Catalytic application of vanadium phthalocyanine in acid-based medium reactions to covert and couple saccharide bi-products

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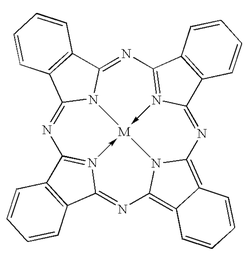
Abstract

Synthesis of vanadium phthalocyanine was completed following a method from literature. Characterization of the complex was established using a combination of FITR, XPS and XRD. Subsequently to synthesis, the compound was studied in the conversion of fructose into different molecules. The capability to convert fructose into other compounds is an important process when synthesizing organic compounds such as levulinic acid. Levulinic acid is an important starting material in the synthesis of biofuels, precursor for pharmaceuticals, plasticizers, THF derivatives and valerolactone. The reactions were performed under acidic conditions in atmosphere using strong acids which included nitric, sulfuric and hydrochloric acid. The products synthesized from the reactions were periodically sampled for analysis using GC-MS in a twenty-four-hour timeframe. The reactions showed a series of compounds being produced within the timeframe of analysis; however, the majority of the fructose was converted into levulinic methyl ester and heptadionic acid. Results exhibited a combination of reactions occurring which include chain growth (coupling or the formation of carbon-carbon bonds) and de-cyclization of the sugar. The reactions indicate the metal-porphyrin systems play a catalytic role in the generation of organic molecules from biological materials such as sugars, cellular materials, cell walls, etc.

Methods

Sythesis of vanadium phthalocyanine via reflux

The metal-porphyrin catalyst was synthesized via a reflux apparatus using vanadyl sulfate hydrate, phthalic anhydride, ammonium chloride, urea and ammonium molybdate tetrahydrate that was grinded up in a mortar and pestle to a homogenous powder. After reflux, plenty of washes using ethanol and methanol were conducted to remove impurities of the catalyst before using it for reactions. Finally, the product was dried out via vacuum oven and characterized using FTIR, XPS and XRD.



Catalytic reactions under acidic conditions

Upon synthesizing the vanadium phthalocyanine, reactions were conducted at a microscale to observe and document changes occurring as reactions were put into reflux under vacuum. Refluxes were run in 24 hour periods with samples extracted periodically. The reactions consisted of using 1 mmol of the metal-porphyrin, 1 mmol of a sugar (glucose, fructose or xylose), 1 ml of acid (hydrochloric, sulfuric, nitric or hydrobromic) and 30 to 40 milliliters of methanol as a solvent for the reflux. Vacuum was achieved by using a Schlenk line system to purge oxygen out and pump inert nitrogen gas into the vessel.

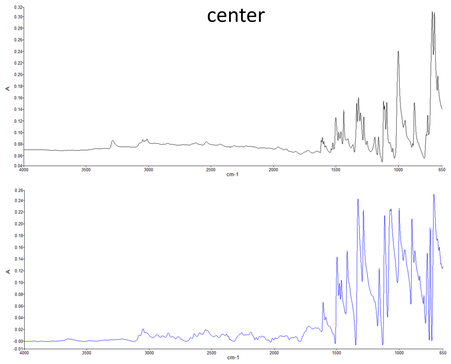
Analysis using GC-MS

GC parameters: Samples are analyzed at run-times of 20 minutes from a start of 50 degrees Celsius with a ramp rate of 25 degrees per minute till 300 degrees is reached

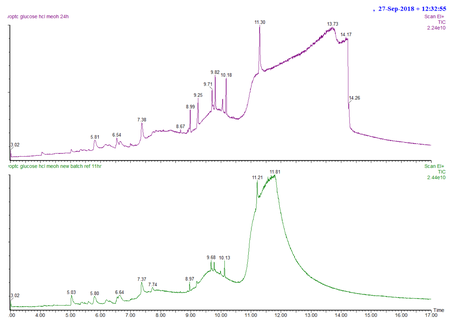
MS parameters: Samples are analyzed at run-times of 20 minutes from masses of 28 to 600 EI+ for fragments measured from 0 to 100 abundance.

Results

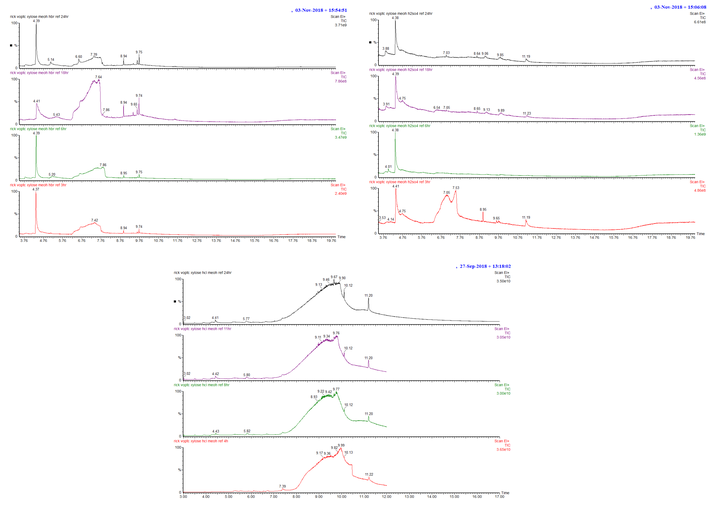
IR spectra for phthalocyanine ring without (black line) and without (blue line) vanadium center



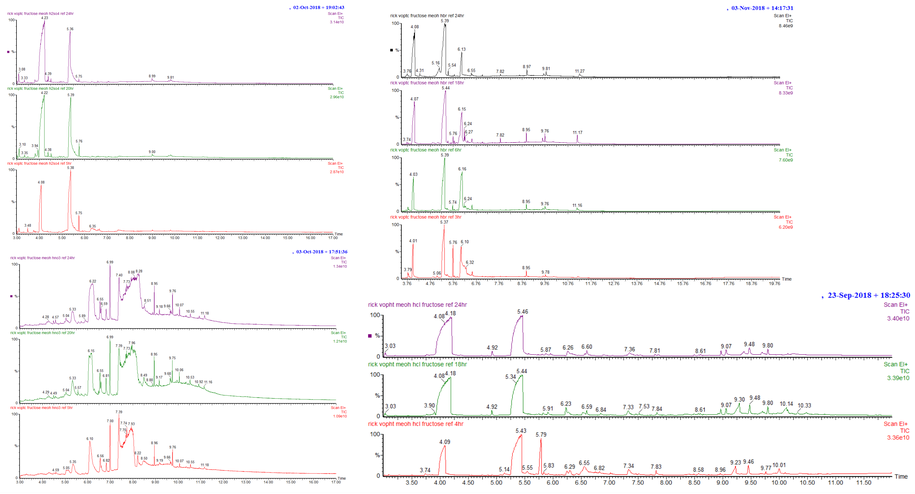
Vanadium phthalocyanine reactions with glucose



Vanadium phthalocyanine reactions with xylose

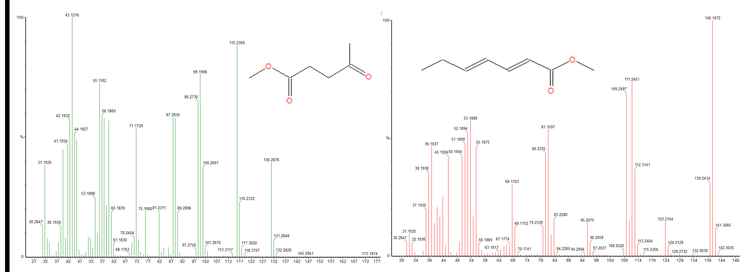


Vanadium phthalocyanine reactions with fructose



Results (cont.)

Mass spectra for desired products of levulinic methyl ester and heptanedioic acid



Discussion

The desired products seen throughout the reactions in abundance were levulinic methyl ester and heptanedioic acid. Levulinic acid would appear around the time of 4 minutes and heptanedioic acid around 5 minutes expressed in the GC/MS spectra.

From the results, we observed that glucose was difficult to break open the ring to oxidize and produce desired fragmentations.

Fructose and xylose both showed to be able to break open and produce fragmentations. Fructose was assumed to be favorable since the sugar is a five member ring and thought to be easier to oxidize rather than a 6 member ring sugar.

The acid producing the most of the desired products was sulfuric and hydrochloric acid. Proceeding into future reactions, these acids are favored to be used for monitoring future reactions and reproduce desired results.

Future works

Moving forward into further reactions, fructose and xylose will be the favored sugars to run with sulfuric and hydrochloric acid in the vanadium catalytic refluxes.

Other phthalocyanine complexes will be used to see if similar results are observed with an interest in nickel phthalocyanine. Similar trends of analysis will be implemented to confirm or differentiate similar tendencies confirmed in the vanadium study.

Repeating of results, kinetics, macro scaling and extraction of products for the reactions will be the next steps in the research.

Acknowledgements

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