcyclohexane was the dominant product from 4-ethylphenol HDO. Benzofuran HDO resulted in primarily 2,3-dihydrobenzofuran, and only Pd-USY and Ru-USY were capable of ring cracking and further deoxygenation.
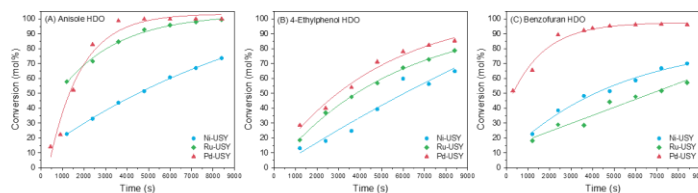

Figure 2. Conversion of (A) anisole, (B) 4-ethylphenol and (C) benzofuran as a function of time over metal-USY catalysts.

Three individual mechanisms were proposed for anisole, 4-ethylphenol and benzofuran HDO. Each mechanism included hydrogenation and deoxygenation steps. Kinetic modelling enabled us to show that Pd-USY was most effective for both hydrogenation and dehydration reactions. Further work focused on application of a mesoporous USY support to improve metal accessibility, and performance of HDO in a differential fixed bed reactor.

Conclusions

Hydrodeoxygenation of three biomass model compounds was performed using three transition metals supported on USY zeolite. The three catalysts were characterized using a number of techniques to determine metal location, morphology and dispersion. Pd-USY was the most effective HDO catalyst. Kinetic modelling showed that this was due to high hydrogenation potential and dehydration activity. Zeolite supported transition metals were created, characterized and shown to be feasible for HDO of bio-oil.

References

Czernik, S., Bridgwater, A. V, 2004. Overview of Applications of Biomass Fast Pyrolysis Oil. Energy & Fuels 590–598.

Mu, W., Ben, H., Ragauskas, A., Deng, Y., 2013. Lignin Pyrolysis Components and Upgrading-Technology Review. Bioenergy Res.