

P1: CO₂ utilisation focused on market relevant dimethyl ether production, via 3D printed reactor and solid oxide cell based technologies

^{I*}Middelkoop, V., ^{II}Pérez Gil, S., ^{III}Bonura, G., ^{IV}Sotoodeh, S., ^VAbbenhuis, E.

*lead presenter

^I vesna.middelkoop@vito.be, VITO, Belgium

^{II} TECNALIA, Spain

^{III} ITAE CNR, Italy

^{IV} Feyecon D&I BV, The Netherlands

^V Hybrid Catalysis BV, The Netherlands

This poster will showcase a newly started project, CO2Fokus (www.CO2Fokus.eu), that brings together six research organisations and six industrial partners. The project is developing cutting-edge technology able to convert industrial CO₂ into DME, a valuable gas extensively used in the chemical and energy sectors providing an alternative to fossil fuel derived feedstock.

To this end, innovative 3D printed multichannel catalytic reactors and solid oxide electrolyser cells are being developed and will be tested in an industrial environment, with a CO₂ point source at end-user facilities to evaluate its integration and operation under process relevant conditions.

The use of DME as a fuel is particularly important, since it can fulfill the ever-increasing demand for alternative, carbon-neutral, environmentally-friendly fuels and chemical and energy carriers, reducing the dependence on non-renewable sources.



These projects have received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement n. 838061
This presentation reflects only the author's views and neither Agency nor the Commission are responsible for any use that may be made of the information contained therein



P2: Heterogeneous catalysis in the fluorochemical industry

^{I*}Rees, C.N. & ^{II}Sharratt, A.P.

*lead presenter

^Iclaire.rees@kouraglobal.com, Koura Global (formerly Mexichem Fluor), U.K.

^{II} Koura Global, U.K.

Chromia-based catalysts are the workhorses of the modern fluorochemical industry and are typically used to effect halogen exchange reactions between chlorocarbon feedstocks and hydrogen fluoride. These reactions only occur at commercially useful rates under fairly extreme conditions of temperature and pressure, where the need to handle anhydrous hydrogen fluoride becomes a real challenge. Thus, a catalyst scientist working in the fluorochemical industry faces a unique set of challenges and must adopt a range of strategies to be successful. This poster will describe these challenges and the typical approaches that must be adopted to overcome them, using the example of refrigerant gas HFC-134a (1,1,1,2-tetrafluoroethane) production. It will also describe how the company came to develop an industry leading heterogeneous catalyst, operating the most efficient catalytic processes in the industry.

Fluorochemicals possess many unique and valuable properties and find applications in many fields such as refrigeration, pharmaceuticals and as monomers for polymers with a range of useful properties. In many of these applications it is their unique physical properties combined with their low toxicity and stability that makes them so valuable, but their manufacture often involves processes operating at the limits of process technology. The first challenge industrial fluorochemical catalyst science needs to overcome is designing a catalyst that will stand these process conditions whilst achieving and maintaining useful rates of reaction and selectivity. Catalysts based on chromia have proved again and again to offer the best balance of properties. The development of promoted chromia catalysts within Koura Global has underpinned the subsequent development of world class process technology for the manufacture of second generation refrigerants such as HFC-134a (1,1,1,2-tetrafluoroethane), see reaction scheme in Figure 1.1 These catalysts have proved to be remarkably active, stable and robust but have been under continuous development for c.a. 20 years are now in their tenth variant.

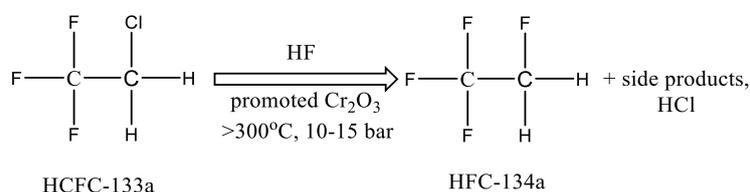


Figure 1. Example of a commercial catalytic vapour-phase hydrofluorination reaction.

This presentation will focus on how the challenges of developing these catalysts were met during the development of second generation fluorochemicals (HFC's, the ozone friendly replacements for CFC's). It will also touch on the greater challenges posed by the current focus on replacing these second-generation products with third generation products designed to address concerns over the global warming potential of HFC's. In the telling of this story the audience will come to appreciate some of the difficulties encountered in developing catalyst science in this area:

- Managing the hazards of and handling hydrogen fluoride

- Catalyst preparation, characterisation and testing
- Test rig development and design (Figure 2)
- Activity, life and stability testing and the development of high throughput test methods to do so
- The difficulties of trying to do fundamental catalyst science



Figure 2. High-throughput atmospheric catalyst screening rig for hydrofluorination chemistry.

References:

- ¹ Sharratt, A. (priority 2008). *Catalyst and Process Using the Catalyst*. US9556079 (B2).

P3: Hydrogenation, hydrogenolysis and hydrodeoxygenation of furan derivatives over noble metal catalysts in the gas phase

I, II* Althikrallah, H. A., II Kozhevnikova, E. F. & II Kozhevnikov, I. V.

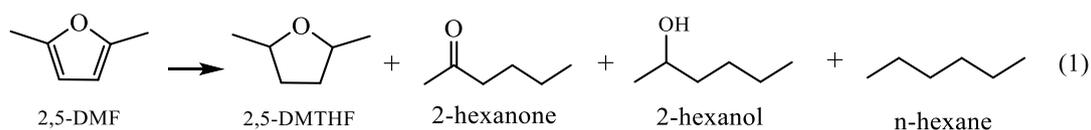
*lead presenter

^I halhekrallah@kfu.edu.sa, Department of Chemistry, King Faisal University, Saudi Arabia

^{II} kozhev@liverpool.ac.uk, Department of Chemistry, University of Liverpool, L69 7ZD, University of Liverpool, U.K.

As fossil fuel reserves become depleted, considerable attention is being given to the use of biomass as a sustainable feedstock. Fine chemicals and fuels can be synthesised using furanic compounds such as furfural, 2-methylfuran, 2,5-dimethylfuran, etc., which are a family of cellulosic or hemicellulosic platform compounds. These compounds require upgrading to produce chemicals and fuels. Hydrogenation, hydrogenolysis and hydrodeoxygenation are effective upgrading processes in the furan chemistry.

Hydrotreatment of furanic compounds over Pt, Pd, Ru, Cu and Co catalysts under relatively mild conditions (90–200 °C, 0.1 MPa) gives ring hydrogenation and ring cleavage products (eq. (1)). In hydrotreatment of 2,5-dimethylfuran (2,5-DMF) over Pt in the liquid phase, ring cleavage is favoured over ring hydrogenation. Use single-line spacing and leave a line gap between paragraphs. This helps your text to be read easily. If you would like to insert a figure you can do so. Use the *insert picture* command and *paste special* as an enhanced metafile for ease of handling.



The general aim of this work is to investigate the gas-phase hydroconversion (hydrogenation, hydrogenolysis and hydrodeoxygenation) of 2,5-dimethylfuran (DMF), chosen as a model for biomass-derived furanic compounds, over carbon-supported noble metal catalysts (Pt, Pd, Ru and Rh). The first aim of this study is (i) to compare the efficiency of noble metal catalysts in the gas phase DMF hydrogenation with that in the liquid phase and (ii) to clarify the reaction network for the gas-phase hydrogenation. The second goal is to investigate the hydrodeoxygenation of DMF in the gas phase over bifunctional metal-acid catalysts comprising noble metals and the acidic heteropoly salt CsPW. The catalysts were characterized by BET, XRD, ICP and CO chemisorption. All the reactions were carried out in a fixed-bed continuous flow reactor in the temperature range of 70–100 °C and 1.6 kPa 2,5-DMF partial pressure using H₂ as a carrier gas at ambient pressure (1 bar).

It is demonstrated that the bifunctional hydrotreatment pathway is more efficient than the monofunctional metal-catalysed pathway. The Pt/C + CsPW physical mixture was found to be a very efficient catalyst for the selective one-step hydrodeoxygenation of 2,5-DMF under mild conditions via the metal-acid bifunctional catalysis, providing almost 100% yield of n-hexane.

P4: Heterogeneous H₂-driven biocatalysis in batch and flow

¹*Thompson, L.A., ¹Reeve, H.A. & ¹Vincent, K.A.

*lead presenter

¹ lisa.thompson@chem.ox.ac.uk, University of Oxford, U.K.

High selectivity under mild reaction conditions makes enzymes a valuable tool for greener, more efficient chemical production.¹ However, many redox enzymes require expensive cofactors (NADH or NADPH) to operate and the enzymes can be difficult to recover from solution, which can inhibit the uptake of biocatalytic processes. To overcome this, cofactor recycling and enzyme immobilisation methods have been developed. Common cofactor recycling methods employ additional enzymes and sacrificial substrates, generating a large amount of waste. Enzyme immobilisation can allow for easier recovery and re-use of the catalyst, and make them amenable to use in flow reactors. However, many immobilisation methods require modification to the enzyme or use non-commercial supports.

Here we describe a heterogeneous biocatalytic cofactor recycling system that uses H₂ gas to regenerate NADH.^{2,3} The sequence of enzymes is simply adsorbed onto a carbon support, which allows transfer of electrons between the enzymes. This can be applied to a range of carbon supports (nanoparticles, electrodes, carbon nanotubes), depending on the reactor design. As such, we have developed a flow reactor with the enzymes supported on carbon nanotubes for H₂-driven biocatalytic ketone reduction and reductive amination.⁴

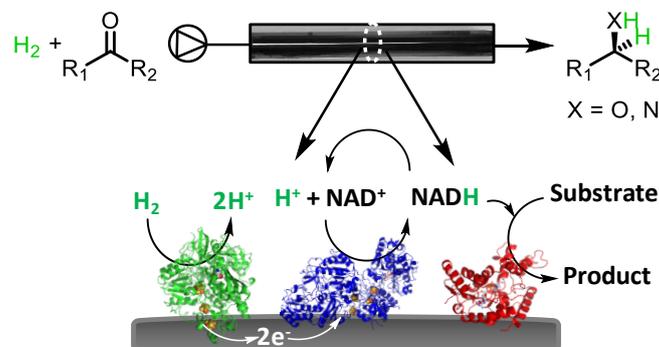


Figure 1: Heterogeneous H₂-driven biocatalysis with built-in cofactor recycling in a continuous carbon nanotube flow reactor.

References:

¹ Sheldon, R. and Woodley, J. (2018). Role of Biocatalysis in Sustainable Chemistry. *Chem. Rev.* 118(2), pp. 801-838.

² Reeve, H., Lauterbach, L., Ash, P., Lenz, O. and Vincent, K. (2012). A modular system for regeneration of NAD cofactors using graphite particles modified with hydrogenase and diaphorase moieties. *Chem. Commun.* 48(10), pp. 1589-1591.

³ Reeve, H., Lauterbach, L., Lenz, O. and Vincent, K. (2015). Enzyme-Modified Particles for Selective Biocatalytic Hydrogenation by Hydrogen-Driven NADH Recycling. *ChemCatChem.* 7(21), pp. 3480-3487.

⁴ Zor, C., Reeve, H., Quinson, J., Thompson, L., Lonsdale, T., Dillon, F., Grobert, N. and Vincent, K. (2017). H₂-Driven biocatalytic hydrogenation in continuous flow using enzyme-modified carbon nanotube columns. *Chem. Commun.* 53(71), pp. 9839-9841.

P5: Monomers for biodegradable plastics - green production by heterogeneous catalysts

¹*Meacham, S. G. & ¹Taylor, R. A.

*lead presenter

¹ samuel.g.meacham@durham.ac.uk, Durham University, U.K.

Cyclic esters such as lactones and lactides are key monomers for the synthesis of biodegradable polymers. Poly(lactic acid) (PLA) is the most common example, synthesised by ring opening polymerisation of lactide, the cyclic diester of lactic acid. However, PLA production is hampered by the energy-intensive process for synthesising lactide, as well as the resultant polymer's relatively low glass transition temperature (~55 °C).

Heterogeneous zeolite catalysts can selectively produce lactide from lactic acid in a single step.¹ However, their use in synthesis of monomers with greater functionality than lactide has not been reported in detail in the open literature.

In this project, the use of zeolite catalysts has been investigated for the synthesis of a cyclic ester, mandelide, from mandelic acid, a phenyl-functionalised alpha-hydroxy acid. The ring opening polymerisation of mandelide produces degradable polymers with properties similar to that of polystyrene.²

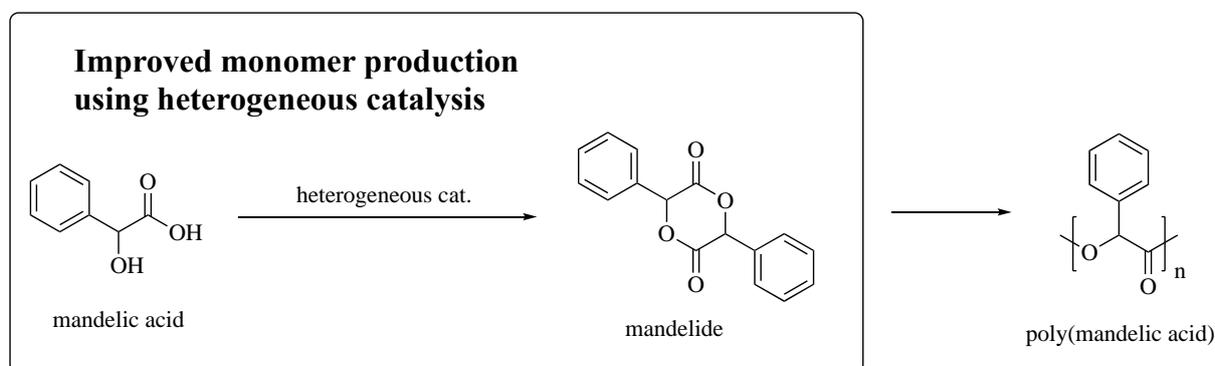


Figure 1. Proposed route to functionalised biodegradable plastics using heterogeneous catalysis to produce functionalised lactide monomers.

References:

¹ Dusselier, M., Van Wouwe, P., Dewaele, A., Jacobs, P. A. and Sels, B. F. (2015) Shape-selective zeolite catalysis for bioplastics production. *Science*, 349(6243), pp. 78-80.

² Liu, T. Q., Simmons, T. L., Bohnsack, D. A., Mackay, M. E., Smith, M. R. and Baker, G. L. (2007). Synthesis of Polymandelide: A Degradable Polylactide Derivative with Polystyrene-like Properties, *Macromolecules*, 40(17), pp. 6040-6047.

P6: Discovery of stable and active catalytic materials via high throughput screening

¹*Carrillo, P., ¹Alvarado, L., ¹ Katsoulidis, A., ¹Zanella, M., ¹Manning, T.,
¹Claridge, J. & ¹Rosseinsky, M. J.

*lead presenter

¹ p.carrillo-sanchez@liverpool.ac.uk, University of Liverpool, U.K.

The rapid development of active and stable heterogeneous catalysts is crucial to successfully tackle the negative impact of climate change and the limited natural resources while satisfying the demands of modern society and increasing population. However, characterization methods (e.g. active metal surface area, particle size and reducibility), and activity and stability tests require long measuring times. Even though theoretical approaches are less time consuming, a theory of the prediction of the catalytic properties of substances has not been able to replace the experimental empirical methods of catalyst discovery. Here we present a high throughput (HT) proxy-based protocol to identify stable, active catalysts by synthesizing hundreds of samples per month and measuring their stability over thousands of hours. The catalysts' stability is assessed by X-ray diffraction measurements of the catalysts phase assemblage (metal to support diffracted intensity ratio) and particle size (line width analysis). This approach has been used to identify "hits" samples that can be scaled-up for activity and selectivity analyses to yield active and stable catalysts.

P7: VerSoX: a versatile soft X-ray beamline at Diamond Light Source

¹*Ferrer, P., ¹Venturini, F., ¹Grinter, D., ¹Quevedo, W., ¹Roi, K., ¹Arrigo, R. & ¹Held, G.

*lead presenter

¹pilar.ferrer-escorihuela@diamond.ac.uk, Diamond Light Source, U.K.

VerSox is a Diamond Light Source bending magnet beamline that cover a diverse range of scientific areas. These include studies involving heterogeneous catalysts under realistic conditions, pharmaceuticals and biomaterials, environmental and space science studies on liquids and ices, heritage conservation, and the study of electronic and photonic materials. VerSox investigates the chemical nature and composition of the near-surface regions of the samples, which are to be investigated using soft X-ray photoelectron spectroscopy (XPS) and Near Edge X-ray absorption spectroscopy (NEXAFS) in pressure ranges that will vary from UHV to less standard Near Ambient Pressure (NAP) conditions.

P8: Model catalytic hydrogenation reaction of an alkyne using palladium on naturally derived mesoporous carbons produced sustainably at scale.

¹*Goodlet, G., ¹Powell, N.A. & ¹Smith, R.A.P.

*lead presenter

¹gregory.goodlet@matthey.com, Johnson Matthey, U.K.

The use of tuneable mesoporous carbons to fabricate palladium catalysts for the hydrogenation of a specific alkyne was investigated. The nature of the sustainable carbons produced in the EU-funded *Porous4App* project (Horizon 2020 Grant No. 686163) was explored by using these as supports for palladium catalysts in the hydrogenation of 1-hexyn-3-ol. A comparison of these novel carbon catalysts with a standard activated carbon catalyst showed significant differences which are to be further investigated.

P9: Dehydration of ethanol to ethylene over heteropoly acid catalysts in the gas phase

I, II*Al-Faze, R., IIKozhevnikova, E. F. & IIKozhevnikov, I. V.

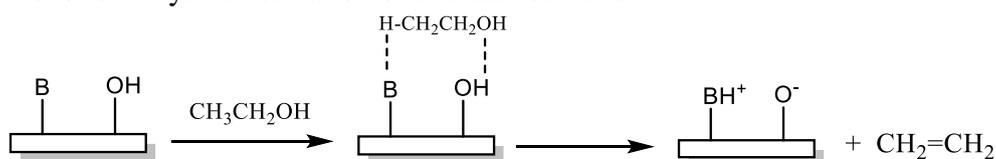
*lead presenter

^Irawan.faze@gmail.com, Taibah University, Medina, Saudi Arabia

^{II}Department of Chemistry, University of Liverpool, L69 7ZD, U.K.

The dehydration of ethanol has long been of interest to produce ethene and diethyl ether (DEE) from non-petroleum renewable feedstock. Ethene is the feedstock for about 30% of all petrochemicals, and DEE is a valuable chemical and a green fuel alternative. The current method of producing ethylene is the steam cracking of fuels, however with the current rise in global emissions of greenhouse gases, attention has turned to new, renewable methods of producing ethylene.

HPAs have been found to exhibit higher catalytic activities in these reactions than oxide and zeolite catalysts, in agreement with the relative acid strength of these catalysts. Solid Keggin-type heteropoly acids $H_n\{XW_{12}O_{40}\}^{n-}$ (HPA) have very strong Brønsted acid sites, stronger than those in zeolites and metal oxides. Alharbi et al. showed that HPAs exhibit a higher catalytic activity than HZSM-5 in dehydration of ethanol to DEE and ethene at low temperatures, with reaction turnover rate for both catalysts determined by the strength of catalyst acid sites. The dehydration of ethanol into ethene follows the mechanism shown in scheme 1. There is also a side product formation of diethyl ether (DEE). The mechanism of DEE formation may be represented by two different pathways termed associative and dissociative pathway. This research aims to investigate the catalytic activity of bulk and silica-supported HPA catalysts in the dehydration of ethanol to ethene and diethyl ether (DEE) in the gas phase, whilst optimising the conditions for ethylene formation over DEE formation.



Scheme 1. Reaction pathway for ethanol-to-ethylene dehydration.

The HPA catalysts included bulk $H_3PW_{12}O_{40}$ (HPW) and $H_4SiW_{12}O_{40}$ (HSiW), as well as HPW and HSiW supported on SiO_2 at 10-60 wt% loading, prepared by wet impregnation method. Silica was chosen as the support due to its large surface area and weak interaction with HPA. The catalysts were characterized by several techniques such as BET, XRD, FTIR, ICP, and NH_3 adsorption microcalorimetry. Dehydration of ethanol was studied in a continuous flow fixed-bed reactor with on-line GC analysis described previously in the temperature range of 100-200°C at 1.5-13.6 kPa ethanol partial pressure using N_2 as a carrier gas. It was found that ethanol conversion increased with increasing the HPA loading, passing a flat maximum between 25-60% HPA loading. This can be explained by increasing the strength of catalyst active sites and decreasing the surface area, which cause the opposite effect on ethanol conversion. HSiW catalysts exhibited higher activity than HPW catalysts probably due to the larger number of proton sites in HSiW compared to HPW. Conversion varies across different ethanol partial pressures also were obtained. Alcohol dehydration follows the Langmuir kinetics with reaction order in alcohol between 0 and 1. Because of this the conversion decreases with increasing the partial pressure of ethanol. Under the conditions studied, we observed stable catalyst performance at a high ethanol partial pressure of 13kPa.

P10: Oxidative desulfurization of model diesel fuel catalyzed by carbon-supported heteropoly acids

^IGhubayra, R., ^INuttall, C., ^IHodgkiss, S., ^IRogers, C., ^ICraven, M.,
^{II}Kozhevnikova, E. F. & ^{II}Kozhevnikov, I. V.*

*lead presenter

^I reem.ghubayra@liverpool.ac.uk, Department of Chemistry, University of Liverpool, L69 7ZD, U.K.

Our work investigate heterogeneous catalysis by Keggin-type HPAs ($H_3PMO_{12}O_{40}$, $H_3PW_{12}O_{40}$ and $H_4SiW_{12}O_{40}$) supported on activated carbon (HPA/C) for the biphasic oxidative desulfurization of model diesel fuel (heptane) by aqueous 30% H_2O_2 . We report a highly efficient catalyst, $H_3PMO_{12}O_{40}/C$, for the oxidation of benzothiophenes (benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT)) to the corresponding sulfones by H_2O_2 . This catalyst shows a higher catalytic activity for the oxidation of benzothiophenes than other recently reported heterogeneous ODS catalysts in similar systems. Strong adsorption of $H_3PMO_{12}O_{40}$ onto the carbon support stabilizes the HPA structure and prevents the HPA from leaching. In addition, our kinetic and infrared spectroscopic studies provide new insights into the mechanism of ODS reaction on carbon-supported HPAs.

P11: Real-time chemical imaging of working catalysts, fuel cells and batteries

I,II,III*Vamvakeros, A., IV,VMatras, D., IJacques, S. D. M., III di Michiel, M., VI Middelkoop, V. & I,II,VBeale, A. M.

*lead presenter

I antony@finden.co.uk, Finden Limited, Merchant House, Abingdon, OX14 5EG, U.K.

II Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, U.K.

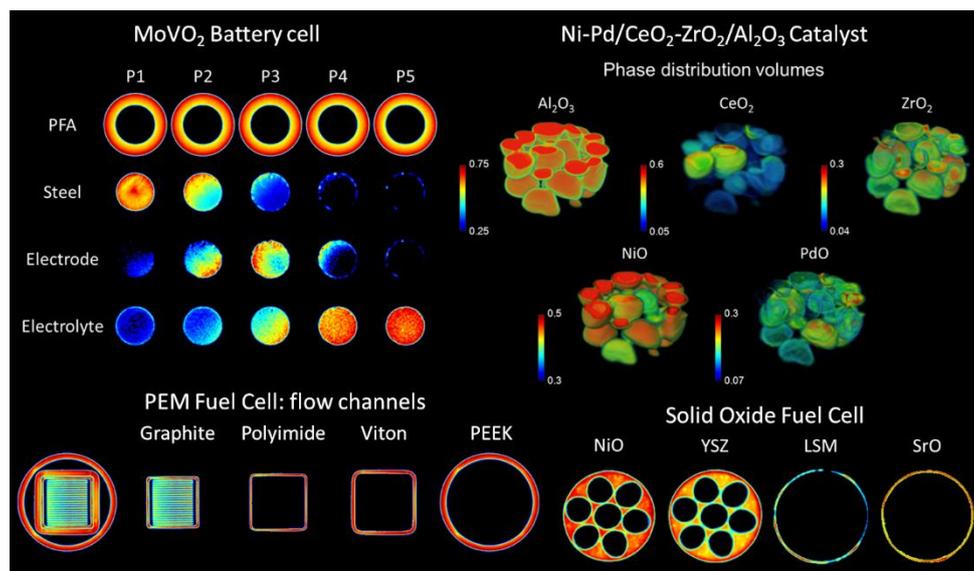
III ESRF - The European Synchrotron, Grenoble, 38000 France.

IV School of Materials, University of Manchester, Manchester, Lancashire M13 9PL, U.K.

V Research Complex at Harwell, Harwell Science and Innovation Campus, Rutherford Appleton Laboratory, Didcot, Oxon, OX11 0FA, U.K.

VI Flemish Institute for Technological Research, VITO NV, Boeretang 200, 2400 Mol, Belgium.

In the past decade, a lot of effort has been put into developing novel reactor cells that allow for chemical imaging of functional materials and devices under industrially-relevant operating conditions. It is now possible to obtain the desired spatially-resolved chemical information by combining X-ray scattering and spectroscopic techniques with computed tomography^{1,2}. Such techniques are considered to fall under the umbrella of “chemical tomography” as each pixel in the reconstructed images corresponds to a chemical signal. The main advantage of these techniques though lies on the fact that they allow to track the chemical changes taking place in a functional material or device under operating conditions as a function of time and/or chemical environment. As demonstrated in the following Figure, we will present different case studies where we have applied the X-ray diffraction computed tomography (XRD-CT) technique to study functional materials and devices, ranging from batteries to fuel cells and catalysts³⁻⁷.



References:

¹ Beale, A.M. et al., 2014, *Coordination Chemistry Reviews*, 277, 208

² Vamvakeros, A., et al., 2015, *Chemical Communications*, 51, 12752-12755

³ Vamvakeros, A., et al., 2018, *Nature Communications*, 9, 4751

⁴ Matras, D., et al., 2019, *The Journal of Physical Chemistry C*, 123, 1751-1760

⁵ Finegan, D. P., et al., 2019, *Nano Letters*, 19, 3811-3820

⁶ Martens, I., et al., 2019, *Journal of Power Sources*, 437

⁷ Li, T., et al., 2019, *Nature Communications*, 10, 1497.

P12: Cascade conversion of bio-derived platform chemicals with multifunctional zeolitic materials

^{I*}Raynes, S.J., ^{II}Taylor, R.A.

^Isamuel.raynes@durham.ac.uk, Durham University, United Kingdom

^{II} Durham University, United Kingdom

Introduction

As of early 2017, more bio-derived ethanol is produced in the United States than demand for gasoline blending and exports exists.¹ Due to the wide array of reaction networks that are accessible, ethanol is an extremely versatile platform molecule.² Hence, excess bio-derived ethanol has the potential to be a cheap, convenient and renewable carbon source from which to produce high value chemicals that are typically derived from fossil fuels. Zeolites, microporous aluminosilicate materials, are considered to be promising alternative materials to many current generation catalysts owing to their distinctive properties. Due to the multitude of potential modification techniques and their unique ability to confer shape-selectivity to reactions through channels and cages of molecular dimensions, catalysts can be attained that target production of small linear molecules such as ⁿbutanol and 1,3-butadiene. Zeolites have been suggested to perform these transformations in a single reaction process due to their ability to incorporate several disparate active centers into their frameworks and channel system.³⁻⁵

Materials and Methods

Metal modified mordenites ($M_xO_y/Na-MOR$, Si/Al = 7) and other zeolites were prepared by impregnation with the respective metal nitrate solution followed by drying and calcination at 550 °C under static air. Alkali metal exchanged zeolites were prepared by an ion-exchange process in which the zeolite was washed with 0.3M metal nitrate solution ($\times 10$) followed by drying and calcination at 550 °C under static air. Heteroatomically substituted zeolite materials were prepared by either a hydrothermal synthesis method or by dealumination in nitric acid followed by remetallation under inert conditions with the desired metal chloride solution in dichloromethane. Reactions under flow conditions were performed using a HEL FlowCAT flow reactor feeding ethanol *via* an HPLC pump (feed rate = 0.01 mL min⁻¹). All catalysts were pretreated at 673 K under flowing He or N₂ (40 mL min⁻¹) before being adjusted to the desired reaction temperature (473-673 K). On-line analysis was performed by GC-MS-BID (Shimadzu QP2010) equipped with BPX90 (SGE Analytical) or RTX-VMS (Restek) columns for MS and ShinCarbon ST (Restek) column for BID.

Results and Discussion

Dehydrogenation of ethanol to acetaldehyde, the initial step of many cascade reactions, was explored over a multitude of metal impregnated and exchanged mordenite catalysts. It was found that ZnO impregnation yielded the highest acetaldehyde productivity and carbon selectivity of all catalysts tested at 673 K (see Figure 2). Exchange of Na⁺ cations for other alkali metals showed a significant decrease in the productivity of ethylene, a competing side product. The catalyst ZnO/Na-MOR-(7) showed good resistance to reaction with hydrous ethanol (95%) and good stability over time. It was observed that whilst acetaldehyde productivity remained constant, productivity of ethylene decreased exponentially, leading to increased acetaldehyde selectivity over time (see Figure 2).

Additionally, heteroatomically substituted (Sn, Zr, Mg, Zn) MFI and bimetallic (Al/Sn, Al/Ti) MOR zeolites have been synthesised by various means and screened for their activity in ethanol cascade conversion both with and without ZnO impregnation. The addition of ZnO is shown to

be significant; whilst Sn-MFI showed low ethanol conversion and low selectivity to cascade reaction products, ZnO/Sn-MFI showed much higher ethanol conversion and higher selectivity to C₄ products.

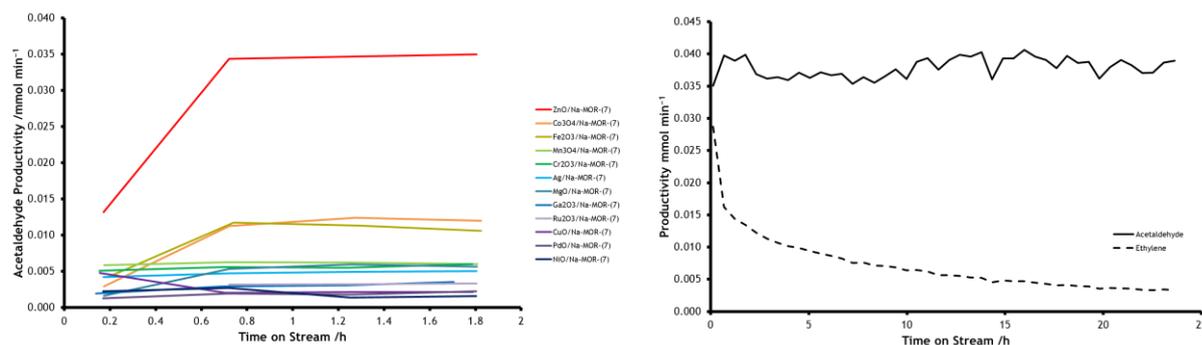


Figure 2 Left: The productivity of acetaldehyde from ethanol over time for mordenites impregnated with various metal oxide species, here ZnO (red line) is shown to be superior to all others tested. Right: Productivities of acetaldehyde (solid line) and ethylene (dashed line) from ethanol over ZnO/Na-MOR-(7). Whilst acetaldehyde productivity remains constant for 24 h time on stream, ethylene productivity is seen to decrease rapidly.

Significance

Whilst various heteroatomically substituted BEA zeolites (Sn, Zr, Ti, Hf) have been shown to achieve good selectivity to butadiene in the literature,^{6,7} few zeolite catalysts have been shown to effectively catalyse the cascade reaction of ethanol to n-butanol. This work explores the effect of zeolite framework (MFI, MOR) on the reactivity of active sites and reaction product distribution. The addition of a dedicated dehydrogenation center is shown to accelerate acetaldehyde production and is expected to increase the turnover frequency of the desired cascade reaction.

References:

- ¹ United States Energy Institute Administration, U.S. fuel ethanol production continues to grow in 2017, (<https://www.eia.gov/todayinenergy/detail.php?id=32152>, accessed: 08/01/18).
- ² Sun, J. and Wang, Y. (2014). Recent Advances in Catalytic Conversion of Ethanol to Chemicals. *ACS Catalysis*, 4(4), pp. 1078-1090.
- ³ Kyriienko, P. I., Larina, O. V., Soloviev, S. O., Orlyk, S. M., Calers, C., Dzwigaj, S. (2017). Ethanol Conversion into 1,3-Butadiene by the Lebedev Method over MTaSiBEA Zeolites (M = Ag, Cu, Zn). *ACS Sustainable Chemistry & Engineering*, 5(3), pp. 2075-2083.
- ⁴ Dai, W. L., Zhang, S. S., Yu, Z. Y., Yan, T. T., Wu, G. J., Guan, N. J., Li, L. D. (2017). Zeolite Structural Confinement Effects Enhance One-Pot Catalytic Conversion of Ethanol to Butadiene. *ACS Catalysis*, 7(5), pp. 3703-3706.
- ⁵ Ennaert, T., Van Aelst, J., Dijkmans, J., De Clercq, R., Schutyser, W., Dusselier, M., Verboekend, D., Sels, B. F. (2016). Potential and challenges of zeolite chemistry in the catalytic conversion of biomass. *Chemical Society Reviews*, 45(3), pp. 584-611.
- ⁶ Palagin, Dennis, Sushkevich, Vitaly L., Ivanova, Irina I. (2016). C-C Coupling Catalyzed by Zeolites: Is Enolization the Only Possible Pathway for Aldol Condensation?. *The Journal of Physical Chemistry C*, 120(41), pp. 23566-23575.
- ⁷ Sushkevich, Vitaly L., Palagin, Dennis, Ivanova, Irina I. (2015). With Open Arms: Open Sites of ZrBEA Zeolite Facilitate Selective Synthesis of Butadiene from Ethanol. *ACS Catalysis*, 5(8), pp. 4833-4836.

P13: 3D printed microstructured reactors for organic chemical production

^{I,II}*Clement, J., ^IMiddelkoop, V., ^{IV}Kellici, S., ^{III}Köckritz, A., ^{III}Bienert, R. & ^{II,V}Beale, A.

*lead presenter

^I clement.jacquot.17@ucl.ac.uk, Sustainable Materials Management, Flemish Institute for Technological Research, VITO, Belgium.

^{II} Department of Chemistry, University College London, U.K.

^{III} Leibniz-Institut für Katalyse, LIKAT, Germany.

^{IV} School of Engineering, London South Bank University, U.K.

^V Research Complex at Harwell, U.K.

A series of tailored, porous catalyst bed architectures optimisation and integrated into a continuous flow reactor for selected selective oxidations in the liquid phase. These novel architectures were micro-structured catalytic beds 3D printed by a direct-write technique, commonly termed micro-extrusion or 3D fiber deposition. The developed 3D structures present several advantage^{1,2} such as a high surface area and tailored porosity (pore size and network), improved mass and heat transfer and reduced pressure drop along the reactor. A well-developed formulation and geometries of 3D micro-structured catalytic reactors could provide operational effectiveness over common packed bed/batch reactors for a lower content in PMG catalysts such as Palladium partially replaced by less active but more sustainable metals such as Cobalt or even Iron. The starting compositions were deposited active catalytic materials onto the appropriate supports..

From the data obtained so far it can be concluded that Fe/Co containing catalysts showed a promising performance (selectivity of more than 60%, conversion of 90% using Fe₁₅Co₁₅/Al₂O₃ for benzyl alcohol selective oxidation into benzaldehyde³ in continuous conditions). There is scope for further by focusing the reaction study on the following: influence of support type, accessibility of the active sites, morphology (pore size) and optimisation of reaction conditions.

References:

¹ Middelkoop, V., Vamvakeros, A., de Wit, D., Jacques, S. D. M., Danaci, S., Jacquot, C., de Vos, Y., Matras, D., Price, S. W. T. & Beale, A. (2019) 3D Printed Ni/Al₂O₃ Based Catalysts for CO₂ Methanation - a Comparative and Operando XRD-CT Study, *Journal of CO₂ Utilization*, 33, p478–487.

² Danaci, S. (2017) Optimisation and Integration of Catalytic Porous Structures into Structured Reactors for CO₂ Conversion to Methane.

³ Gómez-Villarraga, F., Radnik, J., Martin, A. & Köckritz, A. (2016) Synergistic Effect in the Oxidation of Benzyl Alcohol Using Citrate-Stabilized Gold Bimetallic Nanoparticles Supported on Alumina, *Journal of Nanoparticle Research*, 18, 6, <https://doi.org/10.1007/s11051-016-3453-7>.

P14: Non-thermal plasma (NTP) activated heterogeneous catalysts for catalytic CO₂ hydrogenation

¹*Chen, H., ¹Mu, Y., ¹Fan, X. & ¹Hardacre, C.

*lead presenter

¹huanhao.chen@manchester.ac.uk; xiaolei.fan@manchester.ac.uk;

c.hardacre@manchester.ac.uk, Department of Chemical Engineering and Analytical Science, School of Engineering, The University of Manchester, M13 9PL, U.K.

Valorization of CO₂ (e.g. from biogas) via catalytic hydrogenation with renewable hydrogen (e.g. from water electrolysis) into methane is a promising avenue to storage renewable energy in the form of methane and reducing greenhouse gas emissions. Coupling heterogeneous catalysts with non-thermal plasma (NTP) has been recently considered a plausible method for a wide range of challenging reactions. In this presentation, NTP activated catalytic CO₂ hydrogenation was studied in detail using a series of supported Ni or Ru catalysts on porous materials (e.g. Na-BETA zeolite, UiO-66 metal-organic framework, MgAl layered double hydroxide) (Figure 1). Additionally, kinetic studies of NTP activated catalytic CO₂ hydrogenation over heterogeneous catalysts were performed in order to understand the interaction between plasma and catalysts. In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) developed in our group was also specifically employed to probe the surface of catalysts during the NTP activated catalytic reactions aiming at understanding the NTP promoted surface reactions and revealing possible reaction pathways.

Keywords: Non-thermal plasma; Heterogeneous catalyst; Catalytic CO₂ hydrogenation; Kinetic study; In situ characterization

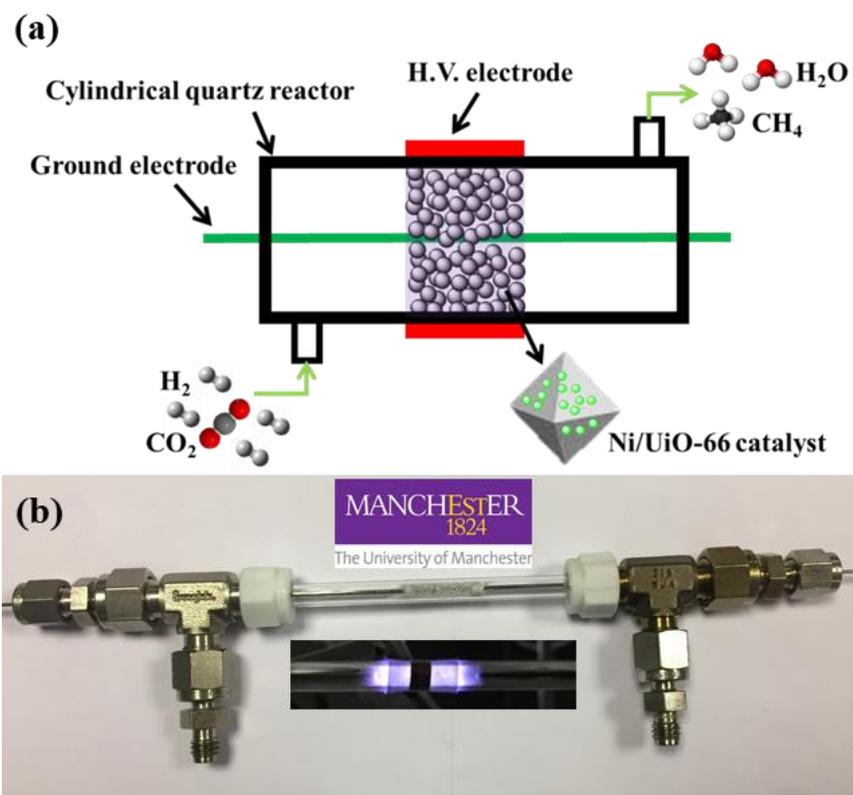


Figure 1. (a) Schematic and (b) photograph of the DBD plasma reactor for catalytic CO₂ hydrogenation.

P15: Chemical imaging of catalytic materials as an emerging tool for improved catalyst design

^{I,II}*Matras, D., ^{III,IV}Vamvakeros, A., ^{III}Jacques, S. D. M., ^Vdi Michiel, M., ^{VI}Middelkoop, V. & ^{II,III,IV}Beale, A. M.

*lead presenter

^I School of Materials, University of Manchester, Manchester, Lancashire M13 9PL, U.K.

^{II} Research Complex at Harwell, Harwell Science and Innovation Campus, Rutherford Appleton Laboratory, Didcot, Oxon, OX11 0FA, U.K.

^{III} Finden Limited, Merchant House, 5 East St Helen Street, Abingdon, OX14 5EG, U.K.

^{IV} Department of Chemistry, University College London, 20 Gordon Street, London, WC1H 0AJ, U.K.

^V ESRF- The European Synchrotron, Grenoble, 38000 France.

^{VI} Flemish Institute for Technological Research, VITO NV, Boeretang 200, 2400 Mol, Belgium.

The development of X-ray imaging techniques for the application to study heterogeneous catalysts under operating conditions has significantly advanced over the past several years¹. Non-destructive scattering/spectroscopic techniques can be now applied to investigate in real-time working catalytic materials in their industrial forms and under industrially relevant conditions of temperature and/or pressure. The obtained spatially-resolved signals provide unique physico-chemical information, impossible to achieve with a standard conventional bulk measurements^{2,3}. In this work, we focus on the application of X-ray diffraction computed tomography technique (XRD-CT) which combines powder X-ray diffraction with the computed tomography. As we recently demonstrated, the combination of brilliant X-rays generated in 3rd generation synchrotrons (such as beamline ID15A in ESRF) with state-of-the-art detectors (Pilatus3 X CdTe 2M) makes it now possible to perform 5D tomographic diffraction imaging experiments (3D spatial, 1D scattering signal and 1D temporal/imposed environment dimensions) with high spatial (<1 μm) and temporal (ms) resolution^{4,5}. X-ray tomographic diffraction imaging can offer an in-depth insight into the solid-state chemical evolution of a working catalyst. The physico-chemical information about the various catalyst components collected under industrially relevant conditions (i.e. catalyst shape and chemical environment) can provide a better understanding of the complex structure-activity relationships and pave the way towards rational design of new catalysts with improved performance.

In this presentation we aim to demonstrate the principles of the XRD-CT technique and its application to operando experiments of selective oxidation reactions, namely oxidative coupling of methane and partial oxidation of methane. As an example, a Na-Mn-W/SiO₂ catalyst was studied during the oxidative coupling of methane reaction with XRD-CT (Figure 1). The results from this study allowed us to identify the reasons behind the catalyst deactivation, resulting from the mobility and volatilisation of active components Na⁺ and WO₄²⁻ at the operating conditions, as well as propose effective solutions of their stabilization and thus improvement in the catalyst long-term stability⁶.

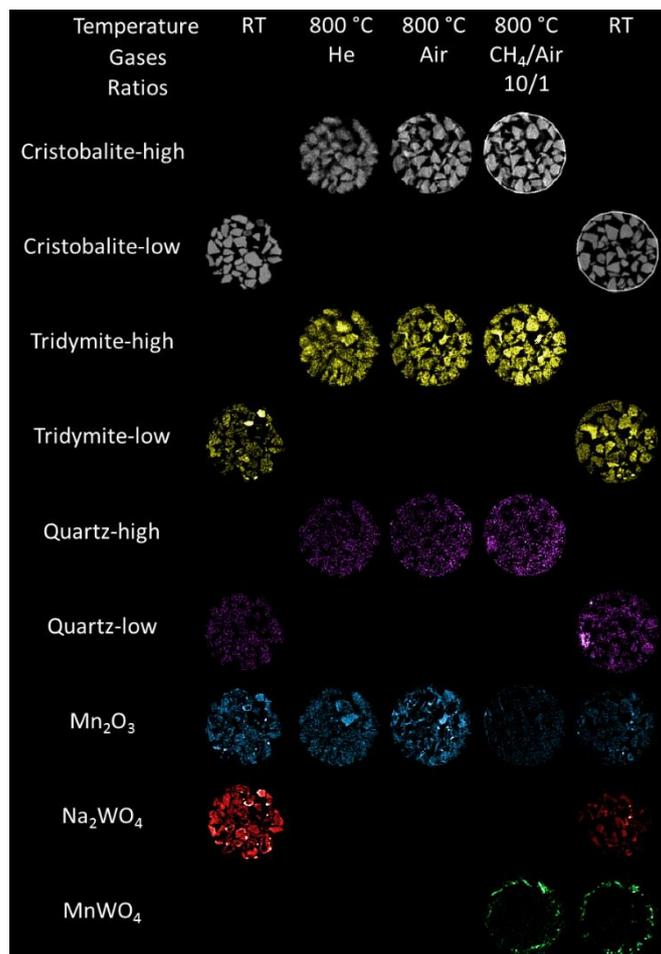


Figure 1 Phase distribution maps created based on the intensities of the scale factors of each crystalline phase⁶.

References:

- ¹ Beale, A.M. et al. (2014) *Coord. Chem. Rev.*, 277, 208.
- ² Matras, D. et al. (2018) *J. Chem. Phys. C*, 122, 2221.
- ³ Jacques, S.D.M. et al. (2013) *Nature Comm.*, 4, 2536.
- ⁴ Vamvakeros, A., et al. (2018) *Nature Comm.*, 9, 4751.
- ⁵ Matras, D. et al., *ACS Catal.*, (submitted).
- ⁶ Vamvakeros, A. et al., *ACS Catal.*, (submitted).

P16: Excellent catalytic behaviour towards hydrogenation reaction of nitrophenols over nickel/N-doped C nanomaterials prepared by polymerized complexing method

¹*Li, P., ¹ Wang, J. & ¹ Jiang, S.

*lead presenter

¹ School of Chemical Engineering, Nanjing University of Science and Technology, 210094 Nanjing, People's Republic of China.

Hydrogenation reduction reaction of nitrophenol to aminophenol is a conventional reaction to reduce the toxicity of nitrophenol and this reaction can be accelerated by using catalyst. Increasing the activity parameter of the catalysts can reduce the cost of the hydrogenation reaction. This work addresses the high activity parameters of Ni/N-doped carbon nanocatalysts toward the hydrogenation reduction reaction of nitrophenols. The Ni/N-doped carbon nanomaterials have been prepared by polymerized complexing method by employing various polyhydric alcohol and plant extracts as bonding agent. The Ni/N-doped carbon nanomaterials have a high activity parameter of $695.8 \text{ s}^{-1} \cdot \text{g}^{-1}$ toward the hydrogenation reduction reaction of 4-nitrophenol by using sodium borohydride as reducing agent, and this activity parameter is almost one order of magnitude higher than those reported in literatures..

Keywords: Hydrogenation reduction reaction; Nitrophenol; Nickel; Polymerized complexing.

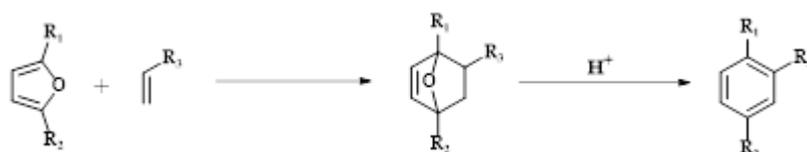
P17: Renewable route to the production of aromatics over sulfonic acid functionalized metal organic framework

¹*Ramesh, S. S., ¹Katsoulidis, A. & ¹Rosseinsky, M.

*lead presenter

¹S.Sringeri-Ramesh@liverpool.ac.uk, Department of Chemistry, University of Liverpool, U.K.

Aromatics are quite essential building blocks in synthetic chemistry for the design of drugs, polymers, cosmetics and other industrially relevant compounds¹. Petroleum feedstocks are currently driving the industrial scale production of aromatics, in view of its limited supply, other renewable resources such as bio-feedstocks is gaining extraordinary importance. Furan derivatives are important bio-based precursors for the green route to the production of aromatics via cascade process involving Diels-Alder reaction and the dehydration. Grounds have already been set in this direction and zeolites with Lewis/Bronsted acid sites were explored extensively in the past to produce paraxylene in a gas phase reaction starting from dimethylfuran and ethylene.¹ We are currently trying to circumvent the use of ethylene as it demands high temperature and pressure by replacing it with the acrylate based dienophiles. Thus, produced aromatics as shown in the scheme below, can be a precursor to produce paraxylene via simple chemical transformation.



We have employed chromium-based mesoporous MOF, MIL-101-SO₃H with sulfonic acid groups provides necessary active sites for catalysis. With 2,5-dimethylfuran (2,5-DMF) and methyl acrylate (MA) as a source of diene and dienophile, we were able to achieve the 30 % conversion to corresponding aromatic, 2,5-dimethyl-methyl-benzoate in neat 2,5-DMF at 90°C. Temperature dependent study indicated that high temperature in addition to the acid sites is imperative for the aromatic formation. We have further investigated other possible reaction pathways at high temperature that are restricting the aromatic yield. We noted the formation of two major products hexanedione and an oligomer based one and we were able to deduce their structures by combined data including NMR and GCMS spectra. With the knowledge of other by products, we further optimized the reaction condition in heptane media by varying diene to dienophile ratios. Interestingly, we noted that on increasing the MA/2,5-DMF ratio, the selectivity towards aromatics was increased from 33% to 57% and it did not change much at higher ratios. The spent catalyst is characterized by PXRD, TGA, CHNS and porosity measurement and it is recyclable up to two cycles. In conclusions, the current study sheds some light on the liquid phase reaction involving the production of substituted aromatics from furanic substrates where zeolites were not of much success before.

References:

¹ Settle, A. E., Berstis, L., Rorrer, N. A., Leshkov, Y. R., Beckham, G. T., Richards, R. M. & Vardon, D. R. (2017) *Green Chem.*, 2017, 19, 3468–3492