

HYDROTREATMENT OF LIGNIN PHENOLIC DERIVATIVES USING Ni-Pd CATALYSTS OVER PILC-Zr TO OBTAIN RENEWABLE JET FUEL

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Highlights

- The hydrotreatment of eugenol and 4-ethylphenol were analyzed as model molecules of a bio-oil.
- The metal loadings of bifunctional catalysts were less than 3 wt. %
- The main products considered in the jet fuel range are ethylbenzene, ethyl, and propyl cyclohexane.

1. Introduction

Currently, the most effective processes for the use of lignocellulosic biomass (LB) in renewable jet fuel include pyrolysis to obtain bio-oil, which is rich in oxygenated aromatic compounds and its subsequent improvement through of a hydrotreatment (HDT). The HDT involves processing the bio-oil in contact with H₂ at medium conditions of T and P and a bifunctional heterogeneous catalyst to remove the oxygen contained in the bio-oil, promoting the cleavage of C-C and C-O bonds. Different research groups report [1-2] that the most stable functional groups in the lignin fraction in bio-oil are C_{Ph-OH} > C_{Ph-OMe} > C_{Ph-OCPh} > C_{Ph-O-Me}, which is why they have used phenolic monomers to analyze the behavior of these functional groups, for example, phenol, m-cresol, anisole, guaiacol, eugenol, etc. Bifunctional catalysts have two active sites: metal sites, responsible for activating H₂, and surface acid sites from the acid support or an oxophilic metal, to activate oxygen [2]. The metal sites can be mono- or bimetallic transition metals and noble metals at low contents, for example, Ni-Pd [1-2] supported on oxophilic metal oxides (Ti, Al, Zr, etc.) or supports with surface acidities such as zeolites, pillared clays and modified mesoporous silicas, [1-2]. Hydrodeoxygenation (HDO), direct deoxygenation, hydrogenation, cracking, trans-alkylation, and hydrogenolysis reactions can be carried out by HDT. In this work, the activity, selectivity, and possible reaction route in the HDT of eugenol (EUG) and 4-ethylphenol (EFL), model bio-oil molecules, were determined using bifunctional Ni-Pd catalysts supported on pillared clays with Zr at 573 K y 3 MPa.

2. Methods

Zirconium-pillared clay (PILC-Zr) was synthesized using the procedure modified by Colín et al. [3]. The metallic phase was incorporated using the solid-state impregnation method, which consisted of adding to the support PILC-Zr the necessary amounts of Ni or Pd acetylacetonate to obtain 1 wt. % in monometallic catalysts and 1:1 weight ratio in Ni-Pd bimetallic catalysts. Before the catalytic evaluation, the calcined catalysts were activated in an H₂ stream at a temperature of 623 K for 1 h. The support and catalysts were characterized by different analysis techniques: XRD and N₂ physisorption. The morphological characterization of the catalysts was carried out through SEM. In addition, H₂-TPR analysis was carried out to determine the reduction temperature and the consumption of the catalysts. The catalysts were tested on the HDT of eugenol and 4-ethylphenol in a batch reactor at 573 K and 3 MPa of H₂ pressure using n-dodecane as a solvent at a stirring speed of 1500 rpm for 6 h [2]. Finally, the liquid phase reaction products were analyzed by GC/MS.

3. Results and discussion

The synthesized supports and catalysts show acceptable textural and structural properties (not shown here) for HDO reactions. The surface area of PILC-Zr increased ten times more than natural montmorillonite, whereas, for impregnated catalysts, it decreased in the order PILC-Zr > 1Ni1Pd > 1Pd > 1Ni. The H₂-TPR results showed that for the PILC-Zr support, there is a reduction peak at 858 K, which could be related to the reduction of Fe³⁺ species present in the clay. This behavior is consistent with that reported by Cheng et al. [4]. At the same time, two reduction peaks were found for the Ni/PILC-Zr catalyst, one at 556 and 858 K. The peak at 556 K would indicate the reduction of NiO species on the catalyst's surface. For the Pd/PILC-Zr catalyst, the first effect observed when increasing the temperature is a negative H₂ consumption. This phenomenon is frequently found in Pd catalysts. The second phenomenon is a reduction shoulder from 643 to 763 K, which is related to a diffuse hydrogen adsorption, confirming that reducing Fe³⁺ with spilled hydrogen species is more straightforward. This effect was also found for the bimetallic Ni-Pd/PILC-Zr catalyst.

For the HDT of eugenol, conversions close to 99% were obtained after 6 h of reaction, finding propyl-cyclohexane as the main product in the case of the Pd and NiPd catalysts on PILC-Zr with selectivity of 29% and 31%. Therefore, the favored reactions were hydrogenation, demethoxylation, and HDO. While in the catalytic evaluation of the HDT of EFL, ethyl-cyclohexane (EC) was found as the main reaction product, indicating the presence of hydrogenation reactions and HDO, in addition to detecting the presence of 4-ethylcyclohexanone (ECA), 4-ethyl-1-cyclohexene (ECO), 4-ethyl-cyclohexanol (ECL) and ethylbenzene (EB). Table 1 reports that a conversion of 91% was achieved for the Pd/PILC-Zr catalyst with a selectivity of 43% to EC after 6 h of reaction. In comparison, the NiPd catalyst reached a selectivity to EC of 21% and a selectivity of 37% to EB. Figure 1 shows the proposed reaction routes for the Pd catalyst and NiPd. In route A, it is suggested that the presence of ECL is obtained from hydrogenation of the aromatic ring followed by dehydrogenation of the aromatic hydroxyl group, thus bringing ECA. In the case of route B, the direct deoxygenation reaction of the EFL is proposed, leading to the formation of EB.

Table 1. Conversion constant, selectivity, and reaction rate in the HDT of EFL using bifunctional mono- and bimetallic Ni, Pd, NiPd catalysts in PILC-Zr

Catalysts*	Conv. (%)	k* x10 ³ [s ⁻¹]	R ²	Selectivity (%)				
				ECA	ECO	ECL	EB	EC
Pd	91	6.8	0.98	0.85	0.18	0.50	-	43
NiPd	54.3	2	0.98	2.51	0.10	0.17	37.04	21
Ni	39.9	1.1	0.97	-	-	-	-	0.61

T = 573K; P = 3 MPa; t = 6 h; V_{C12} = 50 ml; m_{EFL} = 2.5 g; m_{cat} = 0.25 g; *over PILC-Zr

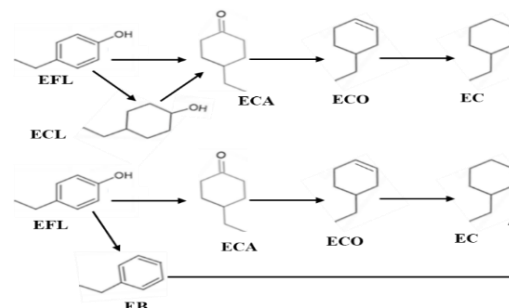


Figure 1. Proposed reaction routes for the HDT of EFL at 573 K and 3MPa A) Pd/PILC-Zr and B) Ni-Pd/PILC-Zr

4. Conclusions

According to these results in the HDT of the EUG and EFL, the presence of propyl-cyclohexane and EC, compounds present in renewable jet fuel, would favor hydrogenation, demethoxylation, and HDO reactions of the hydroxyl-aromatic group, one of the bonds with a high dissociation energy. The latter is the case of the Pd and NiPd catalysts. In the case of EFL's HDT using the bimetallic NiPd catalyst, EB was found in more significant presence, which is attractive like the aromatic product.

References

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Keywords

Bio-oil; hydrodeoxygenation; bifunctional catalysts; lignin phenolic compounds