DFT Insights and Experimental Evaluation of MnCeOx/HAP Catalysts for Efficient Phenol Degradation in CWAO

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Significance and Relevance

Toxic organic pollutants such as phenols in industrial wastewater present significant environmental challenges due to their persistence and toxicity. Catalytic Wet Air Oxidation (CWAO) offers a sustainable approach, converting these pollutants into CO_2 and H_2O under mild conditions. This study investigates $MnCeO_x$ composite catalysts supported on hydroxyapatite (HAP) for Catalytic Wet Air Oxidation (CWAO) of phenol. These materials exhibit excellent activity, stability, and selectivity, achieving nearly complete phenol removal and efficient conversant CO_2 production under mild conditions. The novelty lies in the integration of HAP as a robust support with $MnCeO_x$, exploiting redox activity and oxygen activation to improve wastewater treatment efficiency.

Preferred and 2nd choice for the topic: Water treatement; Materials for Catalysis
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

$MnCeO_x$ catalysts are particularly promising, as their redox properties effectively enhance the degradation of organic compounds[1].
In this study, a novel synthesis procedure for $MnCeO_x$/HAP catalysts was developed to prepare materials characterized by high surface area, superior crystallinity, and excellent redox activity. The use of hydroxyapatite (HAP) enhances the dispersion and stability of the metal oxides. *Ex-situ* and *in-operando* characterization revealed the physicochemical features which represent the key factor for optimizing catalytic systems. The catalysts efficiency in phenol degradation highlights their potential for sustainable wastewater treatment.

Materials and Methods

A coupled redox-precipitation-impregnation route has been exploited to prepare Mn-based catalysts: this approach combines redox reactions for synthesizing MnCeOx followed by impregnation of hydroxyapatite (HAP) to form a composite material. Analytical, morphological, structural and surface properties were investigated by using XRF, XRD, SEM and TEM microscopy, N_2 adsorption/desorption, TGA-MS hyphenated measurements and Raman spectroscopy. *In operando* DRIFT-MS measurements were performed using an environmental chamber located inside IS50 Thermofisher Spectrometer coupled with a Mass Spectrometer. The catalytic performance in phenol degradation was evaluated in a stirred PTFE-lined autoclave at 150°C under oxygen pressures ranging from 0.1 to 1 MPa. Reaction progress and CO_2 selectivity were analyzed by MS-GC and TOC measurements. Additionallty, Density Functional Theory (DFT) calculations were performed to investigate the electronic properties of phenol and its degradation pathways[2].

Results and Discussion

The synthesis method for the novel $MnCeO_x$/HAP catalyst proved highly effective, producing a material with enhanced thermal stability, high surface area, excellent dispersion, and good crystallinity. The catalyst exhibited outstanding performance in phenol removal, achieving high selectivity with minimal intermediate formation and good stability under reaction conditions (T = 150°C, PO_2 = 0.9 MPa, ρ = 0.2). DFT insights provided a deeper understanding of the high catalytic activity in phenol degradation, highlighting the critical role of electronic properties, adsorption behavior, and oxidation mechanisms

in enhancing the catalysts performance for CWAO applications. Theoretical results have been supported by spectroscopic investigations to define the degradation pathways and main intermediates formed during the phenol conversion.

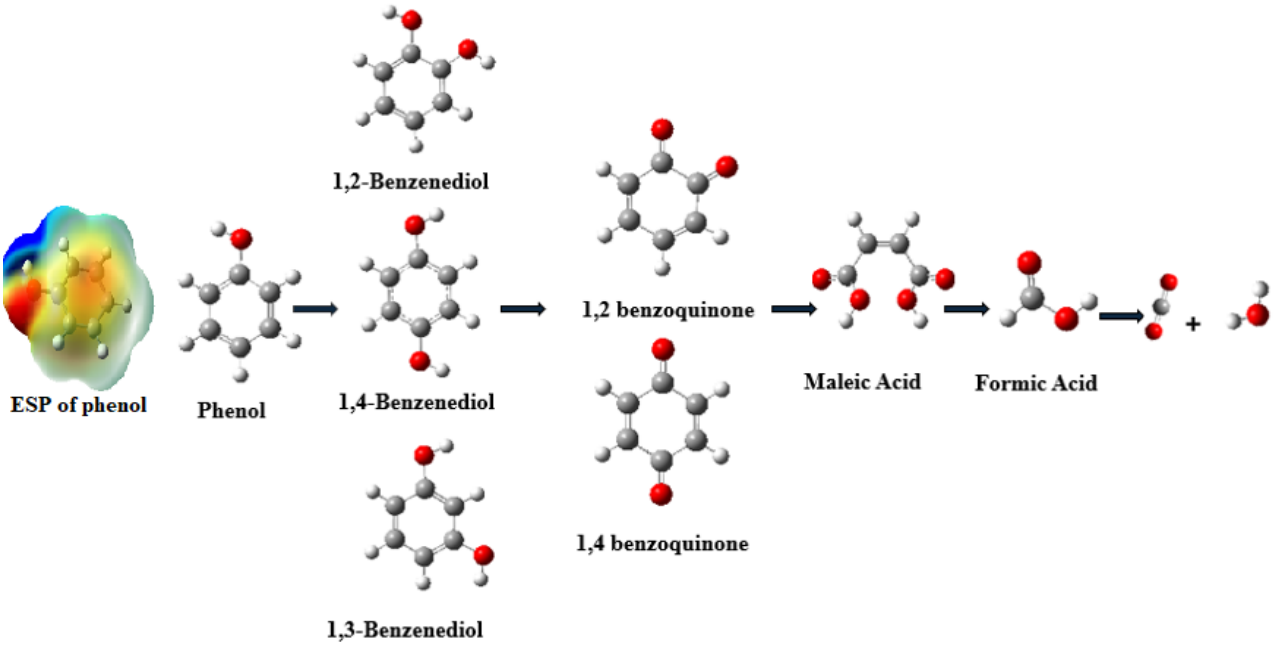

Figure 1: ESP map of Phenol and proposed degradation mechanism in CWAO in the presence of MnCeOx/HAP catalysts.

Conclusion:

$MnCeO_x$/HAP catalysts exhibit high activity and selectivity for phenol degradation under mild CWAO conditions. The synergistic redox properties of Mn and Ce play a critical role in achieving superior catalytic performance, whereas hydroxyapatite (HAP) enhances the dispersion and stability of the metal oxides, such catalysts resulting suitable for sustainable wastewater treatment.

DFT-derived Electrostatic Potential (ESP) map of phenol highlight regions of high electron density providing insights into reactive sites. Computational modeling further proposed a detailed degradation mechanism, elucidating the molecular pathways of phenol oxidation, confirmed by operando spectroscopic investigations.

References

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