

Stable Lewis-acid Catalyzed Depolymerization of Organosolv Lignin in Acetic Acid

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Highlights

- Zr-KIT-5 catalyst depolymerizes lignin dissolved in acetic acid
- Lewis acid sites in Zr-KIT-5 also promote formation of acetylated aromatics
- Acetylation and absence of Brønsted acid sites prevent recondensation of monomers.
- Unlike in water, Zr-KIT-5 catalyst is stable in acetic acid.

1. Introduction

Several lignin deconstruction strategies have been explored including the use of hydrodeoxygenation, hydrogenolysis and acid catalyzed cleavage of the ether linkages [1-2]. The direct production of aromatics from lignin without the use of externally added hydrogen is a desirable strategy considering the high cost and large quantities of hydrogen required in some of these processes [3].

Lewis acidic catalysts, such as metal triflates, have recently been shown to be effective in selective cleavage of ether linkages in lignin [4]. However, catalysts possessing Brønsted acid sites are known to promote undesired re-condensation of the depolymerized products that may form during lignin deconstruction [5]. Indeed, our previous findings indicate that, the high yields of aromatic monomers (7.5 wt% of the initial dealkaline lignin) and overall soluble aromatic species (approximately 77 %) observed over Zr-KIT-5 were higher compared to those observed with ZSM-5 (4.1 % and 67 %, respectively) at identical conditions [3]. Further, the yield of condensation product is lower in Zr-KIT-5 (14 %) compared to H-ZSM-5 (27 %). Complementary GC-MS/FID, gel permeation chromatography (GPC), nuclear magnetic resonance (NMR) and C/H analyses of the product mixtures confirmed that the predominant Lewis acidity of Zr-KIT-5 catalyst deters condensation reactions promoted by the Brønsted acid sites present in zeolites [3]. However, structural degradation and loss of acidity were evident in the spent Zr-KIT-5 catalysts primarily due to a lack of hydrothermal stability and the presence of residual inorganic impurities (Na₂SO₄) in the dealkaline lignin.

These insights motivated us to explore the use of non-aqueous organic solvents to avoid degradation of the Zr-KIT-5 catalyst. The use of a solvents such as acetic acid and formic acid for lignin depolymerization is reported to facilitate the formation of alkylated monomeric aromatics, avoiding recondensation [1]. Accordingly, this work employs acetic acid as solvent to investigate the performance of Zr-KIT-5 catalyst for the depolymerization of organosolv lignin.

2. Methods

Catalytic depolymerization of organosolv lignin (corn stover lignin, supplied by Archer Daniels Midland) was carried out in a stirred 300 mL Parr reactor operated in a batch mode. Typical reaction conditions were as follows: 0.1 g catalyst, 1 g lignin dissolved in 100 mL solvent, 250 °C and autogeneous pressure.

3. Results and discussion

Solvent choice is dictated by its stability at depolymerization conditions and lignin solubility in the solvent. We explored various non-aqueous solvents such as 1,4-dioxane, acetic acid and γ -valerolactone (GVL) for depolymerization of organosolv lignin. While 1,4-dioxane and GVL are not thermally stable at the depolymerization temperature of 250 °C, acetic acid exhibited good stability. In addition, organosolv lignin

has good solubility in acetic acid. Batch depolymerization of organosolv lignin over Zr-KIT-5(Si/Zr =20) catalyst was performed in acetic acid at 250 °C for 4 hours. The GPC spectra (Figure 1a) of the product solution revealed a clear reduction in the molecular weight distribution (MWD). Figure 1b represents various aromatic monomers (including a few that are acetylated) identified from the depolymerized product mixture by GC-MS. Clearly, Zr-KIT-5 catalysts facilitates both depolymerization and acetylation, leading to formation of the stable acetylated monomeric aromatics. The yield of the identified monomers was found to be approximately 6 wt% of the initial lignin charged.

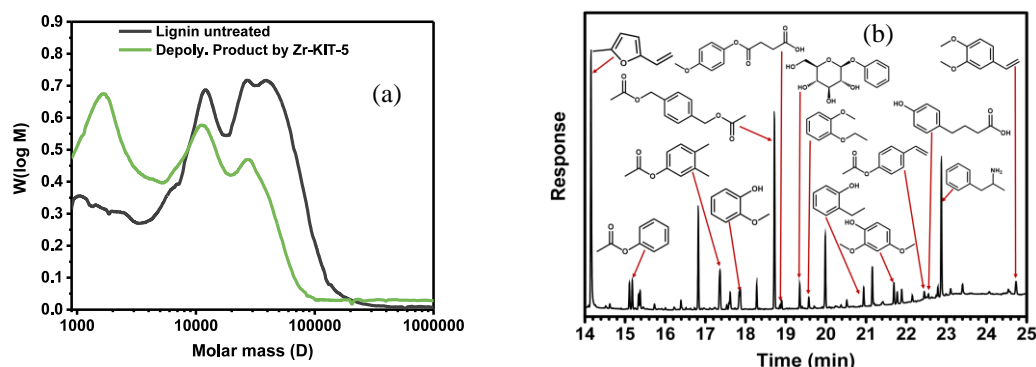


Figure 1. (a) GPC spectra of organosolv lignin and depolymerized product mixture obtained with Zr-KIT-5 catalyst; (b) GC/MS spectra of identified monomeric products in depolymerized product mixture.

The acidity of the spent Zr-KIT-5 catalyst was found to be nearly similar to that of the solvent-treated catalyst in the absence of lignin (Table 1). This is a measure of catalyst stability. Comparative performances of various Lewis acid catalysts (such as Zr-KIT-5, Zr-KIT-6 and metal triflates) for depolymerization of organosolv lignin will be presented. Fundamental insights into the correlation between catalyst acidity and product distribution along with stability and reusability of the catalysts will be presented. Product characterization includes a comprehensive suite of analytical techniques such as thermogravimetric analysis and differential thermogravimetric analysis (TGA-DTA), X-ray diffraction (XRD), X-ray fluorescence (XRF), GC-MS/FID, NMR and GPC. The fresh/spent catalysts are characterized by small angle X-ray scattering (SAXS), N₂-physisorption, NH₃-temperature programmed desorption (NH₃-TPD), XRF and TGA-DTA.

Table 1. Physical characterizations of Zr-KIT-5 Catalyst

Fresh/spent catalyst	Substrate	Solvent	Temp. (° C)	Total acidity (NH ₃ mmol/g)
Zr-KIT-5	-	-	-	0.58
Zr-KIT-5	no lignin	acetic acid	250	0.37
Zr-KIT-5	organosolv lignin	acetic acid	250	0.34

4. Conclusions

Zr-KIT-5 shows promise for deconstructing organosolv lignin into aromatic monomers, which are the precursors needed to make value added products and facilitate a sustainable biorefinery. Lewis-acid sites facilitate both depolymerization and acetylation forming stable aromatic monomers and avoiding condensation.

References

- [1] F. Cheng, C.E. Brewer, *Renew. Sustainable Energy Rev.* 71, (2017) 673–722.
- [2] B.M. Upton, A.M. Kasko, *Chem. Rev.* 116, (2016) 2275-2306.
- [3] K.Y. Nandiwale, A.M. Danby, A. Ramanathan, R.V. Chaudhari, B. Subramaniam, *ACS Sustainable Chem. Eng.* 5, (2017) 7155-7164.
- [4] C.S. Lancefield, I. Panovic, P.J. Deuss, K. Barta, N.J. Westwood, *Green Chem.* 19, (2017) 202-214.
- [5] L. Shuai, B. Saha, *Green Chem.* 19, (2017) 3752-3758.

Keywords

Lignin depolymerization; Aromatic monomers; Lewis acid; Metal triflate.