



From the journal:

RSC Advances

Effects of the novel catalyst $\text{Ni-S}_2\text{O}_8^{2-}\text{-K}_2\text{O/TiO}_2$ on efficient lignin depolymerization†

[Jindong Wang](#),^a [Wenzhi Li](#), ^{*a} [Huizhen Wang](#),^a [Ajibola Temitope Ogunbiyi](#),^a [Xiaomeng Dou](#)^a and [Qiaozhi Ma](#)^b

[Author affiliations](#)

*Corresponding authors

^aLaboratory of Basic Research in Biomass Conversion and Utilization, Department of Thermal Science and Energy Engineering, University of Science and Technology of China, Hefei 230026, PR China

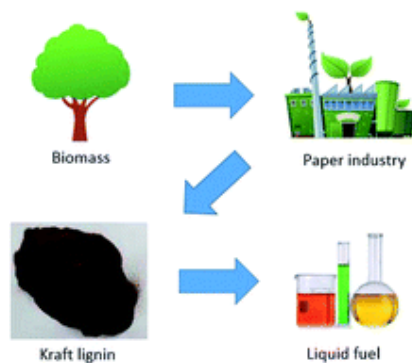
E-mail: liwenzhi@ustc.edu.cn

^bCollege of Materials and Energy, South China Agricultural University, Guangzhou 510000, PR China

Abstract

To improve the utilization of lignin, much effort has been devoted to lignin depolymerization with the aim to decrease waste and enhance profitability. Here, a dual property (acid and base) catalyst, namely $\text{S}_2\text{O}_8^{2-}\text{-K}_2\text{O/TiO}_2$, was carefully researched. Upon loading $\text{S}_2\text{O}_8^{2-}$ and K_2O onto TiO_2 , acid and base sites emerged, and $\text{S}_2\text{O}_8^{2-}$ and K_2O mutually enhanced the acid and base strengths of the catalyst enormously; this indeed facilitated lignin depolymerization. Under appropriate conditions, the yields of liquid product, petroleum ether soluble (PE-soluble) product and total monomer products were 83.76%, 50.4% and 28.96%, respectively. The constituents of the PE-soluble fraction, which are mainly monomers and dimers, can be used as liquid fuels or additives. In addition, after the catalyst was modified by Ni, better results were obtained. Surprisingly, it was found that the Ni enhanced not only the

hydrogenation capacity but also the acidity. The highest high heating value (HHV) of the liquid product (33.6 MJ kg^{-1}) was obtained, and the yield of PE-soluble product increased from 50.4 to 56.4%. The product can be utilized as a fuel additive or be converted to bio-fuel. This catalysis system has significant potential in the conversion of lignin to bio-fuel.



1. Introduction

Increasing awareness of global environmental protection and the finiteness of petroleum-based fuels are among key reasons for seeking a series of promising alternatives to traditional fossil fuels. Biomass, the only carbon-neutral energy source, is renowned as a promising source of synthetic liquid fuels and fine chemicals.¹ However, the scale of the biomass industry is not as large as it should be for many reasons. In China, for example, the lack of proper handling methods of the abundant agricultural crop residues causes many problems; therefore, finding efficient handling methods has drawn much attention.^{2,3} Lignocellulosic biomass contains cellulose, hemicellulose and lignin.⁴ Cellulose and hemicelluloses can be easily converted into fuels or other useful products.⁵⁻⁹ However, the complex, three-dimensional, amorphous polymeric structure of lignin¹⁰ prevents its wide usage in industrial fine chemical production. In fact, little lignin, a byproduct of the paper industry, is efficiently utilized.¹¹ Therefore, the lignin research community is unrelenting in its quest to find efficient methods of lignin depolymerization. Depolymerization is an important method for utilizing lignin well as it can convert lignin into aromatic monomers,^{12,13} which can serve as valuable precursors to obtain further biopolymers or additives for biofuels.^{14,15}

The major thermochemical routes for catalytic lignin transformation are pyrolysis, solvolysis, and hydrothermal catalytic processes.^{16,17} Pyrolysis takes place at high temperatures (over $500 \text{ }^\circ\text{C}$), usually with zeolite catalysts, to obtain liquid fuels and aromatics.¹⁸⁻²⁰ However, high temperature affords low-value char (20 to 40 wt%) and low yields of aromatics.²¹ Lignin solvolysis generates a wide range of monomer products; however, their yields cannot be compared with those obtained by other methods.²³ Hydrothermal catalytic processes for lignin depolymerization have many advantages, such as moderate reaction conditions, high depolymerization efficiency and high conversion rate.^{22,23} Hence, such a process was considered in this work. According to the phase of a catalyst, the catalytic process can be simply divided into two categories, namely homogeneous and heterogeneous catalysis.²³ Homogeneous catalysts generally afford higher production yields; however, due to the difficulty of separation, they are less desirable.²⁴⁻²⁶ Because heterogeneous catalysts can be more easily recycled in most conditions, researchers have paid more attention to heterogeneous catalytic depolymerization of lignin.²⁷ The heterogeneous catalytic process mainly includes acid catalysis, base catalysis, hydroprocessing and oxidation.²² Past studies have mostly focused on the use of mono-

functional catalysts in depolymerization processes. For example, X. Zhang reported a method of hydrodeoxygenation of lignin-derived phenolic compounds over Ni/SiO₂-ZrO₂ catalysts.²⁸ M. Grilc and B. Likozar employed a series of Ni-Mo catalysts for lignin hydrodeoxygenation.^{29,30} Y. Ye used Ru/C to selectively produce 4-ethylphenolics from lignin.³¹ A. K. Deepa and Paresh L. Dhepe carried out solid acid-catalyzed lignin depolymerization to obtain value-added aromatic monomers.³² A. Toledano reduced lignin repolymerization by improving base-catalyzed depolymerization.³³ However, in recent years, researchers have found that combining various catalytic methods at the same time can afford better lignin depolymerization results. S. Riyang employed an acid catalyst, CrCl₃, and a hydrogenation catalyst, Pd/C, together to convert lignin into low molecular weight products.³⁴ H. Ma employed Ni/ZrP in his work.³⁵ Y. Fei used MoC_{1-x} and Cu-MgAlO_z in lignin depolymerization.³⁶ Limarta used Ru/C and MgO/ZrO₂ and L. Jinxing used Ru/C and NaOH in lignin degradation.^{37,38} In the above examples, the researchers combined acid catalysis and hydroprocessing,^{34,36} and other studies combined base catalysis and hydroprocessing.^{37,38} There are reports of joint use of acid catalysis and oxidation^{39,40} and the use of base catalysis and oxidation.^{41,42} Some of these results are shown in Table S8.† Compared with this work, our work has some unique advantages (as shown in Part 3.7).

From previous work, it is known that both acid and base catalytic methods are helpful in lignin depolymerization, and the combination of different catalytic methods may be more effective for lignin depolymerization.^{23,35,37} However, there have been few studies about utilizing combined acid and base catalysts for lignin depolymerization. In this work, acid and base catalysts were combined in a synthesized catalyst, S₂O₈²⁻-K₂O/TiO₂. The effects of the acid and base sites, temperature, and reaction time were investigated. However, in this bond breaking process, many highly reactive carbon intermediates were produced, which can easily polymerize. Because hydroprocessing is known to reduce repolymerization, it was employed in this study after S₂O₈²⁻-K₂O/TiO₂ was modified by Ni. The effects of the solvent type were also studied in this work because the solvent greatly affects these kinds of studies.^{43,44}

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Footnote

1. † Electronic supplementary information (ESI) available. See DOI: [10.1039/c9ra10675h](https://doi.org/10.1039/c9ra10675h)

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Article information

DOI

<https://doi.org/10.1039/C9RA10675H>

Article type

Paper

Submitted

18 Dec 2019

Accepted

12 Feb 2020

First published

27 Feb 2020



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RSC Adv., 2020, **10**, 8558-8567

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