



# Kinetics of the hydrodeoxygenation of cresol isomers over Ni<sub>2</sub>P/SiO<sub>2</sub>: Proposals of nature of deoxygenation active sites based on an experimental study



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## ABSTRACT

The hydrodeoxygenation of cresols (m-cresol, p-cresol and o-cresol) over Ni<sub>2</sub>P/SiO<sub>2</sub> was carried out between 250 and 340 °C under high hydrogen pressure (between 1.6 and 3.2 MPa). XRD demonstrated that the desired Ni<sub>2</sub>P phase was obtained at 450 °C using 4 MPa of H<sub>2</sub>. The catalytic behavior of Ni<sub>2</sub>P/SiO<sub>2</sub> for the transformation of cresols indicated that these compounds were deoxygenated by two different pathways, which involved different reactions such as hydrogenolysis, hydrogenation, dehydration and isomerization. Using these experimental conditions, i.e. under hydrogen pressure, the catalyst used exhibited a remarkable stability, at least during 20 h. An effect of the position of the methyl group in cresol isomers was highlighted, m-cresol being the most reactive whereas o-cresol the less reactive. In addition, an increase of temperature and hydrogen pressure allowed to ensure a high deoxygenation degree of phenolic reactants even at low level of conversion (less than 20%). The participation of different active sites and adsorption modes were proposed to explain the different products observed and their distribution.

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## 1. Introduction

The use of lignocellulosic biomass as a renewable and sustainable source of energy is of growing importance due to the increasing attention on environmental concerns. Such raw materials could be transformed into chemicals and biofuels in a biorefinery [1–4]. The first step required is its depolymerization which can be carried out by several processes, including fast pyrolysis [3,5,6]. The bio-oil produced by fast pyrolysis has to be upgraded by hydrodeoxygenation (HDO) in order to reduce its oxygen content, leading to an oil with better physical and chemical properties such as higher heating values, lower viscosity, stability, pH values, and combustion properties compared to the crude bio-oil [7–11].

The type of catalyst play a key role on the HDO process. Conventional metal sulfides were extensively studied in such reactions due to their great importance in sulfur removal in oil processing

[6,12–14]. Despite of their high activity in deoxygenation, sulfided catalysts have a drawback to process bio-oil since a sulfiding agent must be added to the reactant feed to keep the solid active and stable during the reaction, which could produce undesirable S-containing compounds in the final products [15–17]. Noble metal catalysts could be used as HDO catalyst due to their high activity in oxygen removal. [18–22]. Meanwhile, as they are highly expensive, their use for this purpose may be limited. Alternatively, the non-noble metal (e.g. Ni-based catalysts) are less costly than noble metal catalysts and also show acceptable deoxygenation performance [23–26]. However, Ni-based catalysts are known to promote secondary reactions like hydrogenolysis of C–C bond, methanation and decarbonylation, which results in a loss of carbon and a higher consumption of hydrogen. Transition metal phosphides have been proposed as catalysts for HDO of bio-oil [27–30]. The advantages of transition metal phosphides compared to other catalysts used in HDO are low cost when compared with noble metal catalysts, and the low selectivity for other reactions than deoxygenation with respect to non-noble metal catalysts [31–33].

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Recent studies on deoxygenation of various phenolic model compounds such as phenol [34–36], guaiacol [37–41] and *p*-cresol [42,43] have shown that nickel phosphide based catalysts are effective catalysts in HDO. Zhao et al. [37] investigated the HDO of guaiacol under atmospheric pressure and 300 °C and found Ni<sub>2</sub>P/SiO<sub>2</sub> to be more active to deoxygenation than a metallic phase (Pd/Al<sub>2</sub>O<sub>3</sub>) and a sulfide phase (CoMo/Al<sub>2</sub>O<sub>3</sub>). In addition, the same authors reported the HDO activity for different phosphide phases followed the order: Ni<sub>2</sub>P/SiO<sub>2</sub> > Co<sub>2</sub>P/SiO<sub>2</sub> > Fe<sub>2</sub>P/SiO<sub>2</sub> > WP/SiO<sub>2</sub> > MoP/SiO<sub>2</sub>. Indeed, nickel phosphide appeared as the most promising phosphide phase for HDO of various model oxygenated compounds [32,36,37,44,45], attributed to a higher *d*-electron density of the Ni<sub>2</sub>P phase compared to other phosphide phases [45] but also to the presence of phosphorous that provides “ligand” (or electronic) and “ensemble” (or geometrical) effects on metal sites [39,45,46]. In fact, the ligand effect of P increases the electrophilicity of metal sites favoring the adsorption of oxygenated model compound, facilitating the C–O bond scission [31,45]. In general, catalytic behavior of different transition metal phosphides are interpreted in terms of the electron property of metal site, solid acidity or a combination of both [47]. Another interesting fact is the greater stability of phosphides compared to their parent metals. Indeed, during the HDO of anisole (1.5 MPa and 300 °C), Li et al. [45] assigned the higher stability of Ni<sub>2</sub>P/SiO<sub>2</sub> compared to Ni/SiO<sub>2</sub> to the ligand effect given by P species, which would inhibit the combination of Ni with O and makes nickel phosphide catalyst more stable.

There are different reaction routes proposed for the HDO of phenol and alkylated phenols: direct deoxygenation (DDO) route; hydrogenation followed by dehydration (HYD) and tautomerization. The contribution of each route in the distribution of products is highly dependent on the nature of the active phase, as highlighted in recent reviews [7,10,14]. Over sulfided molybdenum-based catalysts, aromatics were favored over CoMoS phase, whereas the products formed by the HYD route (cycloalkenes and cycloalkanes) were predominated over both MoS<sub>2</sub> and NiMoS phases (under 4–7 MPa, 250–340 °C) [48–51]. Using noble metal based-catalysts (i.e. Pd or Pt) under atmospheric pressure, aromatics appeared as the main deoxygenated products [20,21,52] meanwhile cycloalkanes were the main deoxygenated products under high pressure (10 MPa) [19]. In addition, oxophilic supports like ZrO<sub>2</sub> favored the selectivity to deoxygenated products due to the enhanced hydrogenation of the carbonyl function of the key intermediate suggested to be involved (phenolic tautomer) [20,21,52]. For the phosphide phases, the contribution of each deoxygenated route of phenolic compounds depended on the nature of the M<sub>x</sub>P catalyst (Ni<sub>2</sub>P, MoP, Fe<sub>2</sub>P, . . .) and the experimental conditions [34–36,42,43,53]. Regarding the most active phosphide phase (i.e. Ni<sub>2</sub>P), it was reported that bulk Ni<sub>2</sub>P yielded toluene as the main deoxygenated products from *p*-cresol [42], while methylcyclohexane appeared as the main deoxygenated product using the same reactant and under similar experimental conditions (325–350 °C, 4–4.4 MPa) [43]. Using phenol as model oxygenated molecule, the HYD route was also found to be predominant over different supported Ni<sub>2</sub>P catalysts at 220 °C under 4 MPa [36]. Nevertheless, using the same oxygenated substrate, a modification of the selectivity of Ni<sub>2</sub>P/SiO<sub>2</sub> was highlighted depending on the preparation method to obtain the phosphide phase [35]. These results show that the parameters which govern the selectivity of the Ni<sub>2</sub>P phase are not yet completely known and hence require further investigation.

Therefore, the goal of this work was to investigate the catalytic properties of Ni<sub>2</sub>P/SiO<sub>2</sub> catalyst for the hydrodeoxygenation of cresol isomers as model oxygenated compounds under high pressures of hydrogen (between 1.6 and 3.2 MPa) at temperatures between 250 and 340 °C. The different pathways involved during the transformations of such model molecules were carefully con-

sidered, in particular by using a kinetic model. The nature of active sites present on the nickel phosphide phase and reaction mechanisms were also discussed.

## 2. Experimental

### 2.1. Materials and chemicals

Silica was provided by Sigma-Aldrich. Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Merck), (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> (Vetec) and HNO<sub>3</sub> (Merck) were used as precursors during the synthesis of the catalyst. The chemicals used for the reaction study (*o*-cresol, *p*-cresol, *m*-cresol, *n*-heptane and *n*-dodecane) were also purchased from Sigma-Aldrich. All chemicals were used without further purification. H<sub>2</sub> was provided by Air Liquide.

### 2.2. Catalyst synthesis

Prior to impregnation, silica was calcined under air flow at 800 °C for 5 h. The support was impregnated by nickel phosphide precursors using incipient wetness impregnation method (IWI), according to the procedure described by Yang et al. [31]. A solution containing the amounts of (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O required to obtain a Ni/P molar ratio of 2/1.6 and a nickel loading of 10 wt% was used. After impregnation, the solid sample was calcined under air at 500 °C for 3 h (2 °C min<sup>-1</sup>).

### 2.3. Catalyst characterization

The chemical composition of the solid sample containing Ni<sub>2</sub>P precursors was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using a SPECTRO ARCOS ICP-OES instrument. For this analysis, the sample was digested with concentrated nitric acid and hydrofluoric acid using microwave heating system.

N<sub>2</sub> adsorption–desorption isotherms were measured on a Micromeritics ASAP 2000 analyzer at –196 °C. Prior to N<sub>2</sub> adsorption, the solid samples containing oxide precursors were degassed overnight under secondary vacuum at 200 °C. The specific surface area (*S*<sub>BET</sub> in m<sup>2</sup> g<sup>-1</sup>) was calculated from the adsorption isotherm (*P*/*P*<sub>0</sub> between 0.05 and 0.20) using the Brunauer-Emmett-Teller (BET) method. The total pore volume was calculated from the adsorbed volume of nitrogen at *P*/*P*<sub>0</sub> equal to 0.99. The mesoporous volume was determined using the *t*-plot method. The average mesopore-size distribution was calculated from the adsorption isotherm branch using the Barret-Joyner-Halenda (BJH) method.

X-ray diffraction (XRD) pattern of the catalyst was collected between 2θ = 20 and 80° using a PAN-alytical EMPYREAN powder diffractometer using Cu-Kα monochromatized radiation source (Kα = 1.54059 Å). Phase identification was performed by comparison with the ICDS database reference files. The crystallite size (*D*<sub>c</sub>) of Ni<sub>2</sub>P particles was estimated by the Scherrer equation (Eq. (1)), as already reported [54]:

$$D_c = K\lambda / (\beta \cos\theta) \quad (1)$$

where *K* is the Scherrer constant (0.9), λ is the wavelength of the X-ray radiation (1.54059 Å), β is the width of the peak at half-maximum (FWHM) and θ is the Bragg angle. Prior to analysis, the nickel phosphide phase was obtained by performing the reduction of the catalyst in situ at 450 °C (5 °C min<sup>-1</sup>) under 4 MPa as total pressure during 2 h using pure hydrogen (4.7 NL h<sup>-1</sup>). After activation in situ, samples were cooled down under hydrogen until 25 °C and passivated at this temperature under atmospheric pressure for 3 h by a flow of 5 vol.% O<sub>2</sub> in He (80 mL min<sup>-1</sup>).

In order to estimate the number of active sites and hence to calculate TOF values, CO chemisorption was performed at 30 °C. It was

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