

Lignin Oxidation on CuO: (Electro)chemical Approaches

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Highlights

Lignin was (electro)chemically oxidized by CuO catalyst
Preference to aldehydes generation on both pathways
Electrochemical mechanistic investigation took place
Oxygen vacancies tested by multi-frequency Mott-Schottky

Abstract

Lignin is a macromolecule present in biomass and with practically no industrial application nowadays. In general, it is obtained as a side-product of pulp and paper industry, or bioethanol production, and normally used as fuel for thermoelectricity production. However, this molecule is a natural source of aromatic compounds, which are normally obtained from fossil sources in actual techniques. Because of this, it is of high interest to investigate catalytic processes that can depolymerize lignin to obtain these products. By heterogeneous catalysis, CuO is a potentially good candidate. At temperatures as high as 180 °C, along with high O₂ pressures, CuO can provide good yield to monoaromatic phenol molecules with ketonic or aldehydic carbonyl, or carboxylic acids in para position. In *ortho*, these products can have zero, one or two methoxy groups, depending on the monomeric distribution of the starting macromolecule. Cu oxides are already known in electrochemical literature to be good oxidative catalysts in alkaline media. This approach cannot just find a new way to oxidate the lignin, but also can provide insights into the understanding of general lignin oxidation paths for this catalyst. The electrochemical approach generates the same monoaromatic products observed in heterogeneous catalysis, identified, and quantified by gas chromatography, suggesting a faradic efficiency of 20 % for aldehydes and 4 % for ketones and carboxylic acids each, a similar distribution observed for the heterogeneous catalysis. The catalyst was electrochemically characterized by electrochemical impedance spectroscopy, and capacitive cyclic voltammetry for surface area changes investigation and for the oxide characteristics investigation by multi-frequency Mott-Schottky analysis (mf M-S), which showed a slope of $-6.17 \cdot 10^{13} \text{ F}^{-2}$. The negative slope is a characteristic of intrinsic n-type semi-conductors, and the absolute slope decreased after the potential polarization. This decrease was observed to be dependent on the oxidation potential applied, suggesting that the charge carriers (oxygen-vacancies) are involved in the electrochemical mechanism and probably in the heterogeneous one as well.

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