



Full Length Article

Cross-reactivity of guaiacol and propionic acid blends during hydrodeoxygenation over Ni-supported catalysts

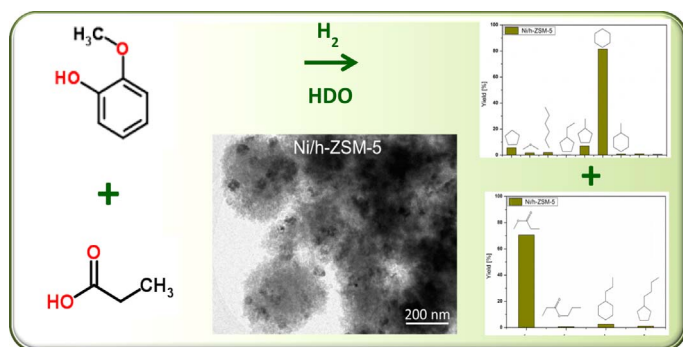


T.M. Sankaranarayanan^a, M. Kreider^a, A. Berenguer^a, S. Gutiérrez-Rubio^a, I. Moreno^{a,b},
P. Pizarro^{a,b}, J.M. Coronado^{a,*}, D.P. Serrano^{a,b}

^a Thermochemical Processes Unit, IMDEA Energy Institute, Avda. Ramón de la Sagra 3, Móstoles, Madrid, Spain

^b Chemical and Environmental Engineering Group, ESCET, Universidad Rey Juan Carlos, Móstoles, Madrid, Spain

GRAPHICAL ABSTRACT



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ABSTRACT

Catalytic hydrodeoxygenation (HDO) is a promising technology for improving the properties of pyrolysis bio-oils. However, the role that intermolecular reactivity between the numerous chemical components of bio-oil plays on the overall performance of the process has been scarcely investigated. In order to gain additional insights into the network of chemical processes taking place during bio-oil upgrading, the present work investigates the hydrodeoxygenation of mixtures of guaiacol and propionic acid using Ni based catalysts supported on solids exhibiting different acidity and textural characteristics: hierarchical ZSM-5 (h-ZSM-5), SBA-15 and Al-SBA-15. In addition, to the products of the HDO of each component of the binary mixture, such cyclohexane and propane, this work shows that hydrodeoxygenation is coupled with esterification, which occurs as a consequence of the in situ formation of methanol by demethoxylation of guaiacol, and other alcohols produced by hydrogenation. Minor contributions of alkylation reactions to the final product distribution are also revealed. Those secondary processes increase the chain length of the products and they contribute positively to avoid carbon losses in the gas phase. Results reported here indicate that the use of acidic supports improves the catalytic behavior leading much higher HDO degree. In this sense, Ni/h-ZSM-5 catalyst shows HDO values close to 100% and significant esterification activity, becoming a very promising catalyst for improving bio-oils properties as advanced biofuel.

* Corresponding author.

E-mail address: juanmanuel.coronado@imdea.org (J.M. Coronado).

1. Introduction

The production of high quality transportation fuels from renewable bio-resources has attracted a great deal of interest in the last years due to its potential environmental benefits achieved by reducing the dependency of petroleum and contributing to the abatement of CO₂ emissions. Besides, biomass also constitutes an attractive feedstock for the production of different platform chemicals [1–4]. In contrast with crops products such cereals grains used for manufacturing first generation biofuels, residual lignocellulosic biomass is less expensive and its utilization does not compete neither with food nor with arable lands. By considering these advantages, thermochemical transformations of this type of resources become both economically and scientifically very attractive [1–3]. Among the routes for the production of biofuels from lignocellulose, one of the most promising is fast pyrolysis, due to its relative simplicity and scalability of the process [5]. However, the so-produced liquid fraction, known as pyrolysis bio-oil, cannot be directly used as a fuel or additive due to their excessive water and oxygen content that result in poor chemical stability and low heating value. Until now, upgrading of pyrolysis bio-oils is still mainly at laboratory scale and a number of technical issues have to be addressed before it can reach commercial development [6,7]. Several catalytic routes have been proposed for enhancing bio-oil properties, including aldol-condensation, ketonization, esterification and hydrodeoxygenation [8]. This last process, which implies the removal of oxygen by hydrogenation at high pressures and moderate temperatures, is considered one of the most effective routes for bio-oil transformation because it can yield fuels more akin to conventional ones derived from fossil resources [9]. Accordingly, great efforts have been devoted to the development of efficient and affordable catalysts for producing hydrocarbons with minimal hydrogen consumption. With this aim, several works have demonstrated the high performance of bifunctional catalysts combining acidic and hydrogenating sites. Thus, catalysts based on noble metals [9,10], metal phosphides [11–15] nitrides [16], carbides [17], sulphides [18,19] or first row transition metals such Co or Ni [20,21] dispersed on zeolites or modified mesoporous silica, have proven to present high activity for hydrodeoxygenation of different feedstocks. However, most of the literature results deals with the conversion of single molecules, which are representative of lignocellulosic depolymerization such as phenol or anisole. Such simplified composition is in sharp contrast with the complexity of pyrolysis bio-oils, which can include more than 400 different molecules, and important side reactions can be overlooked. Thus, little is known about chemical interactions between bio-oil molecules and, therefore, the information about how catalysts' behavior is affected by the competition and the cross-reactivity between the different chemical components is rather limited [22]. In this respect, the large concentration of carboxylic acids in bio-oil can be detrimental for further upgrading because those molecules can hinder the HDO reaction of the phenols and other components by blocking the active surface of the catalyst due to strong adsorption [22]. However, some positive interactions as those leading to esterification of bio-oil components [9], or the promotion of p-cresol conversion [23] have been also reported.

In order to gain further understanding of cross-reactivity of bio-oil molecules, in this work we have investigated the catalytic hydrodeoxygenation of mixtures of two typical components of bio-oils: guaiacol, which is a widely investigated monomer of lignin, and propionic acid, which is one of the most abundant carboxylic acids present in the liquid fraction of pyrolysis [5,7]. Despite the apparent simplicity, this mixture allows exploring the possible intermolecular interactions, including competition for active sites or the existence of new transformations routes, between two of the main chemical families of bio-oils, whereas chemical analysis is still simple enough for keeping good track of all the products. Catalysts based on Ni supported on solids of different acidity and distinctive textural properties have been selected for these tests because of their remarkable HDO activity and affordable

cost. Namely, the support materials used for catalyst preparation are hierarchical ZSM-5, as well as the mesostructured solids SBA-15 and Al-SBA-15.

In this work we have observed limited, but significant cross reactions between the oxygenated aromatics and carboxylic acids. Although overall conversion decreases with respect to the case of using only guaiacol, these processes can be beneficial for the upgrading of bio-oils because they increase the average chain length of the components of the upgraded bio-oil, hindering the removal of small molecules in the gas stream, and can contribute to reduce the overall oxygen content.

2. Experimental

2.1. Support preparation

Pure silica SBA-15 was synthesized following the hydrothermal method described by Zhao et al. [24] using Pluronic 123 (Aldrich) as template and tetraethylorthosilicate (TEOS, Aldrich) as precursor. In a typical synthesis, 8 g of Pluronic 123 (Aldrich) was dissolved in 250 ml of 1.9 M HCl at room temperature. Then, this solution was heated up to 40 °C and, after that, 16.2 g of tetraethylorthosilicate (TEOS, Aldrich) were added. This mixture was stirred for 20 h at 40 °C and, subsequently, subjected to hydrolysis-condensation reaction at 110 °C for 24 h under autogenous pressure. Finally, the filtrated solids were dried overnight at 110 °C and calcined at 550 °C for 5 h using a heating rate of 1.8 °C/min under static air.

Al-containing SBA-15 (Al-SBA-15) was synthesized following a similar procedure but using aluminum isopropoxide (AIP, Aldrich) as Al source [25]. Typically, 8.5 g of TEOS and 0.125 g of AIP were added to 10 ml of an aqueous HCl solution (pH = 1.5). After stirring for 3 h, the homogenous mixture was added to other solution containing 4 g of Pluronic 123 dissolved in 150 ml of HCl at pH = 1.5. The final mixture was stirred for 20 h at 40 °C and, subsequently, subjected to hydrolysis-condensation reaction at 110 °C for 24 h under autogenous pressure. The solid product obtained was filtered, dried overnight and calcined in static air at 550 °C for 5 h with a heating rate of 1.8 °C/min.

The hierarchical ZSM-5 (h-ZSM-5) was obtained following the synthesis route based on the silanization of proto-zeolitic units [26]. Firstly, a clear solution containing tetraethylorthosilicate, tetrapropylammonium hydroxide, aluminum isopropoxide and distilled water, with a molar composition of 1 Al₂O₃:80 SiO₂:14.4 TPAOH:2000 H₂O, was precrystallized under reflux with stirring at 90 °C for 20 h. Then, 8 mol% (referred to the total silica content) of phenylaminopropyltrimethoxysilane was added and left reacting at 90 °C for 6 h. The final solution was crystallized in an autoclave at 170 °C for 7 days. The solid products were recovered by centrifugation, washed several times, dried overnight at 110 °C and calcined in static air at 550 °C for 5 h.

Supported catalysts were prepared by incipient wetness impregnation of 5 wt% Ni (nominal loading) by using aqueous solution of Ni (NO₃)₂·6H₂O (Sigma-Aldrich). After drying, these samples were calcined in static air at 550 °C for 5 h and, finally, all the catalysts were activated by reduction using a hydrogen flow of 60 mL/min at 500 °C for 3 h.

2.2. Characterization

XRD patterns of the supports and catalysts were recorded with a Philips PW 3040/00 X'Pert diffractometer using Cu K α radiation. The actual composition of the prepared samples was confirmed by using ICP-OES analysis on a Perkin Elmer Optima 7300AD instrument after acidic digestion of the solids. TEM images of the materials were acquired using a PHILIPS TECNAI 20T instrument, working at 200 kV. Textural properties of mesostructured solids were determined from N₂ adsorption-desorption isotherms at 77 K using a Quadrasorb system while, for h-ZSM-5 based samples, textural parameters were obtained by means of Ar adsorption-desorption experiments at 87 K measured on

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