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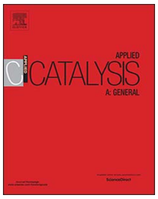

Research Paper

Hydrodeoxygenation of guaiacol over Ni_2P/SiO_2–reaction mechanism and catalyst deactivation

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ABSTRACT

The catalytic hydrodeoxygenation of guaiacol, a phenolic model compound of biomass lignin pyrolysis products, has been investigated under atmospheric pressure in H_2 utilizing a Ni_2P/SiO_2 catalyst. Reaction networks are proposed based on the product distribution as a function of contact time and the temperature programmed surface reaction of adsorbed guaiacol and anisole. Guaiacol is mainly converted to benzene through demethoxylation and dehydroxylation via phenol and anisole as intermediates. Demethylation of guaiacol is a side-reaction, which produces small amounts of catechol. Spent catalyst samples were characterized by means of XRD, XPS, TEM, and temperature programmed oxidation to gain understanding the observed slight deactivation. Coke deposition, sintering, and the altering properties of Ni and P species on catalyst surface all contribute to deactivation, while there is no indication of surface oxidation after reaction. The increase of $Ni^{\delta+}$ or Ni^0 on the Ni_2P surface and the decrease of Brønsted acid sites (i.e. P—OH) are considered to be the major reasons of product distribution changes.

1. Introduction

Population and economic growth are energy demanding processes. A significant percentage of the needed energy is still covered by fossil resources, whose combustion raises environmental concerns by increasing the carbon footprint [1–4]. Therefore, renewable sources of energy and carbon are needed. Biofuels are emerging as a promising alternative to fossil fuels, as they are renewable and contribute to lower CO_2 emissions [1,3,4]. A common approach to obtain liquid fuels from biomass is pyrolysis, which yields an oxygen-rich bio-oil (10–45 wt%) low in stability and heating value, high in viscosity, and immiscible with hydrocarbon fuels [1,5–7]. To convert such bio-oils into useful fuels, a significant part of the oxygen must be removed by Hydrodeoxygenation (HDO). Noble metal [8–11] and transition metal sulfide [12–16] catalysts have been explored for this purpose. Noble metals are rather expensive and they catalyze hydrogenation of aromatic rings [4,17,18], which is undesired in fuel production. Metal sulfides suffer from deactivation due to oxidation or hydrolysis of the active phase unless a sulfiding agent is added [1,6,19,20]. Thus, it is imperative to find alternative catalysts for HDO applications in bio-oil upgrading.

Transition metal phosphides have attracted attention in the last two decades, as they perform well in hydrodesulfurization and hydrodenitrogenation reactions [21–23]. More recently, metal phosphides were also used as catalysts in HDO reactions [2,3,24,25], such as that of guaiacol. Guaiacol is a suitable model compound, as it contains phenolic hydroxyl and methoxy groups like many degradation products of lignocellulose [2,3,25,26]. Oyama et al. investigated the HDO reaction of guaiacol over metal phosphides in a fixed-bed reactor at 300 °C and at atmospheric pressure [3]. Among Ni_2P, Co_2P, MoP, Fe_2P and WP, silica supported Ni_2P showed the highest activity and selectivity towards benzene. Co_2P and WP catalysts converted guaiacol to phenol and benzene via catechol as intermediate, which was argued to be not desirable due to its predisposition towards coke formation. Using Ni_2P catalysts, only anisole and cresol were observed as intermediates. In another study, Oyama et al. [2] investigated the guaiacol HDO reaction at atmospheric pressure over Ni_2P, which was prepared on various support materials, such as SiO_2, ZSM-5, amorphous silica-alumina (ASA) and a fluidized catalytic cracking (FCC) support consisting of USY zeolite embedded in a silica-alumina matrix. The reaction temperature was chosen between 425 and 450 °C, as pyrolysis oil is produced in this temperature range. Catechol accounted for 24% of the products at a conversion rate of 80% on Ni_2P/SiO_2. With increasing Lewis acidity of the support, more catechol was produced. The product distribution when using Ni_2P/ASA suggested that guaiacol was

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converted to phenol via catechol as intermediate. Wu et al. investigated the effect of the support material (Al_2O_3, ZrO_2, SiO_2) on Ni_2P in the guaiacol HDO reaction at 300 °C and atmosphere pressure [24]. Lewis acidic supports (Al_2O_3, ZrO_2) did not only promote coke formation, but did also hinder the formation of the Ni_2P phase due to their strong interaction with phosphorus. Catechol was found to be the major product on Ni_2P/Al_2O_3, Ni_2P/ZrO_2 and Ni_2P/SiO_2 at a guaiacol conversion below 15%. In another study of Wu et al. [25], high yields of catechol (20%) and 1, 2-dimethoxybenzene (37%) were obtained over Ni_2P/SiO_2 at low conversion around 10%.

As different intermediates (e.g., anisole, cresol, catechol, 1, 2-dimethoxybenzene) are observed in the guaiacol HDO, different reaction networks were proposed [2,3,24,25]. In order to gain systematical insight into the reaction mechanism, we did a kinetic analysis of the guaiacol HDO and a temperature programmed surface reaction (TPSR) of guaiacol over Ni_2P/SiO_2. Similar investigations were also done with anisole, the intermediate product in the guaiacol HDO, which have not been reported in previous studies [2,3,24,25]. The TPSR study is, for the first time, applied as a supporting technique for the investigation of reaction mechanism.

We also investigated the origin of catalyst deactivation in more detail. The related discussions in previous works are only developed on the base of XRD characterization [1,24]. In present work, we expand the investigation of catalyst deactivation by using XPS, TEM, and temperature programmed oxidation (TPO) techniques.

2. Experimental section

2.1. Materials and preparation

Commercial silica (silica gel Davisil, particle diameter 90 125 um, S_{BET} = 305 m^2/g) was used as support. $Ni(NO_3)_2·6H_2O$ (Aldrich, 97%) and H_3PO_3 (Aesar, 98%) were used as received to prepare the silica-supported Ni_2P catalyst. HF (VWR, 40%) and HNO_3 (VWR, 65%) were used to prepare solutions for ICP measurements. Catalysts were synthesized according to the method described in our previous study using H_3PO_3 as the source of phosphorus and 450 °C as the reduction temperature [27]. These preparation conditions are proved to generate Ni_2P/SiO_2 catalysts with high activity and stability in thiophene hydrodesulfurization [27]. Specifically, the catalyst precursor was obtained by incipient wetness impregnation of the silica support with an aqueous solution of $Ni(NO_3)_2$ and H_3PO_3. After impregnation, the solid was dried overnight in air at 110 °C. The precursor was reduced at 450 °C for 1 h after heating from room temperature at a rate of 5 °C/min in H_2. The precursor is labeled $Ni(NO_3)_2$-PO_3; the reduced sample Ni_2P/SiO_2. The atomic P/Ni ratio in the precursor is 2.

2.2. Characterization

Metal loading was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis done with a SpectroBlue CCD ICP optical emission spectrometer with axial plasma viewing. Prior to the measurements, around 20 mg sample were heated in a mixture of $HF/HNO_3/H_2O$ (volume ratio1:1:1) until a clear solution was obtained. X-ray diffraction (XRD) patterns were acquired on a Bruker D2 Phaser powder diffraction system using Cu Kα radiation (1.5486 Å) at a voltage of 30 kV and a current of 10 mA. Scans were taken at a rate of 1°/min in the range of $10° \leq 2\theta \leq 80°$. The size of the Ni_2P particles was investigated on a FEI Tecnai 20 transmission electron microscopy (TEM).

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific K-Alpha XPS apparatus equipped with a monochromatic X-ray source (Al Kα = 1486.6 eV). Samples were reduced and sealed in a tubular quartz reactor, transferred to a glovebox without exposure to air, then loaded in an airtight transfer vessel and introduced into the XPS UHV chamber for analysis. The background pressure prior to analysis was 2×10^{-9} mbar. Survey scans were collected at constant pass energy of 200 eV, and region scans at 50 eV. The spectra were calibrated to the Si 2p line at 103.3 eV and fitted with the Casa XPS program.

Temperature programmed desorption (TPD) and temperature programmed surface reaction (TPSR) measurements were performed in a quartz tube reactor. Typically, 15 mg sample were loaded into the reactor and reduced in situ using the same procedure as during catalyst activation prior to the HDO reaction. The reduced sample was cooled to 50 °C and purged with He for 1 h. Adsorption of guaiacol and anisole were done at 50 °C by flushing the catalyst with a guaiacol/He or anisole/He mixture for 1 h, followed by purging with He for 1 h to remove physisorbed guaiacol or anisole. After the adsorption pretreatment, TPD measurement was done by heating samples at a rate of 5 °C/min in a He flow (50 ml/min); TPSR was carried out by heating samples in a H_2/He flow (10 vol%, 50 ml/min) at a rate of 5 °C/min. Temperature programmed oxidation (TPO) of spent catalysts was done by heating samples in a 50 ml/min flow of 10 vol% O_2/He at a rate of 10 °C/min. The effluent flow of the temperature programmed measurements was monitored by mass spectrometry (Pfeiffer Vacuum, QMG422); m/e signals at 78 (benzene), 94 (phenol), 84 (cyclohexane), 108 (anisole), 124 (guaiacol), 110 (catechol), 28 (CO), 44 (CO_2) were collected.

2.3. Catalytic activity measurements

Catalyst testing was done in a continuous fixed-bed reactor with 4 mm internal diameter. Guaiacol (or anisole) was fed by a syringe pump (Hewlett Packard 1050) and evaporated at 170 °C using H_2 as carrier gas before entering the reactor. Prior to reaction, catalysts were reduced in situ in H_2 at 450 °C. During this operation, the reactor effluent was directed to an exhaust line to avoid phosphorus deposition in the analysis section of the setup. After reduction, guaiacol/H_2 or anisole/H_2 mixtures with a molar ratio of 1/50 were fed into the reactor and the effluent from reactor was switched to the gas phase analysis system.

About 60 mg precursor was typically used and the H_2/reactant ratio was kept at 50 for all reactions. The product composition was analyzed by gas chromatography equipped with a flame ionization detector (GC-FID) and a DB-1 (30 m, 0.32 mm, 1.00 μm) column. Catalytic reactions were carried out at 250 °C, 300 °C, and 350 °C at atmosphere pressure. The contact time W/F (h) was defined as the ratio of catalyst mass (g) to the reactant feed flow rate (g/h). In a standard experiment, a W/F of 0.5 h was employed, involving H_2 flow, feed rate and catalyst loading of 20 ml/min, 0.002 ml/min, and 60 mg, respectively. The conversion and yield are defined as

$$X = \frac{(mol\ \ of\ \ guaiacol)_{in} - (mol\ \ of\ \ guaiacol)_{out}}{(mol\ \ of\ \ guaiacol)_{in}} \times 100\%$$

$$S_{aromatic}(i) = \frac{mol\ \ of\ \ product\ \ i}{mol\ \ of\ \ aromatic\ \ products} \times 100\%$$

$$S_{C1}(j) = \frac{mol\ \ of\ \ product\ \ j}{mol\ \ of\,(methanol + methane)} \times 100\%$$

$$Y(i) = conversion \times S_{aromatic}(i)$$

with i and j denoting aromatic and C1 products, respectively.

3. Results

3.1. Catalyst characterization

Table 1 reports the nickel and phosphorus content in the precursor as determined by ICP element analysis. The atomic P/Ni(ICP) ratio is 2, the targeted value in the preparation. The BET surface area of the unreduced precursor is 241 m^2/g, which is lower than the surface area of