

Hydrodeoxygenation of isoeugenol catalyzed by Co/biochar catalyst: reaction network analysis

Lilia Longo^{1*}, Davide Baldassin¹, Päivi Mäki-Arvela², Joan Wärnä², Mark E. Martinez Klimov², Olha Yevdokimova², Kari Eränen², Dmitry Y. Murzin², Michela Signoretto¹

1 Department of Molecular Sciences and Nanosystems Ca' Foscari University of Venice, Via Torino 155, 30172 Venezia, Italy

2 Åbo Akademi University, Johan Gadolin Process Chemistry Centre, Henriksgatan 2, 20500 Turku/Åbo, Finland

**Corresponding author: lilia.longo@unive.it*

Highlights

- Isoeugenol hydrodeoxygenation was studied over Co on rice husk activated biochar (10Co/ARH).
- 64% yield of propyl cyclohexane (PCH) was obtained at 300°C and 30 bar H₂.
- >99% yield of propyl cyclohexanol (PCOL) achieved at 200°C and 40 bar H₂.
- The reaction network was proposed, and a kinetic model was developed for HDO of isoeugenol.

1. Introduction

The use of renewable sources as an alternative to fossil fuels has driven research in academia and industry towards exploitation of lignocellulosic biomass. Lignocellulose utilization requires, however, several processes such as fractionation, flash pyrolysis, liquefaction, hydrolysis, to obtain high yields of the liquid phase (bio-oil) [1]. Bio-oil is a highly viscous and corrosive liquid that necessitates further catalytic upgrading to be exploited as a renewable source of fuels, for example for the aviation industry [2]. Hydrodeoxygenation (HDO) is a catalytic reaction that allows cleavage of the C-O bonds in presence of hydrogen, thus leading to higher added value hydrocarbons. However, due to the complex nature of bio-oil, made of more than 250 compounds with different oxygenated functionalities, model compounds are often exploited to investigate the reactions occurring during HDO. Isoeugenol (IE) is an interesting model compound because it contains a hydroxy and methoxy functionality, an aromatic ring, and a double bond. For the considered reaction, the choice of catalyst is crucial, since it has to activate H₂ (typically with a metal such as Pd, Ru, Ni, Cu etc.) and the C-O bond (typically by Lewis's acidity of the support or oxygen vacancies) [3]. While several catalyst types have been exploited for this reaction; cobalt has not been exhaustively investigated and there are no examples of cobalt supported on active carbon for isoeugenol HDO. The aim of this study is therefore the elucidate the reaction network unveiling the role of the catalyst, namely 10 wt.% Co supported on an activated biochar derived by the slow pyrolysis of rice husk, an important byproduct of the agrifood supply chain [4]. The reaction was investigated at different pressure and temperature conditions and based on the kinetic results a reaction network has been proposed.

2. Methods

The catalyst support was prepared by slow pyrolysis of rice husks (700°C, 5°C/min, 30 min) and activation of the derived biochar by steam (850°C, 90 min). 10 wt.% Co catalyst was prepared by wet impregnation using an aqueous solution of Co(NO₃)₂•6H₂O. The catalyst was annealed at 350°C in Ar for 2 hours. Before every reaction test, an adequate amount of catalyst was pre-reduced in H₂ at 450°C for 2 hours. HDO of IE was conducted in a stainless-steel batch reactor system (Parr Instruments) using n-dodecane as a solvent. The reactions were monitored over time by periodic sampling and analyzing the mixture with GC. The fresh and spent catalysts were characterized by several techniques (N₂ physisorption, SEM, XRD, ICP, TEM, TPR, ammonia TPD).

3. Results and Discussion

N₂ physisorption isotherms showed that the catalyst has a micro-mesoporous structure with a type H4 hysteresis. SEM microscopy revealed a sponge like structure rich in cavities, and a hybrid structure made of layers of silica and carbon. TEM images illustrated a good dispersion of Co on the surface of the support, with a distribution centered on 10 nm. XRD measurements performed before and after reduction confirmed a change of the cobalt phase from CoO to the metallic state with the co-presence of both cubic and hexagonal phases. Ammonia TPD showed three distinct peaks, around 170°C and 450-500°C respectively, revealing the presence of acid sites on the catalyst. To unveil the reaction network of IE HDO, the effect of temperature (175-300°C), pressure (10-40 bar) and reactant concentration (0.01 - 0.1 M) was investigated. Tuning the reaction conditions, it was possible to achieve in hydrodeoxygenation of isoeugenol 64% yield of propylcyclohexane (300°C, 30 bar H₂, 4 hours), a valuable compound for jet fuel. Alternatively, 100% yield of propylcyclohexanol was obtained at 200°C and 40 bar H₂ after 3 hours, (Fig. 1 a,b). Considering the results obtained a reaction network was proposed (Fig. 2). A kinetic model was developed and compared with the experimental observations.

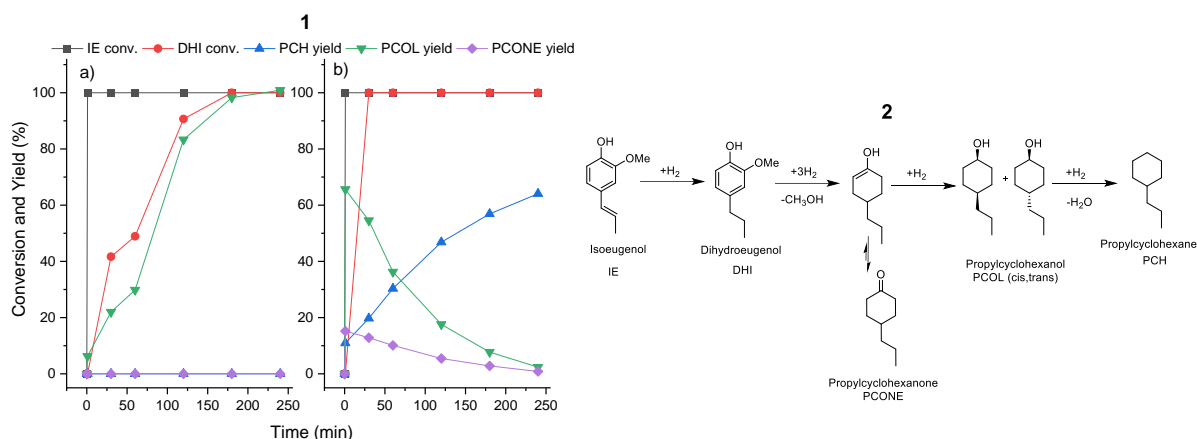


Figure 1. Kinetics in HDO of isoeugenol over 10Co/ARH at a) 200°C, 40 bar; b) 300°C, 30 bar.

Figure 2. Proposed reaction network for isoeugenol hydrodeoxygenation.

4. Conclusions

Activity of a cobalt catalyst supported on rice husk derived activated carbon was investigated. The features of 10Co/ARH were explored and compared to other Co on carbon catalysts, to highlight the role of the metal and the support in the HDO. The kinetic model was developed and compared with the experimental data confirming adequacy of the reaction network.

References

- [1] S. Dutta, ChemSusChem 13 (2020), 2894-2915.
- [2] J. Yang, Z. Xin, Q. He, K. Corscadden, H. Niu, Fuel 237 (2019) 916-936
- [3] M. E. Martinez Klimov, P. Mäki-Arvela, Z. Vajglova, M. Alda-Onggar, I. Angervo, N. Kumar, K. Eränen, M. Peurla, M. H. Calimli, J. Muller, A. Shchukarev, I. L. Simakova, D. Y. Murzin, Energy Fuels 35 (2021) 17755-17768.
- [4] L. Longo, S. Taghavi, M. Riello, E. Ghedini, F. Menegazzo, G. Cruciani, A. Di Michele, M. Signoretto, Catal. Today 420 (2023) 114038.

Keywords

Hydrodeoxygenation, cobalt, biochar, isoeugenol.