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Ternary V(V)-peroxido-zwitterion species catalyze aromatic hydrocarbon oxidation under mild reaction conditions

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Abstract: Vanadium is an element encountered in many abiotic as well as biological systems, thereby attracting considerable attention toward a wide range of processes, including nanotechnology, medicinal chemistry, and industrial (bio)catalysis. Owing to the diverse spectrum of properties linked to a plethora of applications, it has long been known that vanadium is an essential bioelement, intimately participating in various catalytic and inhibitory biological processes. In view of the importance of vanadium in catalysis, efforts have been made in our Laboratory over the years to develop molecular materials targeting vanadium complex systems mimicking the active site(s) of vanadium-dependent enzymes. In this context, the synthesis of catalytic molecular species of vanadium in discrete oxidation states was pursued in the presence of N-methylglycine and N, N'-dimethylglycine in aqueous media and H_2O_2, capable of exerting catalytic activity. The results suggest that such species catalyze benzene oxidation under mild conditions, thereby exemplifying the potential of vanadium in future industrial catalysis.

Introduction

Vanadium catalysts are nowadays a state-of-the-art engineering field, mainly due to the importance of their structural, magnetic and optical properties, and potential applications in catalytic oxidation of various organic compounds in (a)biotic systems. The mono and bis(peroxido)vanadate compounds have been shown to transfer oxygen effectively, thus leading to the synthesis and isolation of valuable organic products, derived through oxidation reactions with enhanced selectivity. To this end, the herein reported hybrid V(V)-peroxido-zwitterionic complex materials bear structural properties supporting catalytic oxidation of industrially important organic compounds. The physicochemical characterization of these materials was carried out by a number of spectroscopic and structural techniques that support catalytic involvement of that element in benzene oxidation under mild reaction conditions. The results collectively project vanadium structural and chemical features formulating its catalytic potency in the selective transformation of benzene into industrially significant products under mild reaction conditions.

Materials and methods

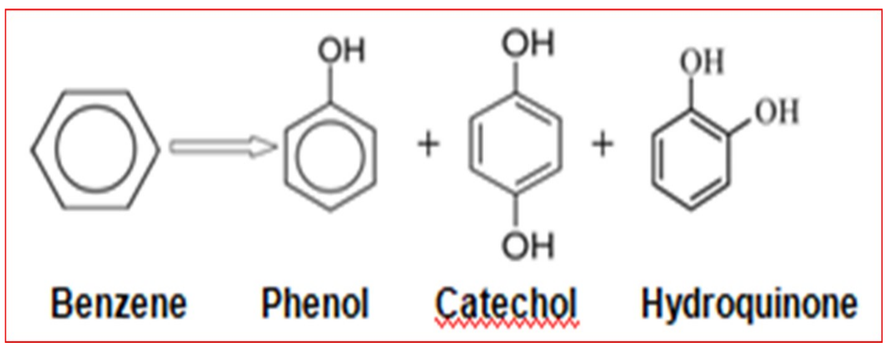
Materials: V_2O_5, N-methylglycine (sarcosine), N,N'-dimethylglycine, hydrogen peroxide solution 30 % (H_2O_2).
Crystallization technique: Layering method, 4 °C.
Physicochemical Characterization: FT-IR, UV-Visible, X–Ray crystallography, Luminescence

Synthesis reaction of V(V)-sarcosine-peroxido catalyst

$$V_2O_5 + C_4H_9NO_2 + 4H_2O_2 + 2KOH \xrightarrow{pH\ 4.5} K_2(H_2O)_2\left[V_2O_2(O_2)_4(C_4H_9NO_2)\right] + 3H_2O$$

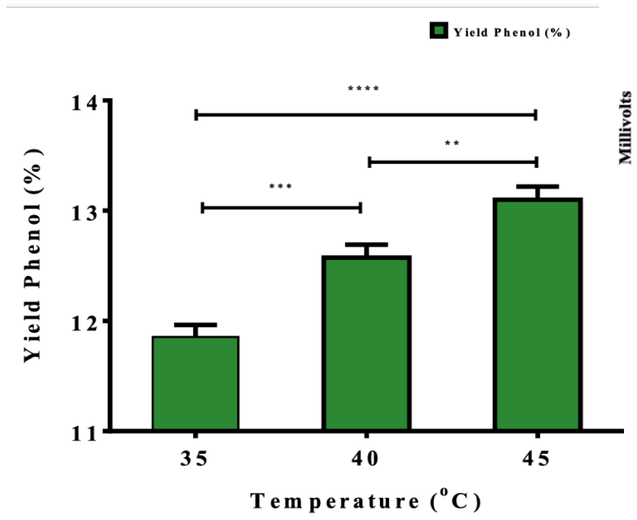
Catalytic action of peroxido-zwitterion- vanadium materials

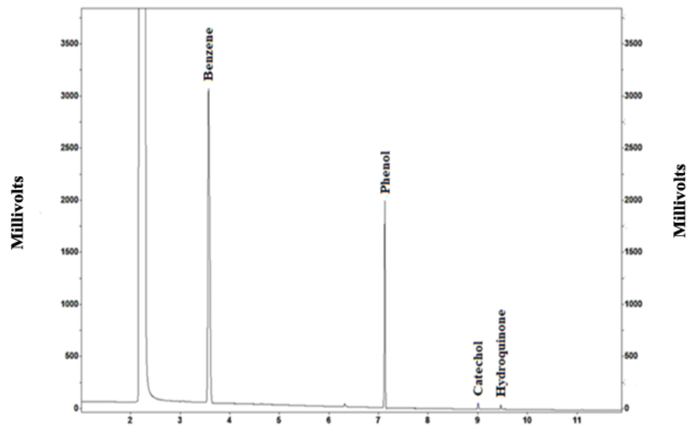
Benzene oxidation mechanism



In this study, we used as a catalyst, the ternary material V(V)-peroxido-sarcosine complex, with molecular formula $K_2(H_2O)[V_2O_2(O_2)_4(L)$ (**1**)], where L = $CH_3N^+H_2CH_2COO^-{\bullet}H_2O$

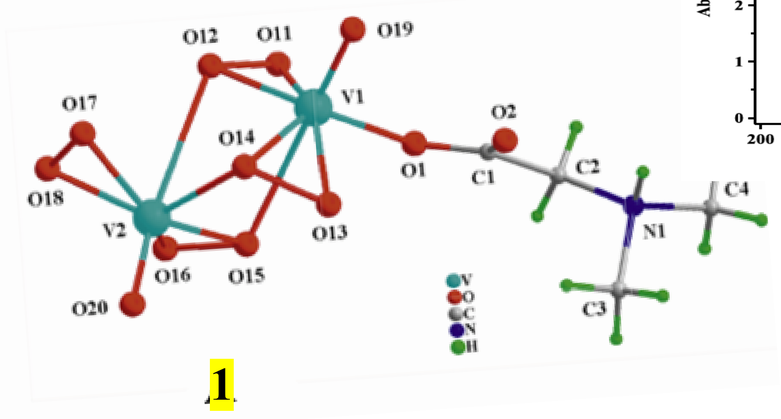
GC sample chromatogram with splitless injection at 40°C



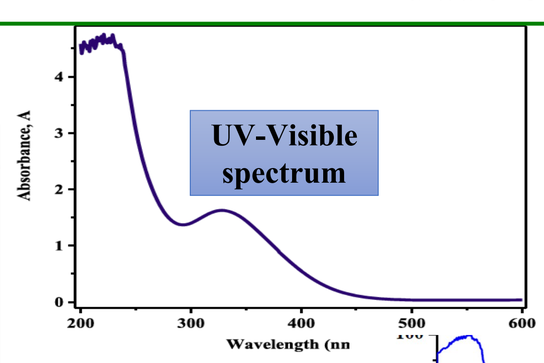


Catalytic work revealed that optimally achieved results were obtained when the catalytic system was formulated as follows: in a 50 mL round bottom flask, placed in a water bath, 0.010 mmol of complex was dissolved in 10 mL solvent (CH_3CN).

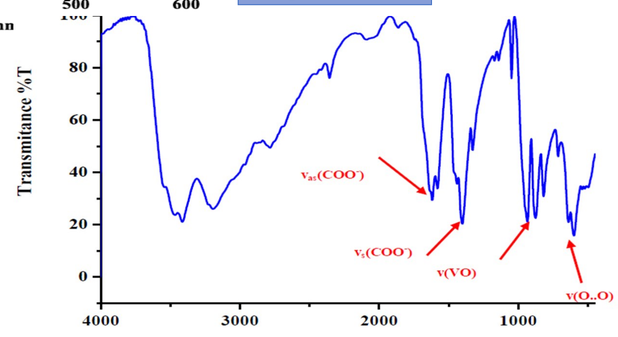
X-ray crystal structure



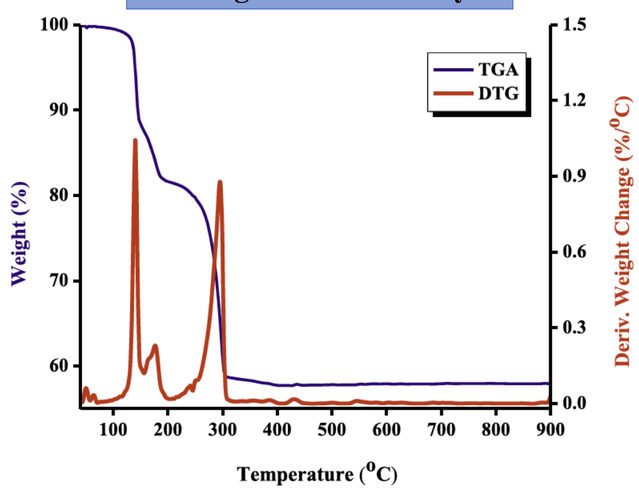
UV-Visible spectrum



FT-IR Spectrum



TGA (A) and DTG (B) thermogravimetric analysis



Conclusions

- Synthetic approaches of the aqueous vanadium-peroxo-zwitterion chemistry reveal the complexity and diversity of mono-dinuclear species purported to possess catalytic properties
- Reactivity of vanadium-zwitterion species with hydrogen peroxide reveals unique modes of coordination of the zwitterion and peroxide ligands to vanadium(V).
- Physicochemical investigation unravels structural dependence and mechanistic information on the reactivity of mono-dinuclear anionic hybrid V(V)-peroxido-zwitterionic complexes acting as efficient catalysts in selective benzene oxidation.
- Structurally diverse vanadium-zwitterion species catalyze benzene oxidation under very mild reactions

Literature

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