Modification of Ordered Mesoporous Carbon materials for Enhancing the Electrocatalytic Oxidation of Phenol to p-benzoquinone

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Significance and Relevance

Selective electrocatalytic oxidation (ECO) offers a promising and sustainable strategy for valorizing phenolic compounds, the primary constituents of lignin biomass. ECO of phenols was mainly studied by employing catalysts based on critical raw materials or heavy metals and oriented to the total mineralization of the organic molecule. This study paves the way to the valorization of a lignin-derived molecule, since phenol is selectively converted to p-benzoquinone, by exploiting available materials such as ordered mesoporous carbons, properly modified by the incorporation of phosphorous as heteroatom. The well-defined structure of these materials should ensure a short transport way for ions and electrons and the presence of the heteroatom, modifying the electron distribution of the carbon network, could improve the electrochemical behaviour.

Preferred and 2nd choice for the topic:
1) Advanced process with electrocatalysis and plasma utilization
2) Green chemistry and biomass transformation, renewable resources conversion
Preferred presentation: Short oral/poster

Introduction and Motivations

Phenolic compounds, the fundamental building blocks of lignin, the second most abundant component of lignocellulose, are considered toxic compounds often found in industrial effluents such as from pulp and paper, plastics, pharmaceutical, pesticide, oil and petrochemical industries. Thus, they represent a hazard for living organism especially for their refractory and, for this reason, most of the last investigations have been addressed to the total degradation.[1] This study explores the valorization of phenol through electrocatalytic oxidation using phosphorus-modified ordered mesoporous carbons free of critical raw materials, selectively producing p-benzoquinone, a compound with several applications.[2] Furthermore, the influence of metal oxides, such as NiO, on selectivity was also examined.

Materials and Methods

Ordered Mesoporous Carbon (OMC) was synthesized using Santa Barbara Silica (SBA-15) as template and glycerol as carbon source. The polymer-template composite was pyrolyzed under nitrogen flow and the silica template was removed by HF treatment. The OMC was then properly modified by introducing phosphorous by following the hard templating method in which 2,7-dihydroxynaphthalene was employed as carbon source while tris(4-methoxyphenyl)phosphine as heteroatom precursor for producing POMC. The deposition of NiO on POMC (NiO@POMC) was performed by wet impregnation and all the resulting materials were analyzed through chemical and structural characterization.

Gas Diffusion Electrode (GDE), used as working electrode, was prepared by depositing by airbrush an ink containing an appropriate amount of the catalyst powder, Nafion® solution (binder) and ethanol onto a Gas Diffusion Layer (GDL).

Chronoamperometric measurements were conducted in a micro FlowCell in a three-electrode configuration by employing 0.1M phosphate buffer solutions at different pH= containing 100mg/L of phenol. Products identification was performed by High Performance Liquid Chromatography (HPLC) and by Gas Chromatography (Micro GC).

Results and Discussion

The XRD showed the characteristic peaks of carbon at 2θ=24° and 2θ=43°of 002 and 100 diffraction planes, typical of graphitic materials. After doping, a slight shift towards lower angles of the 002 crystal plane was registered, pointing out the incorporation of phosphorous in the OMC structure. The diffraction pattern of NiO@POMC reported the typical diffraction peaks of the metal oxide, highlighting that NiO was successfully incorporated in the POMC catalyst. Cyclic voltammetries evidenced that each catalyst is active in the anodic oxidation of phenol to p-benzoquinone, showing in the 1st anodic scan the characteristic peak of phenol oxidation followed, from the 2nd anodic scan, by the formation of another anodic peak ascribable to the oxidation of phenol to p-benzoquinone.

Chronoamperometric tests revealed that phenol conversion increased following the introduction of phosphorous on OMC. A further enhancement in the electrocatalytic perfomances was observed after the deposition of NiO on POMC, which yielded a conversion approaching 60% and a selectivity towards p-benzoquinone of approximately 50%.

This research presents a sustainable and efficient electrocatalytic method for phenol oxidation to p-benzoquinone using heteroatom-doped OMCs. The incorporation of phosphorous and NiO results in a substantial improvement in catalytic performance, attributed to enhanced hydrophilicity, electrical conductivity and the presence of large amount active sites introduced by heteroatom doping and metal centers. Therefore, these results could pave the way for the use of CRM-free carbon materials as anodes for the electrocatalytic valorization of lignin-derived molecules.

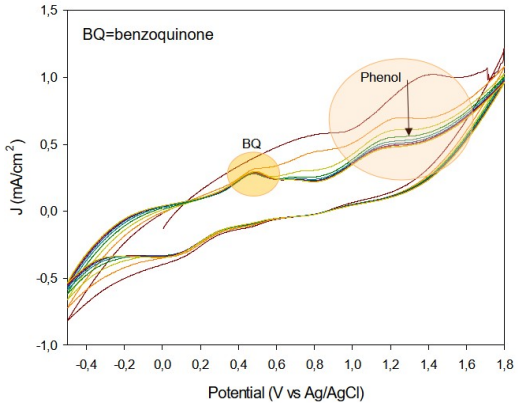

Figure 1. Consecutive cyclic voltammetry scans of NiO@POMC recorded at 10mV/s in 0.1M phosphate buffer solution at pH=3 containing 100mg/L of phenol.

References

1. H. Yapeng et al., *Separation and Purification Technology*. 2019, 212, 802–821
2. O.T. Can, M. Bayrmoglu, *Journal of Hazardous Materials.* 2010, 173, 731-736

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