

Orthogonal Tandem Oxidative Carboxylation of Styrene by VPOM@CTF@PA-4,6 Nanofiber

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Introduction

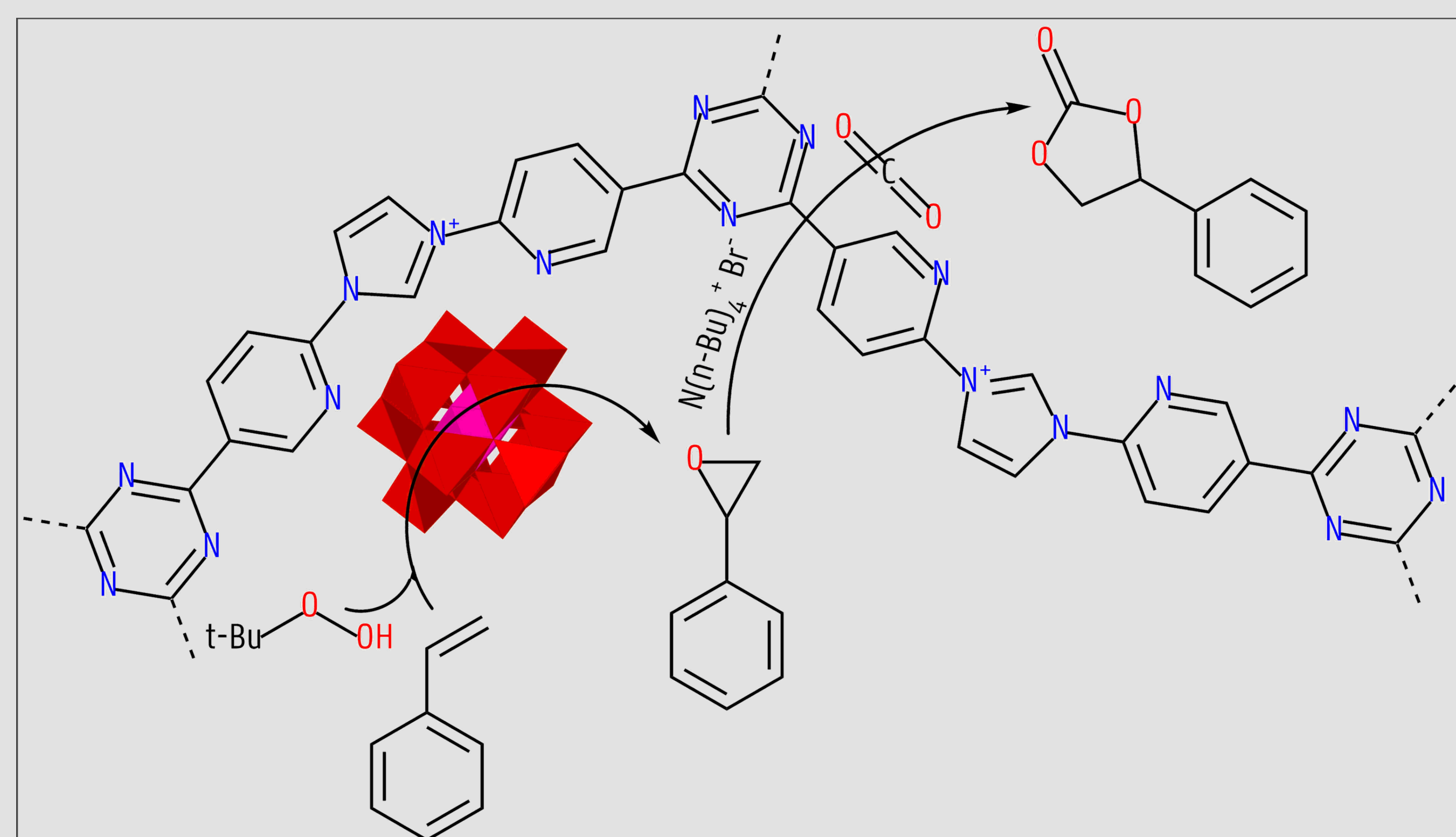
The utilization of CO₂ in the production of value-added chemicals is one way to reduce its emission. In this research, a dual-functional catalyst is envisaged to achieve the orthogonal tandem catalysis of the oxidative carboxylation of styrene to styrene carbonate [1].

This is achieved by incorporating a vanadium-based polyoxometalate, [NH₄]₇[MnV₁₃O₃₈], (VPOM) in an cationic covalent triazine framework (CTF) based on imidazolium moieties. More specifically, the embedded VPOM catalyzes the epoxidation of styrene to styrene oxide with tert-butylhydroperoxide (TBHP) as the oxidant. Simultaneously, CO₂ molecules are efficiently captured and activated by CO₂-philic N-rich triazine groups of the CTFs [2]. Next, the bromide ion of the tetrabutylammonium bromide (TBABr) co-catalyst activates the epoxide via ring-opening. Subsequently the activated CO₂ is inserted to produce the desired styrene carbonate.

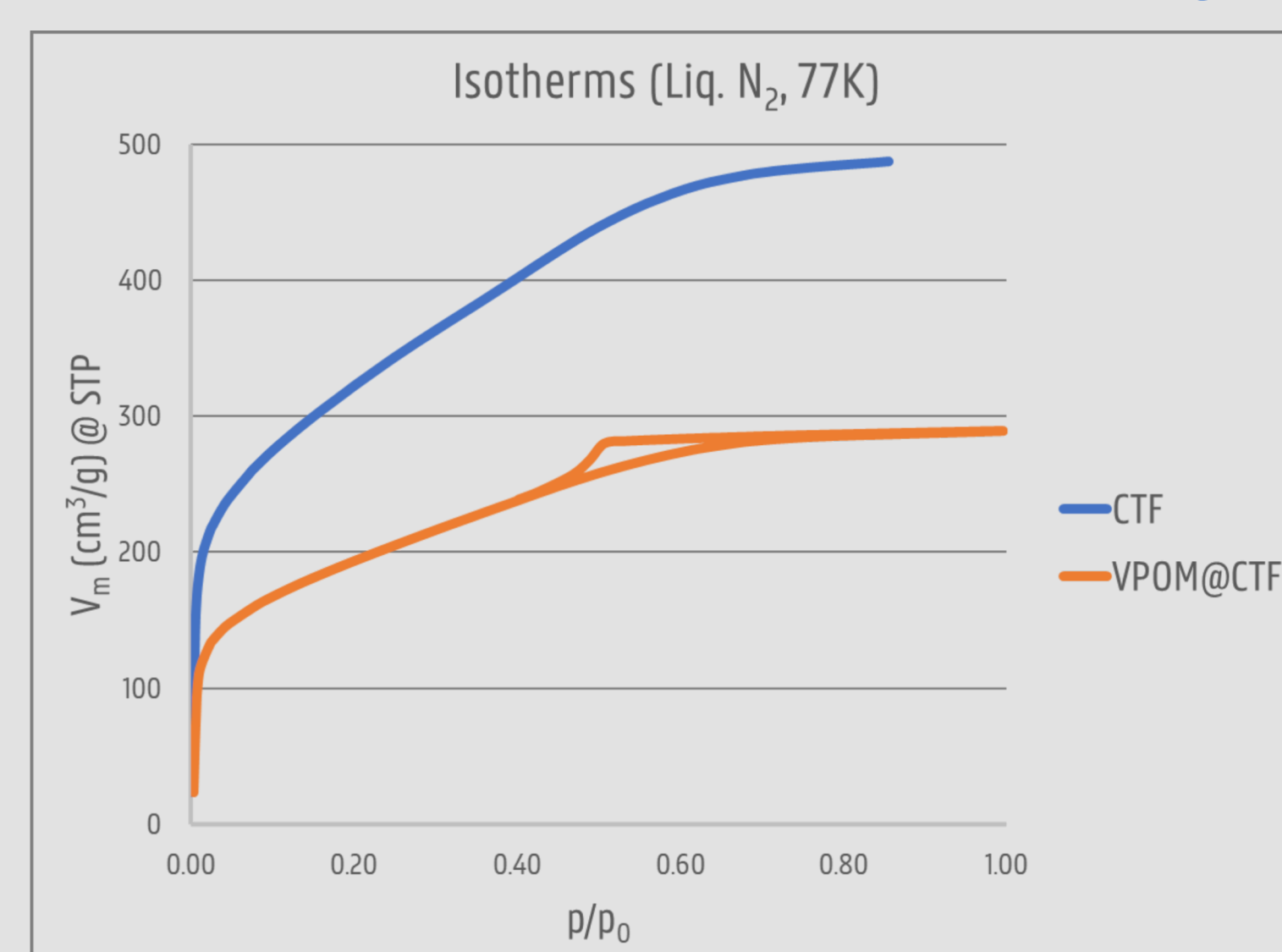
The goal is to make this multistep reaction go to the desired product in one reactor without the need for separation, purification, and transfer of intermediates produced.

The second part of the research is focused on embedding the VPOM@CTF-particles in a polyamide-4,6 (PA-4,6) nanofiber to increase ease of use and catalyst recovery. This is achieved by electrospinning a VPOM@CTF and PA-4,6 solution in formic and acetic acid [3].

Oxidative Carboxylation of Styrene



Proof of Concept: VPOM@CTF Loading



The loading was confirmed by ICP-MS measurement. Up to 25 w% of VPOM is easily anchored in the CTF through ion-ion interaction.

Oxidative Carboxylation: Preliminary Results

Standard reaction conditions

- 1 mmol Chlorobenzene as internal standard
- 1 mmol Styrene as substrate
- Under 0,1 MPa CO₂ with 0,1 mmol TBABr (32,2 mg) co-catalyst
- In 3 mL Acetonitrile as solvent for 48 h at 50 °C

Reaction	TBHP	25 w% VPOM@CTF	Styrene conversion	Styrene oxide	Styrene carbonate	Benzaldehyde	Phenylacetaldehyde
1	1,5 mmol	1,1 mg	67 %	16 %	22 %	39 %	23 %
2	1,5 mmol	5,5 mg	80 %	10 %	25 %	46 %	19 %
3	2 mmol	1,1 mg	73 %	8 %	28 %	45 %	19 %
4	2 mmol	5,5 mg	92 %	6 %	28 %	54 %	12 %

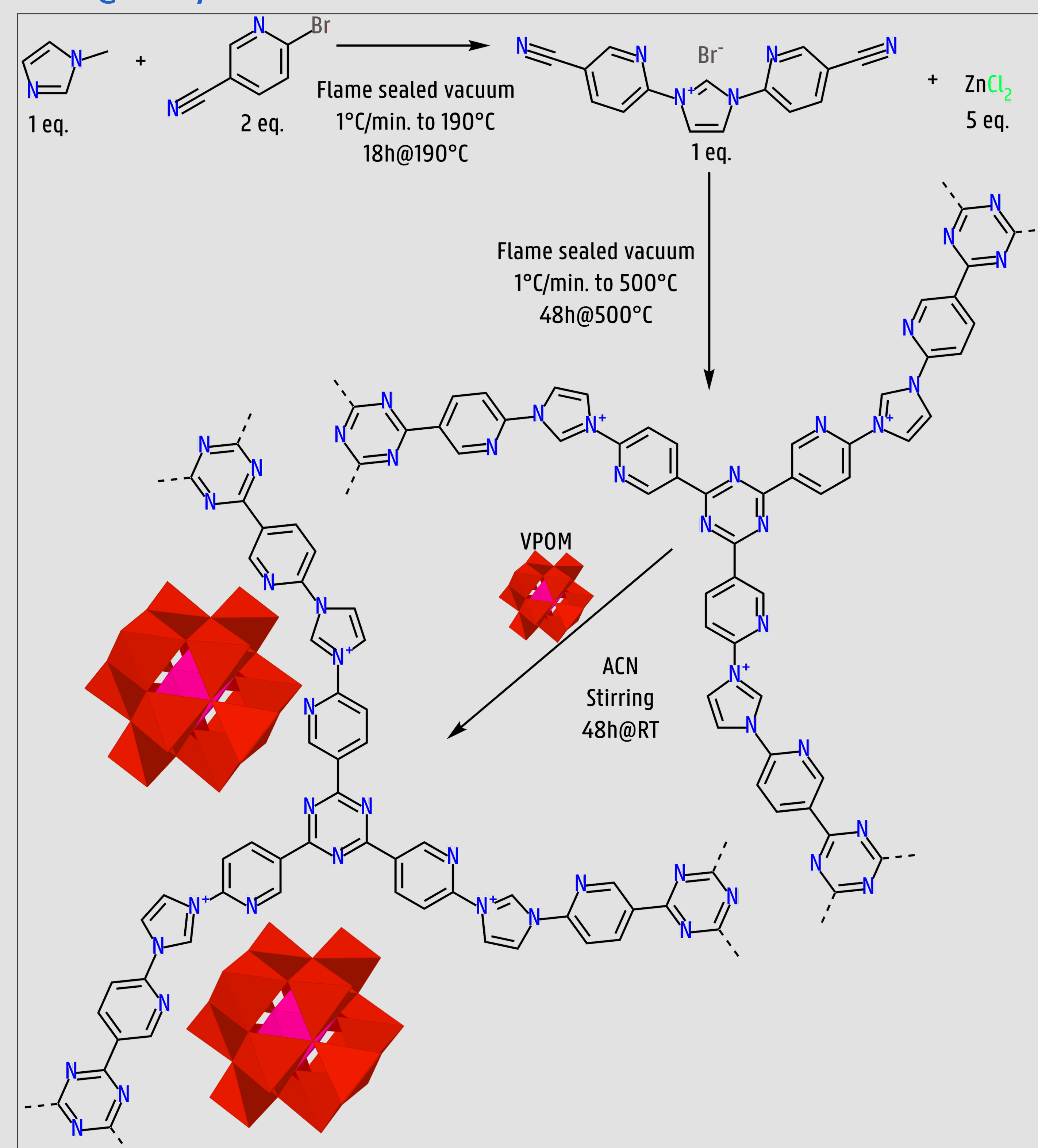
The oxidative cleavage of the C-C bond of the epoxide is a well-known side reaction resulting in the formation of benzaldehyde. The styrene conversion after 48 h is already quite high, but the challenge will be to suppress this over-oxidation and mitigate the benzaldehyde formation.

Conclusion

In this ongoing research a proof of concept for the oxidative carboxylation of styrene by VPOM@CTF@PA-4,6 is shown. The catalytic system consists of a Vanadium-based POM that catalyzes the epoxidation of styrene to styrene oxide. The anionic POM is anchored to a cationic CTF through ion-ion interaction. It is this N-rich CTF together with the TBABr co-catalyst that allows the insertion of a CO₂ molecule in the epoxide ring resulting in the formation of styrene carbonate. To more easily remove the catalyst, it is embedded in a PA-4,6 nanofiber electrospun mat. This system can be thought of as a "catalytic carpet".

The next step in this research is to increase the selectivity for styrene carbonate, expand the range of olefin substrates, embed the VPOM@CTF at a high loading in the PA-4,6 mat and test the recyclability of this system.

VPOM@CTF Synthesis



Proof of Concept: Electrospinning CTF-1@PA-4,6

