

The role of support acidity on the hydrodeoxygenation (HDO) activity of lignin model compounds over sulfided NiMo catalysts

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Introduction

Substantial research focus has been devoted to lignin and lignin derived feedstocks to make green chemicals and fuels [1]. Raw oils from such biomass feedstocks are usually a mixture of mono/di/tri-lignols having large molecular weight compounds with residual C-C and C-O linkages from the original lignin structure including β -O-4, α -O-4, 4-O-5, β -5, β - β etc. in the higher lignols [2]. Hence an efficient upgrading process must achieve simultaneous breakdown of these linkages and subsequent deoxygenation with a robust catalyst to produce stable and quality bio-fuels. In this study, we aimed to understand the influence of support acidity of NiMo based catalysts on the cleavage and hydrodeoxygenation (HDO) activity of typical lignin linkages present in the native lignin.

Materials and Methods

A set of Ni and Mo containing catalysts have been prepared by a wet impregnation process using pre-calcined γ -alumina and USY-zeolite (Silica/Alumina =30). Ammonium molybdate tetrahydrate and nickel (II) nitrate hexahydrate were used as metal precursors. Catalysts were sulfided using dimethyl disulfide at 613K and 2.5 MPa of hydrogen in an autoclave reactor. The liquid feed consisting of 5 mole % benzyl phenyl ether (BPE) or 2-Phenethyl phenyl ether (PPE) (representative of α -O-4 and β -O-4 lignin linkages respectively) in dodecane was used for the investigation at 593K, 5 MPa of H_2 and 1000 rpm stirring speed in the reactor. Temperature programmed desorption of ethyl amine ($C_2H_5NH_2$) was used to quantify the Brønsted acidity of the catalysts [3].

Results and Discussion

With increasing amount of Y-zeolite, Brønsted acidity increased from 264 $\mu\text{mol/g}$ for NiMo/ γ - Al_2O_3 to about 401 $\mu\text{mol/g}$ for NiMo containing Y zeolite. Figure 1 presents the products and intermediates formed during the conversion of reactants. The cleavage of the ether linkages (aliphatic C-O) via hydrogenolysis and hydrolysis yields mainly phenolics (phenol and benzyl phenol from BPE/phenethyl phenol from PPE) and monoaromatics (toluene from BPE/ethylbenzene from PPE). Such cleavage is faster on NiMo-Y with BPE.

Phenol undergoes direct HDO on the sulfided catalyst to produce benzene which can further hydrogenate to yield cyclohexane and methyl-cyclopentane. Interestingly, sulfided NiMo-Y and NiMo-A predominately yield benzene and cyclohexane respectively. Other phenolics undergo HDO/hydrogenation/cracking to give mono and di-ring aromatics/cycloalkanes. For simplicity deoxygenated products are grouped as deoxygenated aromatics and cycloalkanes in figure 1. Clearly, the NiMo-Y catalyst yields less cycloalkane indicating less hydrogenation activity at higher acidity for both BPE and PPE. On the other hand, total deoxygenated aromatics is higher with BPE for NiMo-Y due to high benzene formation. But

for PPE it is low due to low phenolics conversion. Further characterization measurements are being carried out on the catalysts to correlate differing properties of the active phase due to the supports with product selectivities.

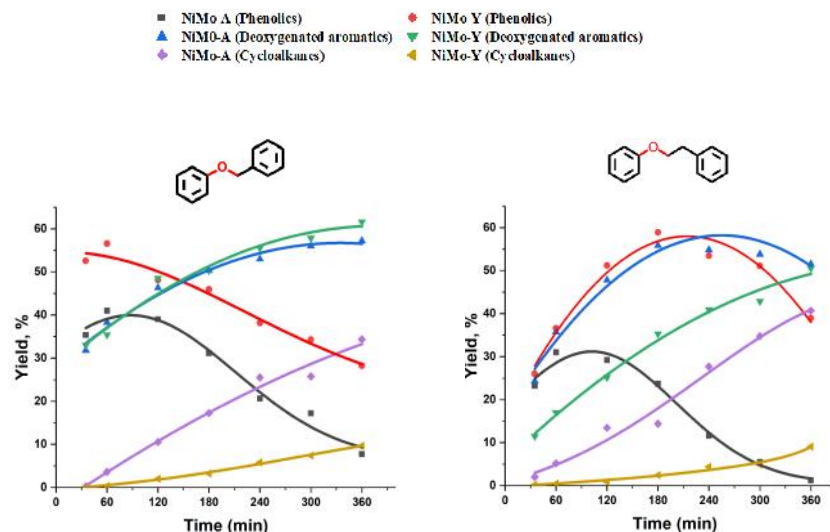


Figure 1. Phenolics, deoxygenated products and cycloalkanes formed during HDO of BPE (left), PPE (right) at 593K, 5 MPa of H_2 in autoclave reactor. Here A denotes γ - Al_2O_3 , and Y=Y-zeolite.

Significance

Support acidity of NiMo based catalysts is an effective tool to control product selectivity during conversion of lignin feedstocks containing β -O-4, α -O-4 linkages into high value fuel additives and chemicals. Toluene/ethylbenzene and cyclohexane products dominate with a γ -alumina support, whereas with USY-zeolite product selectivity strongly shifts to aromatics (more than 75 %) including benzene. A mixed support gave intermediate results, but without benzene.

References

- Schutyser, W., Renders, T., Van den Bosch, S., Koelewijn, S. F., Beckham, G. T., & Sels, B. F. *Chemical Society Reviews*, 47(3), 852-908 (2018).
- Gillet, S., Aguedo, M., Petitjean, L., Morais, A. R. C., da Costa Lopes, A. M., Łukasik, R. M., & Anastas, P. T. *Green Chemistry*, 19(18), 4200-4233 (2017)
- Abdelrahman, O. A., Vinter, K. P., Ren, L., Xu, D., Gorte, R. J., Tsapatsis, M., & Dauenhauer, P. J. *Catalysis Science & Technology*, 7(17), 3831-3841 (2017).