



Unusual catalytic reactivity in new vanadium-peroxido-zwitterion materials

Efrosini Kioseoglou,¹ Antonios Hatzidimitriou,² Athanasios Salifoglou¹

¹School of Chemical Engineering, Laboratory of Inorganic Chemistry and Advanced Materials, Aristotle University of Thessaloniki, 54124, Greece

²School of Chemistry, Laboratory of Inorganic Chemistry, Aristotle University of Thessaloniki, 54124, Greece
E-mai: efi.kioseoglou@gmail.com,



ARISTOTLE
UNIVERSITY OF
THESSALONIKI

Abstract

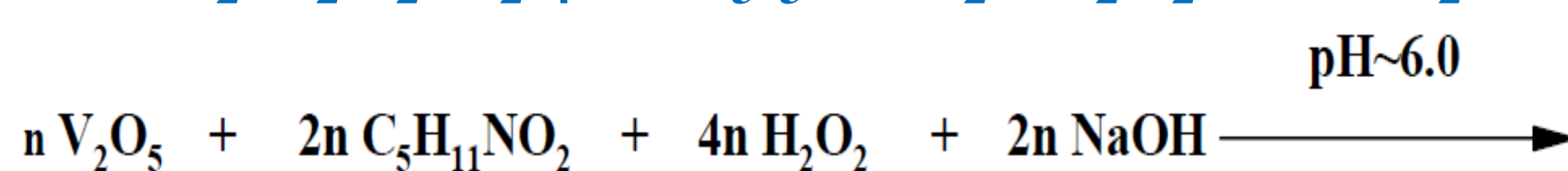
This research involves studies of innovative and well-defined discrete-ternary materials vanadium- (H₂O₂)-trimethylglycine and zwitterions (glycine derivatives), the flexible configuration of which around the vanadium allows control of chemical-catalytic activity in industrial epoxidations of olefins and oxidation of aromatic substrates. The complexes were synthesized in aqueous environment with pH 5.5-6 and crystallized in the presence of ethanol at 4 °C.

Introduction

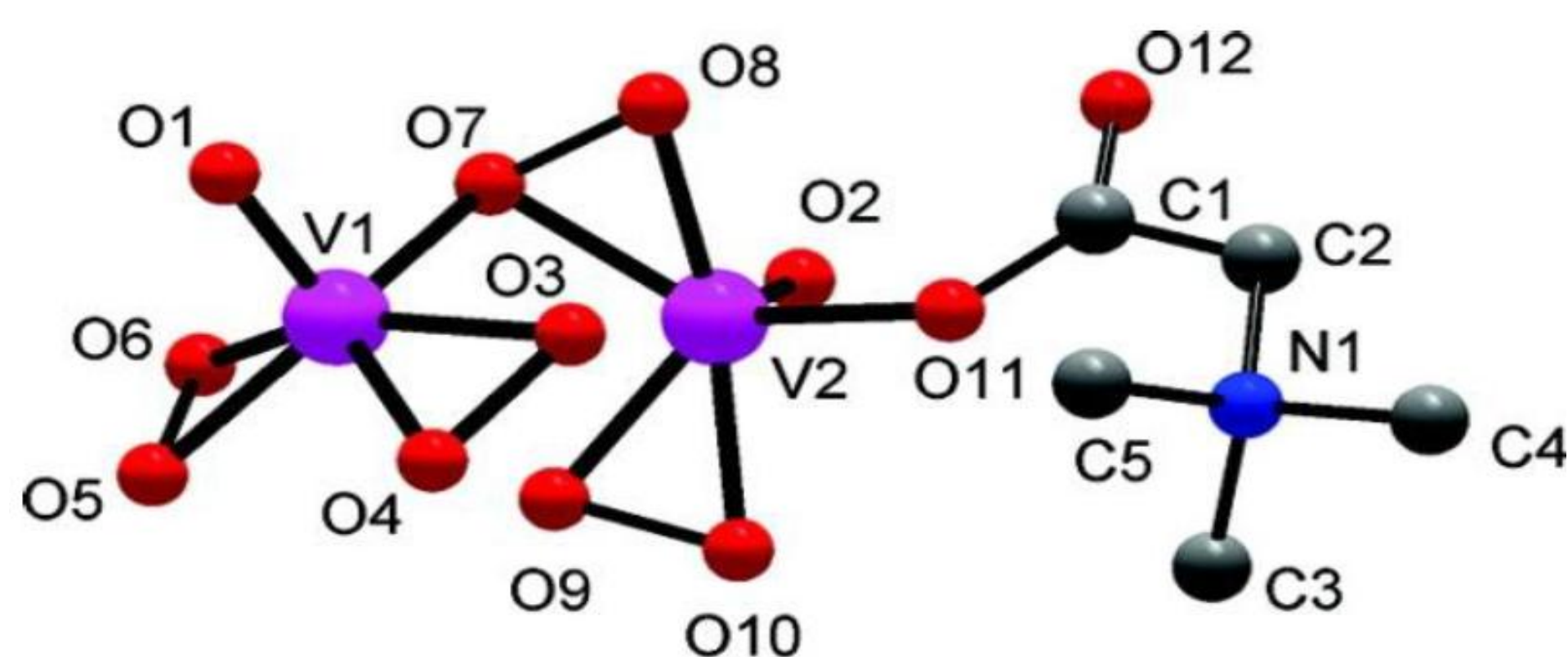
Vanadium catalysts are nowadays a state of the art subject, mainly due to the importance of their structural, magnetic and optical properties, and potential applications in catalytic oxidation of various organic compounds and their relevance in biological systems. The mono and bis(peroxido)vanadate compounds have been shown to transfer oxygen effectively, leading to the acquisition of valuable synthetic molecules, derived through oxidation reactions with enhanced selectivity.^{1,2,3}

Vanadium occurs in the fully oxidized state V(V). The physicochemical characterization of these materials was carried out by elemental analysis, X-ray crystallography techniques, FT-IR, UV-Visible, cyclic voltammetry (CV), NMR and Raman, CP-MAS NMR/NMR (liquid-solid), ESI-MS. It collectively a) provides important information on the properties of the vanadium materials as potential catalysts, in the solid and liquid phase, and b) underlines the structural and chemical features that justify the development of catalytic action of vanadium on discrete substrates with industrial and biological significance.^{4,5,6}

Material and method

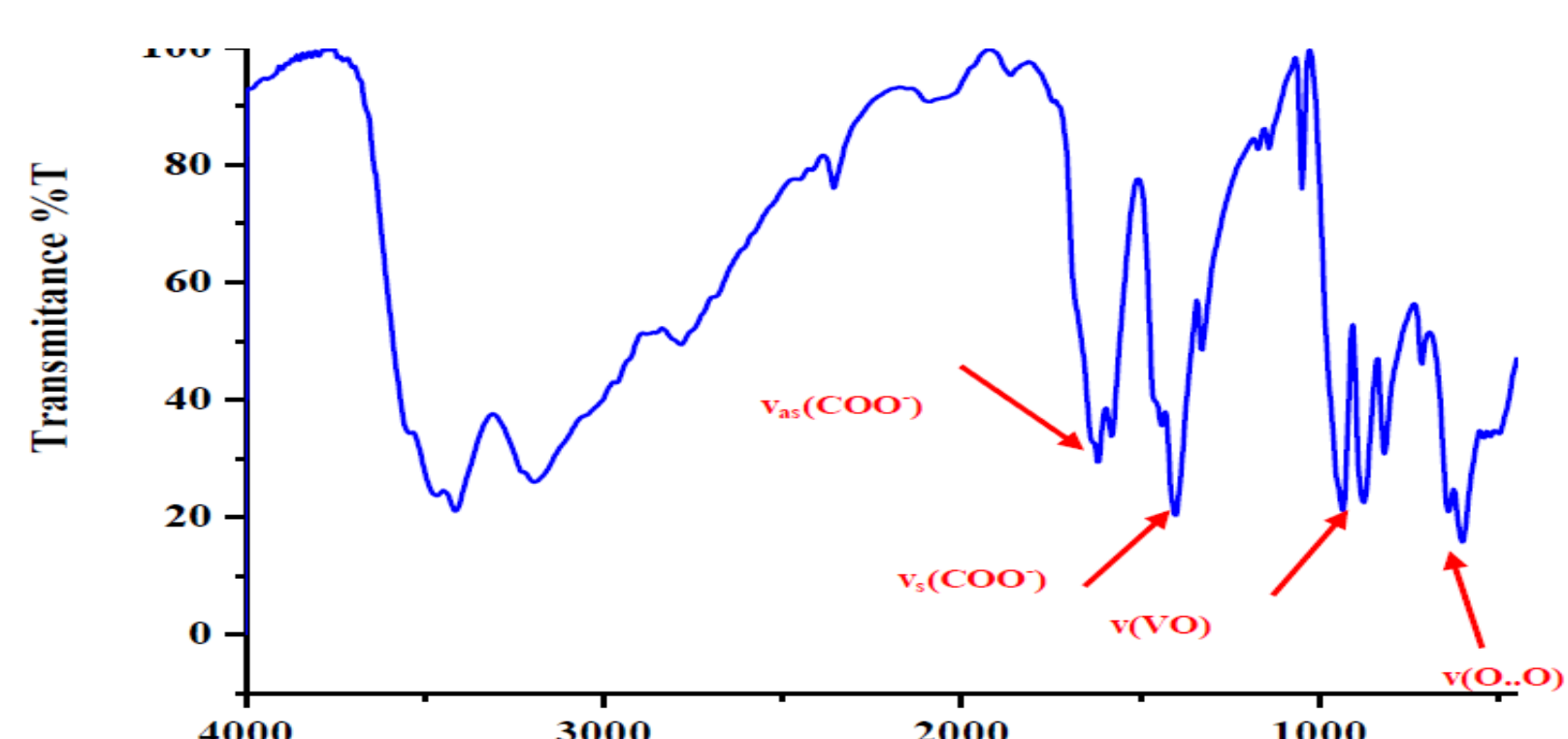


DIAMOND diagram of



FT-IR spectrum of

GC chromatogram with splitless injection



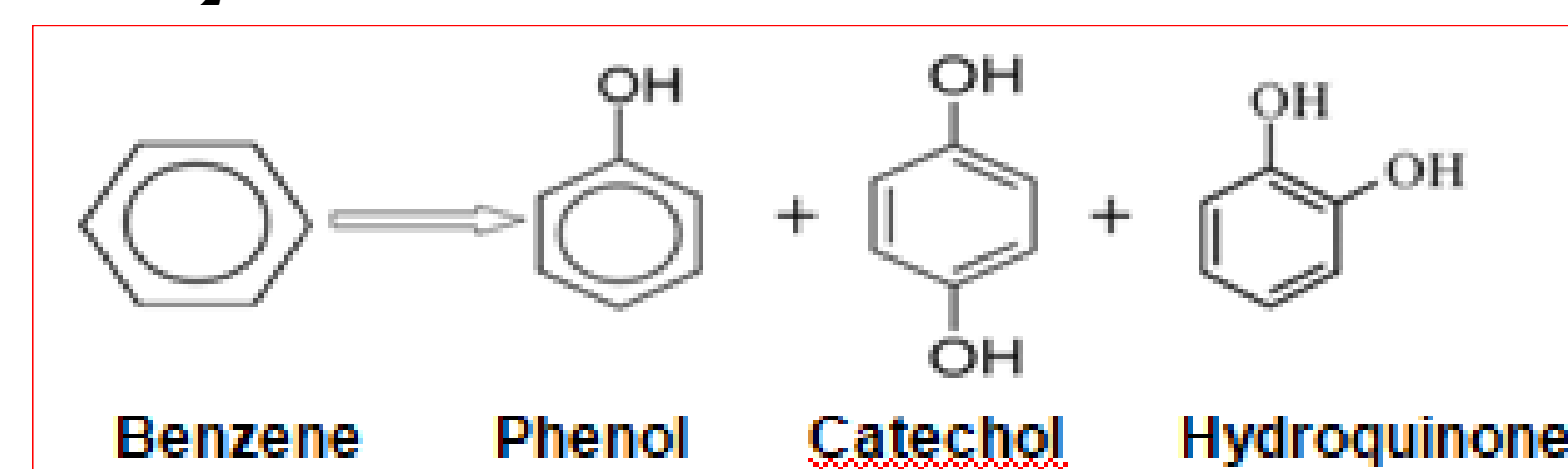
- The FT-IR spectra of the complex revealed the presence of both symmetric and antisymmetric vibration of the carboxyl groups of assembled betaine.
- The antisymmetric vibration strain of carbonyl groups $\nu_{as}(COO^-)$ are presented in 1634 cm^{-1} while the symmetrical $\nu_s(COO^-)$ in the region $1472\text{--}1330 \text{ cm}^{-1}$.
- Finally, the vibration $\nu(O-O)$ due to the presence of O_2^{2-} , appears at 836 cm^{-1} .

Results and discussions

Catalytic action of peroxido-zwitterion- vanadium materials

Benzene oxidation mechanism

In this study we used as a catalyst, the ternary material V(V)-peroxido-betaine, with molecular formula $Na_2[V_2(O_2)_4O_2L_2]$, (1) where $L = Me_3N(+)-CH_2-COO(-)$.



GC sample chromatogram with splitless injection at 40°C

In this study we used as a catalyst also as before the ternary material V(V)-peroxido-betaine with molecular formula $Na_2[V_2(O_2)_4O_2L_2]$, where $L = Me_3N(+)-CH_2-COO(-)$.

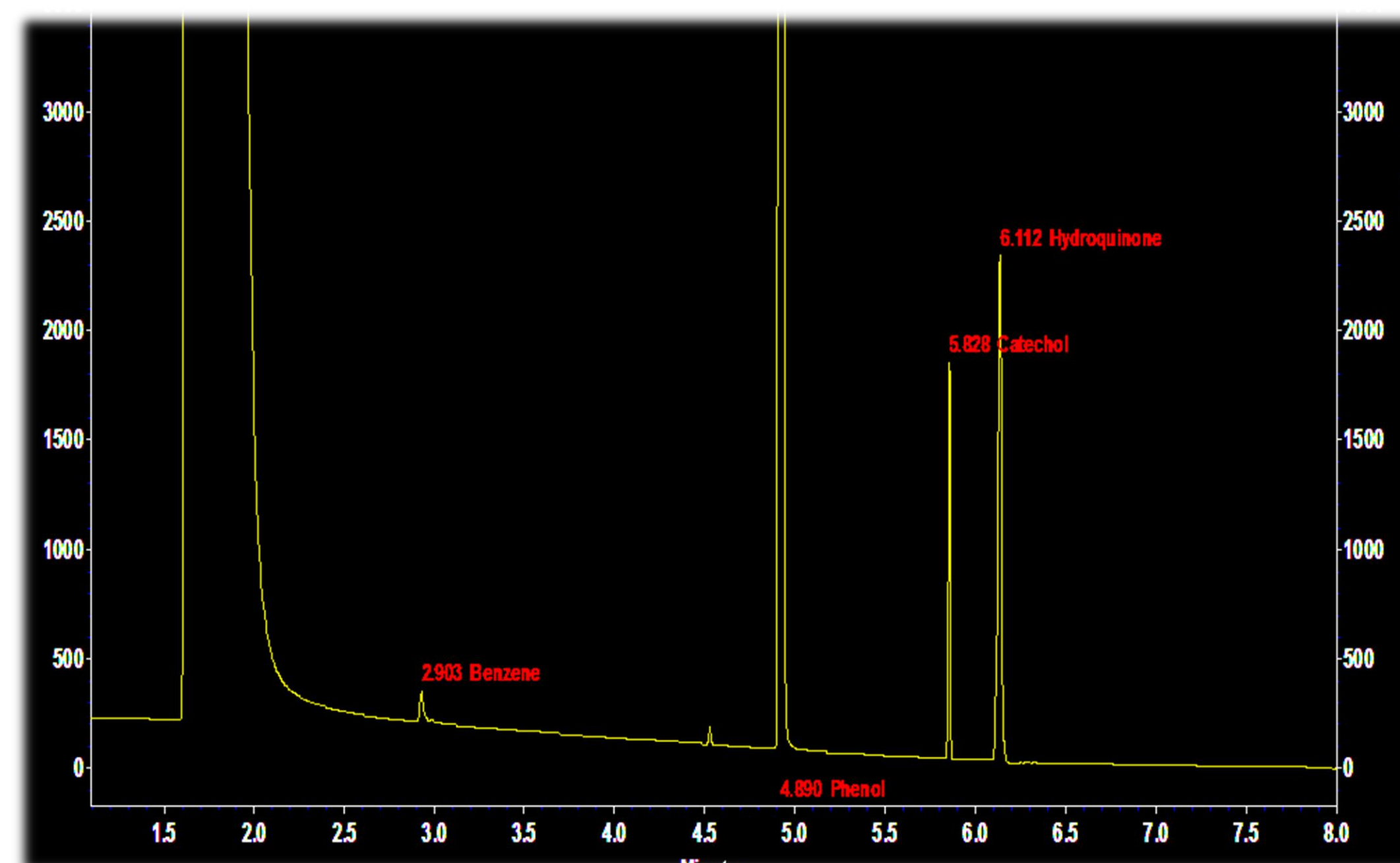


Figure 1. GC-FID chromatogram of Benzene, Phenol, Catechol and Hydroquinone

Conclusion

- Synthetic approaches of the aqueous vanadium-peroxo-zwitterion chemistry reveal the complexity and diversity of mono-dinuclear species purported to possess catalytic abilities
- Reactivity of vanadium-zwitterion species with hydrogen peroxide reveals unique modes of coordination of zwitterion and peroxide ligand to vanadium.
- Physicochemical investigation unravels structural dependence and mechanistic information on reactivity of mono-dinuclear anionic complexes of vanadium with zwitterion on pH.
- Discovery of new and structurally and spectroscopically diverse vanadium-zwitterion species through structural speciation
- Further perusal of synthetic avenues leading to novel vanadium complexes with structural, electronic and spectroscopic properties may provide the physicochemical basis of comprehending and/or potentially predicting the factors governing the catalytic capacity of vanadium in the presence of physiological ligands.

Literature

1. D. Rehder, *Angew. Chem. Int. Ed. Engl.* 30 148-167 (1991)
2. D. Rehder, *Biomaterials* 5 3-12 (1992)
3. R.S. Ray, B. Ghosh, A. Rana, M. Chatterjee, *Int. J. Cancer* 120 13-23 (2007)
4. J. Pessoa, S. Etcheverry, D. Gambino, *Coord Chem Rev.* 301 24-48 (2015)
5. D. Gambino, *Coordination Chemistry Reviews* 255 2193-2203 (2011)
6. S. Petanidis, E. Kioseoglou, M.C. Hadzopoulou, A. Salifoglou, *Cancer Letters* 335 387-396 (2013)