

The Andrew Commemorative Fellowship 2018 Completion Report

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Aims of the fellowship

My Fellowship aimed to bring digital technologies into the formulation of heterogeneous catalysts, to increase efficiency in catalyst development, to develop and use novel process monitoring technologies to enhance understanding of the catalytic processes. Ultimately, to improve catalyst formulation, process efficiency, and reduce the environmental footprint.

The Fellowship comprised 3 Work Packages (WP):

WP1 instrumental studies focusing mainly on liquid-phase adsorption work made possible by automation of the experiments, and on developing novel process control tools for studying formulation of heterogeneous catalysts,

WP2 creating a platform for studying the catalyst poisoning phenomena (as a way of promoting selectivity sacrificing some activity, and as catalyst deactivation).

WP3 advancing the high-throughput experimentation into heterogeneous catalysis development via a combination of rapid (yet scalable) catalyst synthesis, testing, and algorithms for developing a recipe of candidate catalysts based on the existing data and common-sense understanding of the catalyst development techniques.

Progress during the Fellowship

WP1

WP1 focuses on the studies of liquid-liquid adsorption to learn mechanistic insights into heterogeneous catalysis. During the Fellowship, several peer-reviewed research papers have been published on reporting the WP1 work.

A paper published in the Journal of Molecular Liquids [1] reviewed the application and methods of liquid-phase adsorption – the key component of WP1. This review is aimed at increasing awareness of the liquid-phase adsorption and showcased the liquid-phase adsorption applications. A paper published in the Chemical Engineering Journal [2] compared mass transfer phenomena in the packed-bed and catalyst-coated reactors, its effects on conversion and selectivity.

Following the work, I and collaborators studied the effect of liquid-phase adsorption on the anomalous reaction rate acceleration of propylbenzene in the presence of toluene over the Ru/SiO₂ catalyst [3]. Hydrogenation of propylbenzene over Rh/SiO₂ proceeds 120% faster in the presence of toluene. Such an acceleration effect does not agree with the well-accepted Langmuir–Hinshelwood reaction model. In this paper, we examined its mechanism experimentally and computationally. The study results indicate formation of binary propylbenzene-toluene associates increased the adsorption energy of toluene and decreased that of propylbenzene. Lowered adsorption energy reduces the activation barrier for catalytic reaction and intensifies the reaction rate beyond the Langmuir–Hinshelwood model prediction.

In the last work [4] we looked into the alkyne semi-hydrogenation selectivity over Pd and Lindlar catalyst with liquid phase adsorption. The results show that there are strongly-adsorbing alkyne and alkene sites; alkenes react non-selectively over the alkene adsorption sites. DFT studies indicate that the non-selective sites are low-coordination Pd atoms in the nanoparticles.

WP2

WP2 focuses on combining traditional heterogeneous catalysts with homogeneous catalyst modifiers; on developing automation tools and methods to develop efficient catalysts.

During the fellowship, several systems and automation tools have been developed focusing on alkyne semi-hydrogenation catalysts. A broad range of experiments with 4 catalysts, 21 nitrogen modifiers, and 3 substrate alkyne molecules. After considering publication options and discussions with the industrial partner, we concluded to combine two expected publications into one stronger publication.

The work had been presented at the UKCC 2022 conference in person and published [5] in collaboration with a developed collaboration with a Japanese colleague, Dr Shusuku Asano. The published work includes experimental studies and density functional theory calculations for the catalyst – substrate interaction.

WP3

WP3 advancing the high-throughput experimentation into heterogeneous catalysis development via a combination of rapid (yet scalable) catalyst synthesis, testing, and algorithms for developing a recipe of candidate catalysts based on the existing data and common-sense understanding of the catalyst development techniques.

During the Fellowship, a preliminary experimental system had been assembled and preliminary experiments had been performed.

The system performs automatically the following steps:

- (i) synthesis of scalable heterogeneous catalysts, and
- (ii) rapid testing of the catalyst performance – both activity and selectivity under production-relevant conditions, and
- (iii) generation of the improved generation of the catalysts for synthesis based on the testing results.

The algorithms and systems have been developed in Matlab; analytics of the alkyne (substrate) and alkene (reactant) were developed. The spectra of these compounds are shown in Fig. 1. A characteristic band for MBY is the $C\equiv C$ stretching frequency at 2123 cm^{-1} ; for MBE is the $C=C$ bond stretching at 1654 cm^{-1} . There is a negligible signal at 2123 cm^{-1} in MBE or MBA that allows identification and quantification of MBY in the reaction mixture; the same applies for the 1654 cm^{-1} band. Unfortunately, MBA does not have similar characteristic bands so its unique identification in the mixture is impossible.

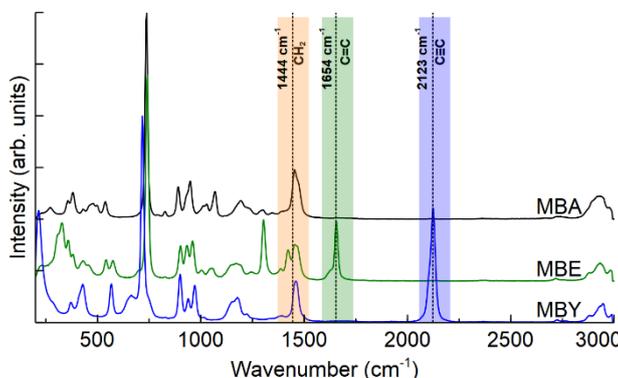


Fig. 1. Raman spectra of the MBA, MBE, MBY compounds as well as the 1:1 (mol) mixture of MBY and MBE key stretching frequencies for $C\equiv C$ at 2123 cm^{-1} and $C=C$ at 1654 cm^{-1} .

The intensity for the 3 compounds is very similar at 1444 cm^{-1} (C-H bending in CH_2 groups) that allowing normalising the spectra to this band intensity. Such normalisation increases signal stability towards variations in the laser power, temperature, presence of solids or gases in the product feed [stoli reference]. Fig. 2 shows the normalisation applied to the MBY/MBE mixture. The intensity of $C\equiv C$ at and $C=C$ relative to the 1444 cm^{-1} band changes linearly with the corresponding concentration shows that quantitative analysis in semi-hydrogenation is possible.

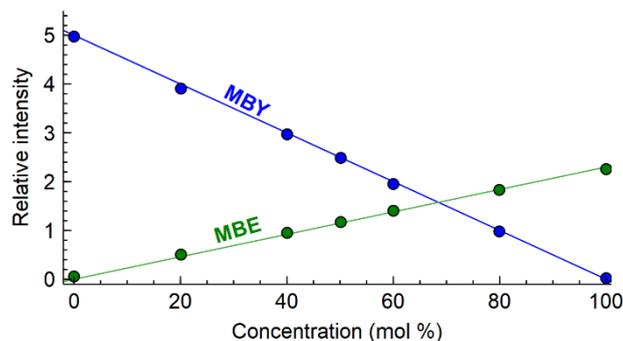


Fig. 2. Intensities of the C≡C (2123 cm⁻¹) and C=C (1654 cm⁻¹) stretching vibration bands relative to the 1444 cm⁻¹ band for the MBY and MBE mixture.

Due to time limitations to perform extended experimental studies, I was unable to fully complete WP3. Yet, a strong collaboration was established with Dr Shusuku Asano and we aim to continue experimental work in Japan. The experimental system had been translated to the collaborator and the genetic catalyst synthesis algorithms.

Conclusion

The Fellowship had been completed successfully and enabled a substantial expansion in the knowledge in the heterogeneous catalysis. The key WP1 on mechanistic understanding exceeded original expectations resulting in 4 publications. WP2 was performed according to plan, and the results had been published in 1 peer-reviewed paper. WP3 progress was slower than expected because of experimental difficulties. Yet, the work had resulted in establishing good collaboration and the work on this work-package is ongoing beyond the project.

References (Published works)

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- [3] N. Cherkasov *et al.*, "Mechanistic origins of accelerated hydrogenation of mixed alkylaromatics by synchronised adsorption over Rh/SiO₂," *React. Chem. Eng.*, pp. 12–14, 2023, doi: 10.1039/d3re00032j.
- [4] N. Cherkasov, D. Y. Murzin, C. R. A. Catlow, and A. Chutia, "Selectivity of the Lindlar catalyst in alkyne semi-hydrogenation: a direct liquid-phase adsorption study," *Catal. Sci. Technol.*, vol. 11, pp. 6205–6216, 2021, doi: 10.1039/d1cy01016f.
- [5] S. Asano *et al.*, "Homogeneous catalyst modifier for alkyne semi-hydrogenation: systematic

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