



# Thermocatalytic conversion of lignin in an ethanol/formic acid medium with NiMo catalysts: Role of the metal and acid sites

Mikel Oregui-Bengoechea<sup>a,\*</sup>, Inaki Gandarias<sup>b</sup>, Nemanja Miletic<sup>b,c</sup>, Sveinung F. Simonsen<sup>a</sup>, Audun Kronstad<sup>a</sup>, Pedro L. Arias<sup>b</sup>, Tanja Barth<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Bergen, Norway, Allegaten 41, N-5007 Bergen, Norway

<sup>b</sup> Department of Chemical and Environmental Engineering, School of Engineering, University of the Basque Country (EHU/UPV), C/Alameda Urquijo s/n, 48013 Bilbao, Spain

<sup>c</sup> Department of Food Technology, Faculty of Agronomy, University of Kragujevac, Cara Dušana 34, 32000 Čačak, Serbia

## ARTICLE INFO

### Article history:

Received 23 February 2017

Received in revised form 31 May 2017

Accepted 3 June 2017

Available online 4 June 2017

### Keywords:

Lignin  
Formic acid  
NiMo catalyst  
Alumina  
Zirconia

## ABSTRACT

NiMo catalysts supported on different sulfated and non-sulfated aluminas and zirconias were studied for the catalytic conversion of lignin in a formic acid/ethanol medium. All the pre-reduced NiMo-support combinations resulted in high conversion of lignin into bio-oil, with over 60% yield (mass%). The NiMo-sulfated alumina catalyst exhibited the highest activity among all the catalysts studied. The overall reaction mechanism of the catalytic lignin conversion was found to be especially complex. The oil yield and its properties are affected by a combination of successive catalytic reactions that are part of the lignin conversion process. Lignin is first de-polymerized into smaller fragments through the cleavage of the aliphatic ether bonds. This reaction can be either catalyzed by Ni<sup>0</sup> species and strong Lewis acid sites within the alumina supports. In the presence of both active species, the Ni<sup>0</sup> catalyzed ether bond cleavage is the prevailing reaction mechanism. In a second step, the smaller lignin fragments can be stabilized by catalytic hydrodeoxygenation (HDO) and alkylation reactions that hinder their re-polymerization into char. Mo was found to be especially active for HDO reactions while all the catalysts studied exhibited significant alkylation activity. The final bio-oil yield is strongly dependent on the aliphatic ether bond cleavage rate; the contribution of those monomer stabilization reactions (i.e. HDO and alkylation) being secondary.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

The use of lignocellulosic biomass as a raw material for the production of renewable fuels and chemicals is growing rapidly. Consequently, there is an increasing interest in the development of integrated models for the efficient valorization of woody biomass (i.e. as lignocellulosic bio-refineries). Over the last decades, most of the effort has been focused on the development of more efficient lignocellulose pretreatment technologies and the subsequent conversion of the cellulose and hemicellulose fraction into bio-ethanol [1–3] and/or value-added chemicals [4]. In contrast, the third component, lignin, is mostly considered a waste and it is normally burned as a low value fuel [5]. However, the expected growth of the production of lignocellulosic-based products will demand the efficient valorization of the lignin sub-product and the conceptual

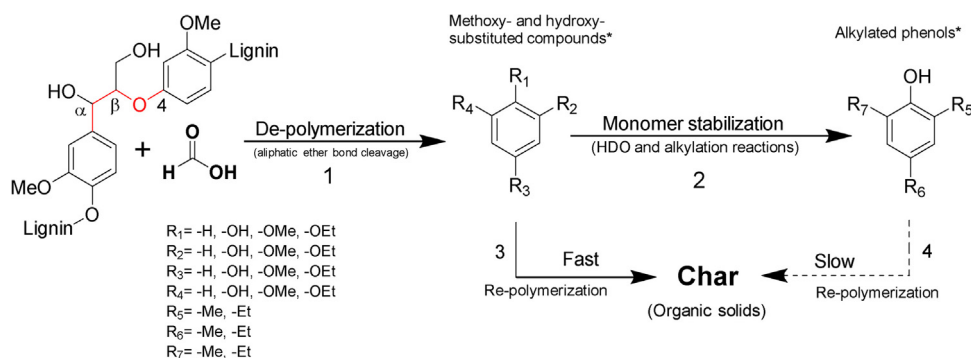
integration of its conversion processes in the so-called bio-refinery concept.

A plausible process that could meet these requirements is the recently developed LtL process [6,7]. Formic acid, one of the main sub-products from the cellulose and hemicellulose hydrolysis and sugar conversion processes [8,9], can react together with lignin in a water or ethanol media to yield a mono-aromatic based oil, with considerable chemical stability and low oxygen content. This process is carried out under severe reduction conditions: formic acid is decomposed mainly into CO<sub>2</sub> and H<sub>2</sub> providing high reaction pressures. Nevertheless, the LtL conversion requires high temperatures, in the range of 300–360 °C, and long residence times for complete lignin conversion. The process severity would imply a high cost at industrial scale, and at present, the oil yields and its quality are not sufficient to produce LtL oils competitive with traditional fossil-based products [10,11].

A possible option in order to decrease the process severity and simultaneously increase the LtL oil yield and quality – i.e. a higher H/C and lower O/C ratio- is the use of heterogeneous catalysts.

\* Corresponding author.

E-mail address: [mikel.oregui@ehu.eus](mailto:mikel.oregui@ehu.eus) (M. Oregui-Bengoechea).



**Scheme 1.** Sequential reaction scheme for the conversion of lignin into bio-oil. \* The term compounds may refer to both monomers and/or oligomers. This is an adapted scheme based on a previous study [29].

Recently Zhang and co-workers [12] described the most important catalytic routes for the conversion of lignin in a reductive environment (hydroprocessing), and the most relevant conversion mechanism were: (i) the catalytic hydrogenolysis of the aliphatic ether bonds of the lignin biopolymer and (ii) the catalytic hydrodeoxygenation (HDO) of the lignin monomers. For the catalytic hydrogenolysis of lignin, Ni-based catalysts are normally the preferred choice (e.g., Raney Ni, Ni/SiO<sub>2</sub>, Ni/activated carbon) [13–15]. In the case of HDO, nonetheless, three different types of catalysts have been studied: monometallic, bimetallic and bifunctional. The monometallic catalysts consist mainly of Mo-supported catalysts [12]. The bimetallic systems refer typically to the combination of mixed sulfides of Co, Ni, Mo and W. Nevertheless, sulfided catalysts are not entirely adequate since they increase the amount of sulfur containing compounds in the liquid products [12,16]. Bifunctional catalysts in turn contain both metal and acid sites [17]. Several combinations of hydrogenating (e.g. Ni Raney, Pd/C, Pt/Al<sub>2</sub>O<sub>3</sub>) and solid-acid catalysts (e.g. HZSM-5 and Nafion/SiO<sub>2</sub>) [18–20], or even bifunctional catalysts (e.g. Ru/HZSM-5, Ni/HZSM-5) [21,22] have been studied, mostly with lignin model compounds as starting materials.

However, very little research has been conducted in the catalytic hydroprocessing of a real lignin feedstock [12,23]; and even less in the formic acid aided lignin conversion [24]. Our research group has studied the effect of different noble metal catalysts (e.g. Ru/Al<sub>2</sub>O<sub>3</sub>, Rh/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>) in the catalytic LtL conversion in aqueous media [10,25]. Nevertheless, recent studies show that using ethanol as solvent systematically gives higher oil yields than water-based systems [26]. Furthermore, ethanol would provide a more suitable environment for the stability of more traditional and cheaper hydrotreating catalysts (i.e. NiMo catalyst), which tend to deactivate in the presence of water [27,28]. In a previous study, we investigated the role of formic acid and the solvent (i.e. ethanol) in the catalytic lignin conversion with a NiMo catalyst supported on a sulfated Al<sub>2</sub>O<sub>3</sub>, a Lewis solid acid [29]. The investigations revealed that the catalytic lignin conversion into bio-oil follows a complex reaction pathway. In the presence of formic acid, lignin undergoes de-polymerization through a formylation-deformylation-hydrogenolysis pathway that leads to the cleavage of its aliphatic ether bonds. The depolymerized monomers and oligomers can undergo subsequent hydrodeoxygenation (HDO) and alkylation reactions. These reactions tend to stabilize the lignin monomers hindering their re-polymerization into char (Scheme 1).

To further explore these processes the catalytic role of the type of metal (i.e. Ni and Mo) and the effect of the Lewis acidity on the lignin de-polymerization (i.e. aliphatic ether bond cleavage) and on the monomer stabilization reactions (i.e. HDO and alkylation) are studied using well-characterized heterogeneous catalysts. Moreover, the relative importance of each reaction path-

way (de-polymerization vs. stabilization) and the influence of the metal-support interaction on the oil yield and oil quality is also assessed. For this purpose, several combinations of non-sulfided monometallic (i.e. Ni and Mo) and bimetallic NiMo catalysts supported on zirconia and  $\gamma$ -alumina are evaluated. Sulfated zirconia [30,31] and alumina [32] are also used as catalyst supports to further explore the effect of the Lewis acidity strength in the reaction mechanism. The recyclability of the NiMo catalyst in the LtL conversion process is also examined.

## 2. Experimental

### 2.1. Chemicals

Formic acid (>98%), tetrahydrofuran (>99.9%), ethyl acetate (99.8%), hexadecane (>99.8%), sulfuric acid (95–97%), anhydrous sodium sulphate (>99.0%) and zirconium (IV) hydroxide (97%) were purchased from Sigma Aldrich and used as supplied.  $\gamma$ -alumina (>97%), nickel(II) nitrate hexahydrate (99.9% Ni) and ammonium molybdate tetrahydrate (99.98% Mo) were purchased from Strem Chemicals Inc. and used as received. The Technical College of Bergen supplied rice straw lignin from a strong acid carbohydrate dissolution pre-treatment. The lignin was ground and sieved (<500  $\mu$ m) prior to use. The elemental composition and the inorganic ash content of the rice straw lignin are given in Table S1, *Supplementary Information*.

### 2.2. Synthesis of the catalyst

#### 2.2.1. Synthesis of the supports

**2.2.1.1. Non-sulfated alumina.**  $\gamma$ -alumina was dried at 100 °C for 24 h prior to use. This support is denoted as AL.

**2.2.1.2. Non sulfated zirconia.** ZrO<sub>2</sub> was obtained by calcining Zr(OH)<sub>4</sub> at 600 °C for 4 h with a heating ramp of 3 °C/min. The resulting support is denoted as ZR.

**2.2.1.3. Sulfated alumina.**  $\gamma$ -alumina was subjected to a thermal treatment in air at 450 °C for 4 h with a heating ramp of 3 °C/min. The calcined alumina was impregnated (4 cm<sup>3</sup> sulfuric acid/cm<sup>3</sup> of pore) with a sulfuric acid solution (mass fraction of 0.5%) and stirred for 24 h. The solution was dried at 80 °C for 24 h and the resulting solid was calcined at 600 °C for 4 h with a heating ramp of 3 °C/min. The resulting sulfated alumina is denoted as SAL.

**2.2.1.4. Sulfated zirconia.** Zr(OH)<sub>4</sub> was impregnated (5 mL/g) with a sulfuric acid solution (0.5 M) and stirred for 2 h. The solution was dried at 80 °C for 24 h and the resulting solid was calcined at 600 °C

Download English Version:

<https://daneshyari.com/en/article/6453977>

Download Persian Version:

<https://daneshyari.com/article/6453977>

[Daneshyari.com](https://daneshyari.com)