Highly-Efficient and Magnetically-Separable ZnO/Co@N-CNTs Catalyst for Upgrading Lignin and Its Derived Species

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PURPOSE OF THE ABSTRACT
Lignin-derived bio-oils (LBOs) produced using fast pyrolysis and high-temperature, high-pressure liquefaction is not completely suitable as a liquid transportation fuel because of their undesirable physicochemical properties, such as low calorific values, high corrosiveness, instability, and high viscosities. Till date, several approaches have been proposed to remove oxygen from the lignin or its derived species, in which heterogeneous catalyst-based hydrotreatment is recognized as a prominent process than the rest in water media. Here, a highly-efficient and magnetically-separable bimetallic ZnO and Co nanoparticles (NPs) deposited on N-doped carbon nanotubes (ZnO/Co@N-CNTs) catalyst, synthesized by the direct carbonization of the bimetallic Zn/Co zeolitic imidazolate framework (Zn/Co-ZIF), was studied for the effective hydrogenation (HD) and hydrodeoxygenation (HDO) of LBO, lignin and its derived species. During the carbonization of Zn/Co-ZIF, Zn was dislocated from the framework to the particle surface to form amorphous ZnO NPs and metallic Co NPs, which activated the growth of the N-CNTs. Because of the highly Lewis acidic amorphous ZnO, high HD/HDO ability of metallic Co NPs, and high wettability of the N-CNT, an almost complete conversion of vanillin into its corresponding deoxygenated species, creosol, was achieved in an aqueous medium without the production of byproducts under mild reaction conditions (150 °C, 0.7 MPa H2, a reaction time of 2 h). When kraft lignin and bio-oil derived from concentrated strong acid hydrolysis lignin were converted over ZnO/Co@N-CNTs, high degrees of deoxygenation of 74.2% and 34.4%, respectively, could be achieved at 350 °C, 5.0 MPa H2, and a reaction time of 6 h in water. The mild reaction conditions, use of a non-noble metal catalyst, and use of water as the solvent make it possible to develop a cost-effective, easy to scale up, and environmental-benign process for biofuel and biochemical production.
FIGURE 1
Figure 1
Schematic representation of the synthesis of the bimetallic ZnO/Co@N-CNT catalyst by the direct carbonization of Zn/Co-ZIF.

FIGURE 2
Figure 2
GC-TOF/MS chromatograms of the LBO before and after the reaction over ZCI1-700.

KEYWORDS
Biofuel upgrading | Lignin | Hydrodeoxygenation | Co-Zn/N-CNT

BIBLIOGRAPHY