Journal of the Taiwan Institute of Chemical Engineers 000 (2017) 1–8

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Hydrodeoxygenation of 4-methylguaiacol over silica-supported nickel phosphide catalysts: The particle size effect

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ARTICLE INFO

Article history:
Received 5 October 2016
Revised 3 February 2017
Accepted 12 February 2017
Available online xxx

Keywords:
Nickel phosphide
Hydrodeoxygenation
Particle size effect
4-methylguaiacol

ABSTRACT

Lignin is a natural-made heteroaromatic polymer, which can be transformed into bio-based aromatics. Catalytic hydrodeoxygenation (HDO) depolymerizes lignin through selective oxygen extraction. This study investigated HDO of 4-methylguaiacol, a lignin model compound, over silica-supported nickel phosphide catalysts with controlled scale of active site. Catalyst characterizations, including N_2 physisorption, ICP, XRD, TEM, XPS, H_2-TPR, NH_3-TPD, CO chemisorption, CO-TPD, and H_2-TPD, were performed. HDO of 4-methylguaiacol was conducted in a H_2-pressured, batch-type reactor, and the reaction network was proposed. The H_2 uptake of Ni_2P was discovered to play a key role in mediating reaction routes such as demethoxylation and hydrogenation in the reaction network. Therefore, nickel phosphide catalyst is deemed to have particle size effect in 4-methylguaiacol HDO.

1. Introduction

Transforming abundant, renewable lignocellulosic biomass into fuels and chemicals alleviates our fossil fuel addiction. Among the three major components (cellulose, hemicellulose, and lignin) of lignocellulosics, lignin is a potential feedstock for aromatic synthesis. Catalytic hydrodeoxygenation (HDO) is promising in lignin and its derivatives (*e.g.*, bio-oils) upgrading [1].

HDO is a process by which oxygen-containing feedstocks can be selectively reduced by hydrogen, yielding water as the major byproduct. High H_2 partial pressures (2–20 MPa) and moderate temperatures (200–300 °C) are usually required. To overcome hydrogen deficiency in biorefineries, atmospheric- [2–4] or low-pressure [5–7] HDO process and using liquid hydrogen sources (such as formic acid and decalin) for in situ H_2 generation [8–13] are investigated. Detailed reaction conditions and exploited catalysts in lignin HDO can be found in earlier reviews [1,14–16].

Using a model compound as lignin representative is necessary to understand HDO chemistry at molecular level. Guaiacol ($C_7H_8O_2$), anisole (C_7H_8O), and cresol (C_7H_8O) are the most encountered lignin representatives because they contain functional groups of lignin structure, such as methoxyl and hydroxyl, and are frequently identified in bio-oils [17]. Applying these species in HDO allows us to understand how the functional groups evolved, making it possible to correlate the nature of HDO catalyst and its performances.

Transition metal phosphide catalysts, *e.g.*, Ni_2P and MoP, were recently deployed in HDO of lignin fragments because of its effectiveness in analogue reactions like hydrodesulfurization [18] and hydrodenitrogenation [19]. The acidic/metallic nature of metal phosphide acts as a bifunctional center: the metal site mediates C_{aryl}–O hydrogenolysis and hydrogenation, while acid site (*e.g.*, Brønsted acids of phosphorous) promotes dehydration and transalkylation [3,4,20,21]. Ni_2P is effective in HDO of lignin derivatives. Oyama et al. [2] surveyed a series of SiO_2 supported transition metal phosphides (including Ni_2P, Co_2P, Fe_2P, WP, and MoP), and found that Ni_2P is the most active in guaiacol HDO. Ni_2P/SiO_2 also possessed a better durability than commercial Pd/Al_2O_3 and sulfided $CoMo/Al_2O_3$ catalysts due to its superior coke resistance. The Chen group [22,23] investigated effects of crystalline size and Mo substituted Ni_2P in methyl laurate and anisole HDO. Small Ni_2P size had a negative impact on HDO activity due to strong interaction between Ni and P [23]. Doping Mo in Ni_2P could also hamper anisole conversion caused by the Mo-Ni interaction [22,24]. Our group investigated kinetics and mechanism of guaiacol HDO over Ni_2P supported on SiO_2, ZrO_2, and Al_2O_3 [3]. Using differential kinetic analysis, small Ni_2P particles are found to be intrinsic active in deoxygenation, while large Ni_2P clusters are prone to demethylation.

Compared to guaiacol and anisole, little attention has been paid on HDO of alkylated guaiacols, particularly 4-alkylguaiacols. The Lercher group employed a series of bifunctional catalysts, including Raney Ni + Nafion/SiO_2 [25], Pd/C + H_3PO_4 [26], and

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http://dx.doi.org/10.1016/j.jtice.2017.02.020
1876-1070/

Please cite this article as: P.-J. Hsu, Y.-C. Lin, Hydrodeoxygenation of 4-methylguaiacol over silica-supported nickel phosphide catalysts: The particle size effect, Journal of the Taiwan Institute of Chemical Engineers (2017), http://dx.doi.org/10.1016/j.jtice.2017.02.020

Pd/C + HZSM-5 [27] in HDO of 4-methylguaiacol to methylcyclohexane and methanol. They reported metal-promoted hydrogenation coupled with acid-promoted hydrolysis/dehydration can produce nearly 100% deoxygenated hydrocarbon products. Comparatively, 4-methylguaiacol HDO over sulfided $CoMo/Al_2O_3$ yielded mostly methylated phenols with trace ring-saturated products, suggesting demethylation and dehydroxygenation dominated [28].

4-alkylguaiacols are potential precursors of novel polymer monomers derived from lignin [29]. For example, alkylated caprolactone can be synthesized through asymmetric Baeyer–Villiger oxidation of 4-alkylcyclohexanone [30,31], a derivative of alkylated guaiacols through demethoxylation, hydrogenation, and dehydrogenation routes [29]. Moreover, steric effect caused by alkyl species can lead to different HDO results of alkylated guaiacols compared to non-alkylated counterparts [28]. Since most lignin fragments carry alkyl functionalities, an in-depth investigation of alkylated guaiacols HDO is necessary.

In this work, silica-supported Ni_2P with different dispersions were synthesized and tested in HDO of 4-methylguaiacol. By loading the same amount of nickel phosphide on silica with sequentially decreased surface area (*i.e.*, SBA-15, high-surface-area SiO_2, and low-surface-area SiO_2), the active site domain can be manipulated in an increasing order. Changing size of active phase varies partial positive charges of Ni cations ($Ni^{\delta+}$, known as the ensemble effect) [32,33] on the surface, making Ni_2P catalyst to have particle size effect in 4-methylguaiacol HDO.

2. Experimental

2.1. Chemicals

$Ni(NO_3)_2{\cdot}6H_2O$ (Alfa Aesar, 99%) and $(NH_4)_2HPO_4$ (J.T. Baker, 99%) were used as the precursors of nickel phosphide. The precursors were dissolved in deionized water as aqueous nickel phosphate solution with a Ni/P molar ratio of 0.5. A loading of 1.7 mmol Ni per gram of support (~12.6 wt% Ni_2P) was employed.

Low-surface-area silica (SiO_2-L, Cabosil L-90), high-surface-area silica (SiO_2-H, Alfa Aesar), and SBA-15 were used as the supports. SBA-15 was synthesized using the method developed by the Ryoo group [34]. In brief, 4.0 g of Pluronic P123 (Sigma-Aldrich) was dissolved in 76.0 g deionized water and 2.3 g of 37% hydrochloric acid at room temperature. After vigorous stirring, 8.6 g of tetraethoxysilane (TEOS, 99%) was added with continued stirring overnight. The mixture (TEOS: P123: HCl: $H_2O = 1: 0.016: 0.54: 100$ in molar ratio) was transferred to a bomb and treated in a hydrothermal condition at 100 °C for 24 h The collected paste was dried at 80 °C for 12 h and then calcined to 550 °C (3 °C/min) for 4 h

After impregnating aqueous nickel phosphate solution, the powder was dried at 120 °C for 1 h and calcined at 500 °C for 6 h The particles were reduced in an 80% H_2/N_2 stream (150 mL/min) from 30 to 670 °C (2 °C/min) and kept isotherm for 1 h. The reduction procedure transformed the phosphate into a phosphide [19]. After reduction, the sample was cooled to ambient temperature in a He stream (100 mL/min), and was passivated under a 2% O_2/He (40 mL/min) stream for 1 h.

2.2. Characterization of catalysts

N_2 physisorption was performed on a Micromeritics ASAP 2020 gas-adsorption analyzer at −196 °C. Approximately 0.1 g of a sample was dehydrated at 300 °C for 1 h prior to the measurement. Total surface area was calculated based on the Brunauer–Emmett–Teller (BET) method. Inductively coupled plasma-atomic emission spectrometry (ICP-AES, Kontron Model S-35) was used to measure the compositions of Ni and P. Powder X-ray diffraction (XRD) was conducted on a diffractometer (Rigaku D/Max-IIB) with Cu $K\alpha$ radiation, excited at 40 kV and 40 mA. High resolution transmission electron microscopy (HR-TEM) images were acquired using a JEOL JEM-2010 microscope at 120 kV. X-ray photoelectron spectroscopy (XPS) was performed using a Kratos Axis Ultra DLD equipped with a 180° hemispherical sector and a focused monochromatic Al-$K\alpha$ X-ray (1486.7 eV) source. Each sample was sputter-cleaned with an Ar^+ beam for 5 min prior to the measurement. Binding energy shift was corrected by using the C 1s signal of adventitious carbon at 284.6 eV. The XPS spectra were deconvoluted using a Nonlinear Curve Fit tool provided by Origin 8.1 using a Gaussian model. A Micromeritics Autochem II chemisorption analyzer with a thermal conductivity detector (TCD) was used to measure H_2-temperature-programmed reduction (TPR), H_2-temperature-programmed desorption (TPD), NH_3-TPD, and CO pulse chemisorption with subsequent CO-TPD. Before the test, each sample was dehydrated in a He stream (30 mL/min) for 1 h at 150 °C. Approximately 0.1 g of calcined precursors, *i.e.*, $Ni_xP_yO_z/SiO_2$, was tested in H_2-TPR using a 10% H_2/Ar stream (100 mL/min) from 100 to 1000 °C (5 °C/min). For the remaining temperature-programmed characterizations, approximately 0.1 g of passivated Ni_2P catalyst was pre-reduced at 450 °C for 1 h then cooled to 100 °C before the test. For NH_3-TPD, a 10% NH_3/He stream (30 mL/min) was used to flush the sample at 100 °C for 1 h. The NH_3-treated sample was then purged with He for 40 min at 100 °C to remove weakly adsorbed NH_3. NH_3-TPD was measured from 100 to 700 °C at a rate of 10 °C/min in a He stream. CO chemisorption was performed at ambient temperature. Pulses of 10% CO/He were repeatedly injected into the system until achieving a breakthrough. The CO uptake was calculated based on the difference of the sum of pulse areas between a tested catalyst and a known volume. The CO-TPD was executed immediately after CO pulse chemisorption with a 15 °C/min heating rate in a He stream.

2.3. HDO activity evaluation

Reactivity tests were performed in a 300 mL stirred-batch autoclave (Parr Model 4561). The temperature was set at 250 °C with an agitation rate of 500 rpm. Approximately 60 mL solvent (n-hexadecane), 1.5 mL reactant (4-methylguaicol or cresol), and 0.1 g passivated catalyst (200–120 mesh; 0.074–0.125 mm) were used per trial. After transferring the mixture of solvent, reactant, and catalyst into the system, the autoclave was flushed with an Ar stream (60 mL/min) for 10 min and then purged with a H_2 stream (60 mL/min) for 30 min to expel residual air. Once the reaction temperature was achieved, the system was pressurized to 4 MPa with H_2. Different reaction time periods, ranging from 1 to 10 h, were used. Gaseous products, mostly methane and methanol, were analyzed by a parallel-dual-column gas chromatography (GC, SRI 8610C) with a 60-m MXT-1 capillary column and a HayeSep D packed column; liquid compounds including toluene (C_7H_8), methylcyclohexane (C_7H_{14}), cresol, 4-methylcyclohexanol ($C_7H_{14}O$), guaiacol, 2,4-dimethylphenol ($C_8H_{10}O$), 3-methylanisole ($C_8H_{10}O$), and 4-methylguaiacol were analyzed by a GC–MS (Agilent 5890, DB-5MS capillary column, 60 m × 0.25 mm). Internal and external mass transfer resistances of tested catalysts were examined with different catalyst particle sizes and stirring rates (see Figs. A1 and A2 of Appendix). Both resistances were negligible. Deposited coke was analyzed using the weight loss of spent catalyst by a thermogravimetric analyzer (TA Q600). The sample was dried in a 10% O_2/He stream at 150 °C for 30 min, followed by a 10 °C/min heating rate to 600 °C to burn out residual coke.

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