# Upgrading of pyrolysis bio-oil using nickel phosphide catalysts

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## ARTICLE INFO

## ABSTRACT

Pyrolysis bio-oil is a promising source of liquid fuels, but requires upgrading to remove excess oxygen and produce a satisfactory fuel oil. Nickel phosphide has been shown to be an active composition for hydrodeoxygenation (HDO) of bio-oil model compounds. In this study, nickel phosphide catalysts were used for direct upgrading of an actual pyrolysis bio-oil derived from cedar chips. The activity of $Ni_2P$ deposited on an amorphous $SiO_2$ support for HDO was first verified using the model compound, 2-methyltetrahydrofuran (2-MTHF), at the temperature of the pyrolysis oil treatment of 350 °C. The $Ni_2P/SiO_2$ catalyst showed high activity for 2-MTHF hydrodeoxygenation under atmospheric pressure hydrogen with low cracking activity.

Fast pyrolysis and catalytic upgrading were conducted sequentially using a laboratory-scale, two-stage system consisting of a fluidized bed pyrolyzer and a fluidized bed catalytic reactor both operating at 0.1 MPa, with a hydrogen partial pressure of 0.06 MPa. It was found that the $Ni_2P/SiO_2$ catalyst was moderately effective in upgrading the biomass pyrolysis vapors and producing a refined bio-oil with decreased oxygen content. The moderate deoxygenation of the bio-oil was confirmed by elemental analysis and Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) analysis. Gas chromatography–mass spectrometry (GC–MS) analysis showed that the treated bio-oil mainly consisted of phenolic compounds, and the MS spectra before and after upgrading suggested that reactions including hydrodeoxygenation, hydrogenation, decarbonylation, and hydrolysis occurred during the upgrading. Furthermore, $Ni_2P$ supported on ZSM-5 zeolite eliminated oxygen in the bio-oil with smaller reduction in the oil yield than $Ni_2P$ supported on $SiO_2$. The deoxygenation activity of the nickel phosphide catalysts was higher than that of conventional catalysts such as $Ni/SiO_2$, Pd/C and an FCC-catalyst.

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## 1. Introduction

Biomass-derived fuels have been attracting great interest because of their short $CO_2$ cycle, and the abundance of bioresources on earth [1], and because biofeedstocks are the only renewable energy source that can be readily converted into liquid fuels [2]. Liquid fuels are indispensable, especially in the transportation sector, because electrical energy is difficult to store and distribute. There have been many methods established to convert biomass into liquid fuels such as thermal, biological and physical processes. Fast pyrolysis is a thermal decomposition process which is conducted at moderate temperature (∼500 °C) and short reaction time (∼2 s) to give high yields of bio-oil [3]. Fast pyrolysis of biomass to bio-oil is one of the most efficient thermal processes to obtain liquid fuel from biomass and has already been demonstrated and semi-commercialized [4,5].

Although fast pyrolysis is a promising method to obtain bio-oil, the high content of oxygenated molecules in pyrolysis bio-oil is a problem. The high oxygen content in bio-oil results in low heating value, immiscibility with hydrocarbon fuels, and chemical and thermal instability [6,7]. Therefore, pyrolysis bio-oil must be upgraded to remove oxygen to obtain a satisfactory fuel oil. One promising upgrading method is hydrotreatment of bio-oil using hydrodeoxygenation (HDO) catalysts [8–10]. There have been many studies of HDO catalysts, for example, transition metal sulfides (e.g. NiMoS, CoMoS) [11], noble metals (e.g. Ru, Rh, Pd, and

Pt) [12,13] and base metals (e.g. Fe, Ni and Cu) [14]. However, problems of deactivation or expense, in the case of the noble metals, have also been reported for these catalysts [9,15,16].

Transition metal phosphides of base metals have recently attracted attention as HDO catalysts [17,18]. In particular, nickel phosphide has been shown to be a highly active catalyst for HDO of model compounds such as guaiacol [19], dibenzofuran [20], and 2-methyltetrahydrofuran (2-MTHF) [21]. Advanced methods such as extended X-ray absorption fine structure (EXAFS) have been used for structural characterization including in situ analysis during reactions [22,23]. Many studies over nickel phosphide catalysts have been conducted to elucidate the reaction mechanism of HDO on these model compounds. Differing from these fundamental studies, in this research, nickel phosphide catalysts were used for the hydrotreatment of an actual pyrolysis oil.

A two-stage reactor consisting of a pyrolyzer and a catalytic reformer is effective and practical for vapor phase upgrading [24,25]. In this process, pyrolyzed vapor is introduced directly to the catalytic reactor and upgraded bio-oil is obtained continuously. This two-stage process is sometimes called 'ex situ catalytic fast pyrolysis', while catalytic fast pyrolysis conducted in one pyrolyzer that contains a catalyst is called 'in situ catalytic fast pyrolysis' [26]. Because the term "in situ" for catalysis studies refers to examination of catalysts in their working state, here the term "two-stage reactor" will be used for the ex situ system.

Two-stage catalytic fast pyrolysis using H-ZSM-5 zeolite has been conducted and a decrease in oxygenated compounds in the resulting bio-oil was reported, though the oil yield also decreased from 34 wt% to 27 wt% [27]. A Co doped ZSM-5 zeolite was also tested, and in this case, the oil yield decreased from 37 wt% to 17 wt%, while the oxygen content also decreased from 39 wt% to 28 wt% [28]. As described above, the catalyst studies for bio-oil synthesis via two-stage catalytic fast pyrolysis have mainly focused on zeolites or mesoporous materials, but the results obtained are not sufficient for bio-oil processing because of the limited deoxygenation activity or rapid catalyst deactivation [29–32]. Therefore, there is a need for more research on HDO catalysts.

In this study, the effectiveness of nickel phosphide catalysts for the upgrading of actual pyrolysis oil was investigated using a two-stage reactor. At first, the activity of a $Ni_2P/SiO_2$ catalyst for HDO was verified using the model compound 2-MTHF at the conditions of the pyrolysis oil treatment of 350 °C and atmospheric pressure. Then, a laboratory-scale, two-stage reactor at atmospheric pressure (hydrogen partial pressure 0.06 MPa) was used for fast pyrolysis and successive catalytic upgrading. The work here departs from conventional studies in that hydrogen was used in the pyrolysis reactor, rather than an inert gas, in order to make possible subsequent catalytic upgrading. The deoxygenation activity of a $Ni_2P/SiO_2$ catalyst toward pyrolysis bio-oil was investigated and compared to other metal catalysts and also acid catalysts.

## 2. Experimental

### 2.1. Materials

The precursors for $Ni_2P/SiO_2$ and $Ni/SiO_2$ catalysts were provided by Japan Gas Chemical Catalysts and Chemicals Ltd. (JGCCC). The nickel content of both $Ni_2P/SiO_2$ and $Ni/SiO_2$ catalysts was 1.16 mmol/g-support. The silica–alumina and FCC-catalysts were also provided by JGCCC. A ZSM-5 zeolite of Si/Al ratio 1500 (HSZ-890HOA) was obtained from the Tosoh Nikkemi Corporation and was also employed as support material for $Ni_2P$. The chemicals $Ni(NO_3)_2 \cdot 6H_2O$ (Sigma–Aldrich, 99.999%), $(NH_4)_2HPO_4$ (Sigma–Aldrich, >99.0%), $HNO_3$ (TCI, 67%), and the catalyst 5 wt% Pd/C (Sigma–Aldrich) were used as received. The chemicals used as

reactants were 2-methyltetrahydrofuran (Sigma–Aldrich, >99.0%) and benzene (TCI, >99.0%).

### 2.2. Catalyst preparation

The $Ni_2P/SiO_2$, $Ni_2P/ZSM-5$, and $Ni/SiO_2$ catalysts were synthesized by temperature-programmed reduction (TPR) of supported precursors. The precursor of $Ni_2P/ZSM-5$ was prepared by incipient wetness impregnation and subsequent calcination. An aqueous solution for impregnation was prepared by dissolving $(NH_4)_2HPO_4$ and $Ni(NO_3)_2 \cdot 6H_2O$ in distilled water. The amount of water was determined to be equal to the pore volume of the ZSM-5 (0.18 $cm^3/g$). The nickel content was 1.16 mmol/g-support, and the initial P/Ni molar ratio was 2, similar to those of the $Ni_2P/SiO_2$ and $Ni/SiO_2$ precursors. The extra phosphorus is needed for complete phosphidation [33,34] and improved dispersion [35] of the catalyst. Part of the excess P is volatilized as $PH_3$ during reduction [36] and part remains as hydrogen phosphates on the support [37]. For example, for 10 g of ZSM-5, 3.06 g $(NH_4)_2HPO_4$ and 3.37 g $Ni(NO_3)_2 \cdot 6H_2O$ were dissolved in 1.8 g of distilled water. A small amount of $HNO_3$ aqueous solution (67%) was added to the mixture until the precipitate formed in the solution was dissolved. The amount was 2.5 mL for the case of 10 g of ZSM-5. The obtained transparent green solution was used to impregnate the ZSM-5 support, which was dried at 120 °C for more than 10 h. Then, the impregnated support was dried at 120 °C for 12 h and calcined at 500 °C for 4 h. After the calcination, the precursor was pelletized and sieved to a size of 650–1180 μm.

The TPR was conducted at the same conditions for $Ni_2P/SiO_2$, $Ni_2P/ZSM-5$ and $Ni/SiO_2$ catalysts. A quantity of 10 g of precursor was reduced at one time. A flow of 33 vol% $H_2/N_2$ at a flow rate of 0.15 L/min g-precursor was used, and the temperature was raised to 600 °C for $Ni_2P/SiO_2$ and $Ni_2P/ZSM-5$ and 500 °C for $Ni/SiO_2$ at a heating rate of 3 °C/min. The final temperature was maintained for 2 h, after which the samples were cooled to room temperature in $N_2$ flow. The gas was then changed to 0.5 vol% $O_2/N_2$ at a flow rate of 1 L/min and the catalysts were passivated for 4 h.

### 2.3. Catalyst characterization

X-ray diffraction (XRD) analysis was conducted to determine the crystal structure of the catalysts. The diffractometer (Rigaku, RINT-2400) was operated with Cu Kα monochromatized radiation generated at 40 kV and 100 mA. Scans were obtained at a speed of 2°/min with step width of 0.02° for 2θ values from 10° to 80°.

Transmission electron microscopy (TEM) images of $Ni_2P/SiO_2$ and $Ni/SiO_2$ were taken to observe the morphology of supported nanoparticles using a JEOL JEM 2000EXII microscopy at 200 kV. A carbon-coated copper grid was used as a substrate and the catalyst was dispersed in ethanol and put on the grid.

The Brunauer–Emmett–Teller (BET) specific surface area and pore volumes were calculated from isotherms of nitrogen adsorption at liquid nitrogen temperature obtained using a BELL Japan Bellsorp-mini II. Before the measurement, samples were pretreated at 200 °C in vacuum for 2 h.

X-ray photoelectron spectroscopy (XPS) measurements were carried out using a JEOL JPS-9000 instrument with a Mg Kα X-ray source and a spherical section analyzer. For the measurement, the catalyst samples were ground and pelletized (diameter: 10 mm, thickness: c.a. 1 mm).

### 2.4. Study of catalytic activity with a model compound

Activity measurements using the model compound 2-methyltetrahydrofuran (2-MTHF) were conducted in a tubular fixed-bed reactor (quartz, inner diameter of 0.8 cm) at atmospheric