IChemE Andrew Fellowship – Final report

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1. Introduction

This report summarises the work done between March 2019 to March 2023 with the financial support of Andrew Fellowship. The report will first introduce the background of the research. The main achievements of the research are summarised, and these are followed by an assessment of how the initial proposals have been met. Finally, future plans of research are briefly described.

The aim of the study is to obtain experimental insight into Fischer-Tropsch synthesis (FTS) and ultimately optimise this catalytic process. FTS is a heterogeneous catalytic reaction and is the key step in producing synthetic fuels and chemicals from low-carbon resources[1]. In the low-temperature operation of FTS, carbon monoxide CO and hydrogen H_2 are primarily converted to linear alkanes[2]. To obtain insight into this reaction, it is necessary to investigate the catalyst performance under *operando* conditions. Previous *operando* studies of FT catalysis have mainly focused on the intrinsic activity and selectivity of the catalyst[3]. However, the catalysts used in industrial operations are usually in the form of millimetre pellets where the catalyst behaviour is substantially affected by mass transfer. In attempting to understand the FTS process occurring at industrially relevant conditions, the following questions need to be addressed: What are the diffusion coefficients of reaction species in catalyst pores under the reaction conditions? How is the intrinsic catalytic behaviour modified by including the active sites in catalyst pellets? Water and oxygenates are produced; how are they present inside catalyst pores and how do they affect catalyst surface?

The research carried out in the period of the Fellowship addresses these questions by developing and applying advanced magnetic resonance (MR) techniques to characterise FTS under *operando* conditions. The main achievements are summarised in the following sections.

2. Achievements

The studies during the time of the Fellowship have led to following publications:

Zheng, Q. et al. Operando magnetic resonance imaging of product distributions within the pores of catalyst pellets during Fischer-Tropsch synthesis. *Nature Catalysis* 6, 185-195 (2023)[4].
Zheng, Q. et al. In situ characterization of mixtures of linear and branched hydrocarbons confined within porous media using 2D DQF-COSY NMR spectroscopy. *Analytical Chemistry* 94, 3135-3141 (2022)[5].
Zheng, Q. et al. Experimental determination of H_2 and CO diffusion coefficients in a wax mixture confined in a porous titania catalyst support. *Journal of Physical Chemistry B* 124, 10971–10982 (2020)[6].

2.1 Diffusion of H_2 and CO in wax-saturated pores

During FTS, the catalyst pores are saturated by liquid hydrocarbon products through which reactants H_2 and CO diffuse. The diffusion coefficients of H_2 and CO determine their

concentrations in pores and therefore are important parameters in FTS modelling. However, experimental determination of the diffusion coefficients in pores saturated by wax and under reaction conditions has not been reported. In this study, the diffusion coefficients of H_2 and CO diffusing in titania pores saturated by a wax mixture were measured at typical reaction conditions of FTS using pulsed-field gradient (PFG) nuclear magnetic resonance (NMR) methods.

The diffusion coefficients of H_2 and CO within the wax-saturated pores were measured in the range $(1.00-2.43) \times 10^{-8}$ and $(6.44–8.50) \times 10^{-9}$ m^2 s^{-1}, respectively, in the temperature range of 140–240 and 200−240 °C for H_2 and CO, respectively, at a pressure of 40 bar. The wax mixture was typical of a wax produced during FTS and had a molar average carbon number of 36. It is shown that the hydrogen diffusion coefficient within this wax mixture was consistent, to within experimental error, with the hydrogen diffusion coefficient measured in pure single-component n-hexatriacontane (n-C_{36}) wax; this result held when the wax mixture was in the bulk liquid state and also when it was confined within the porous titania. The tortuosity of the porous titania was also measured using PFG NMR and found to be 1.77; this value was independent of temperature. The ability of existing correlations to predict these experimentally determined data was then critically evaluated. It is found that parameterized correlations based on the rough hard sphere model, having accounted for the experimentally determined tortuosity factor, predicted the H_2 and CO diffusion within bulk and confined wax to within 3%. The study is illustrated in Fig. 1.
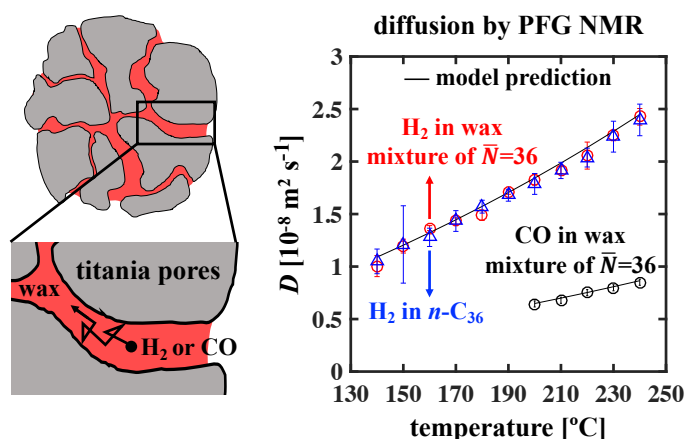

Figure 1. Diffusion of H_2 and CO in wax-saturated titania pores. The figure at the right shows the diffusion coefficients of H_2 and CO as measured in the experiment and predicted by the correlations.

2.2 Differentiating saturated hydrocarbons, oxygenates and water inside pores

Comprehensive understanding of the reaction mechanism requires characterisation of different product species in pores under *operando* conditions. The products of FTS primarily consist of n-alkanes and water, along with minor products of branched alkanes and oxygenates. Discrimination and characterisation of such complex mixtures from within catalyst pores are extremely challenging. This is partially because most products species have similar molecular structure and hence similar NMR chemical shifts. In addition, the NMR signal line broadening for species confined in porous catalysts results in spectra indistinguishable for different product species. Recently, a method has been developed and validated to determine the carbon number

distributions of *n*-alkane mixtures confined in pores; this is achieved by differentiating *n*-alkanes of different carbon chain lengths by their diffusion coefficients[7]. However, discrimination between *n*-alkanes and their branched isomers still remains challenging and the discrimination between water and oxygenates from hydrocarbon products has not been achieved. Following methods have been developed and tested to address these challenges.

The discrimination of branched alkanes from linear alkanes is achieved by applying 2D NMR spectroscopy. It has been shown that the 1D projection spectrum, which is obtained by projecting a 2D correlation spectroscopy (COSY) spectrum along its diagonal, is unaffected by line broadening and therefore retains high-resolution information of species in pores[8]. This method was applied to analyse the 2D double-quantum filtered (DQF) COSY spectra of liquid mixtures of linear and branched alkanes confined within a porous titania (Fig. 2). Two case studies were considered. First, mixtures of 2-methyl alkanes and *n*-alkanes were investigated. It is shown that estimation of the mole fractions of branched species present was achieved with a root-mean-square error of prediction (RMSEP) of 1.4 mol%. Second, the quantification of multicomponent mixtures consisting of linear alkanes and 2-, 3-, and 4-monomethyl alkanes was considered. Discrimination of 2-methyl and linear alkanes from other branched isomers in the mixture was achieved, although discrimination between 3- and 4- monomethyl alkanes was not possible. Compositions of the linear alkane, 2-methyl alkane, and the total composition of 3- and 4-methyl alkanes were estimated with a RMSEP < 3 mol %. The approach was then used to estimate the composition of the mixtures in terms of submolecular groups of CH_3CH_2, $(CH_3)_2CH$, and $CH_2CH(CH_3)CH_2$ present in the mixtures; a RMSEP < 1 mol % was achieved for all groups. The ability to characterise the mixture compositions in terms of molecular subgroups allows the application of the method to characterise mixtures containing multimethyl alkanes. The method reported is generic and can be applied to any system in which there is a need to characterise mixture compositions of linear and branched alkanes. The study is illustrated in Fig. 2.
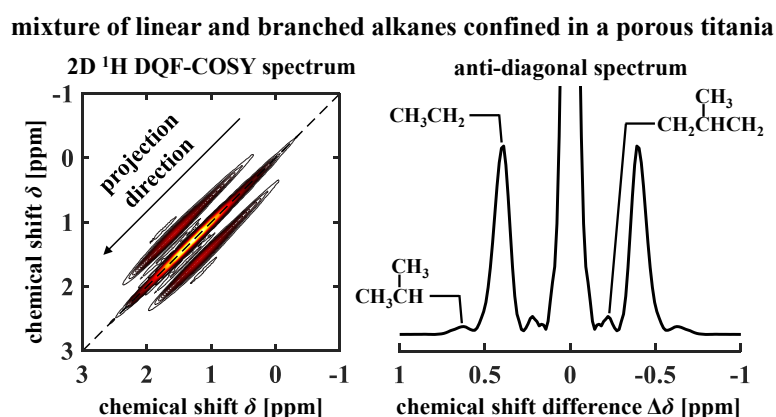

mixture of linear and branched alkanes confined in a porous titania

Figure 2. Discrimination between linear and branched alkanes in a porous titania. The figure at the left shows a 2D DQF-COSY spectrum of a mixture of branched and linear alkanes. The 1D projection spectrum obtained by projecting the 2D spectrum along its diagonal is shown at the right where NMR peaks associated with different submolecular groups are identified. All data were acquired at ambient conditions and the chemical shifts are relative to the ^{1}H resonance of tetramethylsilane.

A disadvantage of 2D NMR spectroscopy is that the signal is subject to long relaxation decay before the acquisition starts hence reduction in signal to noise ratio. This limits the application

of the method; in particular, species such as oxygenates and water, that can strongly interact with the pore surface and therefore have fast relaxation rates, cannot be studied. To overcome this problem, the discrimination of oxygenates and water from hydrocarbon products is achieved by employing a 2D method in which one of the dimensions is the nuclear spin-lattice or T_1 relaxation time, which is a sensitive indicator of surface interaction strength[9]. The second dimension is a chemical shift dimension which characterises the structure of molecules. An example of 2D chemical shift – T_1 relaxation time correlation spectrum acquired under the *operando* conditions of FTS is shown in section 2.3.

2.3 Operando characterisation of FTS

Having developed and tested the methods to achieve chemical information in pores, the FTS was characterised under *operando* conditions using multiple MR techniques. The FT reaction was carried out in a pilot scale fixed-bed reactor of 20 mm inner diameter and packed with 3 layers of Ru/TiO$_2$ catalyst pellets. The reaction was carried out at 220 °C, 37 bar and at 3 feed H$_2$/CO ratios (FR) of 2, 1 and 0.5. Characterisations of reaction products including linear hydrocarbons, oxygenates and water and branched alkanes are achieved, and the conclusions are summarised as follows.
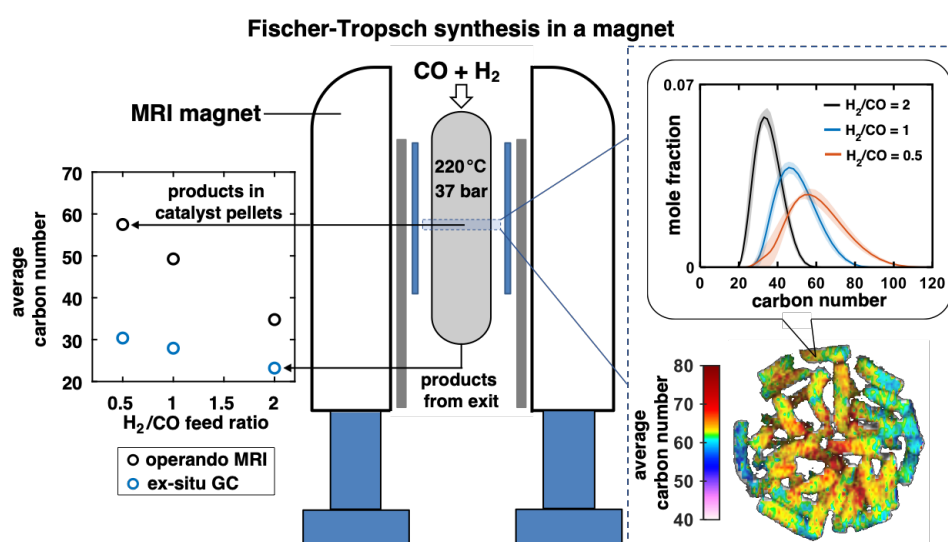

Figure 3. *Operando* determination of product distributions from within catalyst pores during the FT reaction in a fixed-bed reactor. The figure at the left shows the comparison between the average carbon numbers of intra-pellet products and the products collected from the reactor exit. The image at the right shows the spatial distribution of product carbon number in a local catalyst layer and the carbon number distributions measured from an image pixel from inside a catalyst pellet are also shown.

Molecular diffusion and carbon numbers of hydrocarbon products were spatially resolved within the reactor. Spatial resolution was achieved such that product distributions were obtained from inside individual catalyst pellets. Spatial heterogeneity in product distribution within both the reactor and individual pellets was observed. The data highlight the importance of mass transfer on catalyst performance. In particular, a start-up time of up to 3 weeks was required for steady-state to be achieved in the catalyst pores. This is much longer than 50 h as suggested by the GC measurement of effluent gas composition which is conventionally used as an indicator of steady-state behaviour. This observation has important implications for how

catalyst screening studies are performed. Further, the average carbon number present in the pores can be double that in the product wax collected from the reactor exit. Given that the carbon number of intra-pellet products significantly affects the diffusivities and solubilities of H_2 and CO inside the pores and hence the catalyst performance, errors in reaction modelling are expected if the intra-pellet product composition is estimated by that of collected wax which is a common practice in the literature[10]. These results are illustrated in Fig. 3.

To understand how the reaction proceeds inside the catalyst pores it is important to track not just hydrocarbon formation but also water production and the phase and environment in which it exists, because of its impact on catalyst behaviour[11]. However, an experimental characterisation of water directly from within catalyst pores under *operando* conditions has not been reported. Figure 4 shows a 2D spin-lattice T_1 relaxation time – chemical shift spectrum acquired during the reaction in which ^{1}H-containing species which share overlapping chemical shift signals are spectrally-resolved through their T_1 relaxation times. It confirms that oxygenates and water are formed along with hydrocarbons. The chemical shift and T_1 relaxation time of the water signal provide insight into the phase of water. The data suggest a layer of liquid-phase water covering the surface and coexisting with wax. This is consistent with the predictions of molecular dynamic simulations for the case of hydrophilic pores[12]. This had not, until the present work, been confirmed under *operando* conditions. The data of water and oxygenates are being analysed to gain insight into the surface chemistry of the catalyst at different feed ratios.
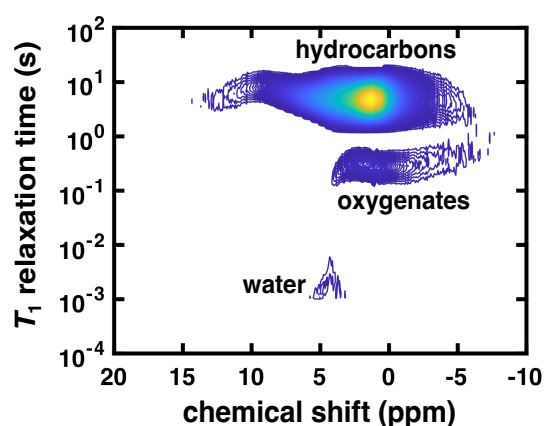

Figure 4. 2D chemical shift – T_1 relaxation time correlation spectrum of the reactor acquired at feed ratio 2. The chemical shifts are relative to the ^{1}H resonance of tetramethylsilane.

The composition of branched isomers in the product mixtures of FTS affects the quality of synthetic fuels[13] and the characteristics of branched alkanes also provide insight into the reaction mechanism of FTS[14]. However, a direct characterisation of branching composition from inside the pores of a working catalyst has not been reported. Branched alkanes were characterised using the DQF-COSY technique introduced in section 2.2. The result confirms the formation of branched alkanes and that the branching groups are predominantly located at the internal of the carbon chain instead of at the chain terminus. The branching composition was determined as 5-10 mol% and it decreased with decreasing feed ratios. This study will be extended to catalysts of different formulations and physical structures.

2.4 Initial proposals for the Fellowship

This section discusses how the initial proposals for the Fellowship are met by the studies described in previous sections. It was proposed to address the following:

1. *Operando* measurement of FT reaction at various operating conditions.
2. Liquid-phase diffusion of H_2 and CO dissolved in FT liquid products confined in pores
3. Water-wax phase behaviour in FT catalyst supports of various pore sizes
4. Diffusion-reaction modelling of FT catalyst

Proposal 1 has been completed with the FTS product distributions characterised at three H_2/CO feed ratios and proposal 2 is accomplished with the diffusion coefficients of H_2 and CO determined in a wax mixture confined in titania pores under the reaction conditions. For proposal 3, the action has been adjusted to focus on detection and characterisation of water under *operando* conditions. The results confirm the presence of a liquid-phase water on the catalyst surface coexisting with wax products in the pore centre. For proposal 4, the modelling of the catalyst is carried out by our industrial collaborators while the work in Cambridge focuses on obtaining experimental insight into the catalyst behaviour which guides the optimisation of the model. For example, to better predict the catalyst behaviour one needs to consider the effect of product carbon number on the diffusion and solubility of H_2 and CO in pores.

3. Conclusion and future plan

Multiple MR techniques have been developed and applied to achieve *operando* characterisation of FTS occurring in a pilot reactor and catalyst pellets of industrially relevant scales. The properties of reactants and major and minor products of FTS were characterised under reaction conditions to provide insight into the kinetics, mass transfer and surface chemistry of the catalytic process. As expected, the effect of mass transfer limitation on catalyst behaviour was found to be significant. Although this effect is already well known in literature, it is the first time to achieve *operando* and quantitative characterisation of a working FTS catalyst of which the behaviour is modified by mass transfer. This will facilitate the optimisation of the process.

Combining the MR capability of flow imaging[15], a complete package of MR capabilities is now available to address transport phenomena and chemical conversion in a working catalytic process. The studies on FTS can be extended to investigate the effects of catalyst formulation and nanostructure, and the effects of other processing parameters such as temperature and water partial pressure on the catalytic conversion. In a wider context, the MR toolkit helps to obtain insight and therefore identify the limitation of a catalyst and process. The information provided can subsequently be used to guide rational design of catalyst and process intensification techniques.

References

1   Panzone, C., Philippe, R., Chappaz, A., Fongarland, P. & Bengaouer, A. Power-to-Liquid catalytic CO_2 valorization into fuels and chemicals: focus on the Fischer-Tropsch route. *J. CO_2 Util.* **38**, 314-347 (2020).

2   James, O. O., Chowdhury, B., Mesubi, M. A. & Maity, S. Reflections on the chemistry of the Fischer-Tropsch synthesis. *RSC Adv.* **2**, 7347-7366 (2012).

3   Meirer, F. & Weckhuysen, B. M. Spatial and temporal exploration of heterogeneous catalysts with synchrotron radiation. *Nat. Rev. Mater.* **3**, 324-340 (2018).

4   Zheng, Q., Williams, J., van Thiel, L. R., Elgersma, S. V., Mantle, M. D., Sederman, A. J., Baart, T. A., Bezemer, G. L., Guédon, C. M. & Gladden, L. F. Operando magnetic resonance imaging of product distributions within the pores of catalyst pellets during Fischer–Tropsch synthesis. *Nat. Catal.* **6**, 185–195 (2023).

5   Zheng, Q., Mantle, M. D., Sederman, A. J., Baart, T. A., Guedon, C. M. & Gladden, L. F. *In situ* characterization of mixtures of linear and branched hydrocarbons confined within porous media using 2D DQF-COSY NMR spectroscopy. *Anal. Chem.* **94**, 3135-3141 (2022).

6   Zheng, Q., Williams, J., Mantle, M. D., Sederman, A. J., Baart, T. A., Guedon, C. M. & Gladden, L. F. Experimental determination of H_2 and CO diffusion coefficients in a wax mixture confined in a porous titania catalyst support. *J. Phys. Chem. B* **124**, 10971-10982 (2020).

7   Williams, J., Zheng, Q., Sederman, A. J., Mantle, M. D., Baart, T., Guedon, C. & Gladden, L. F. *In situ* determination of carbon number distributions of mixtures of linear hydrocarbons confined within porous media using pulsed field gradient NMR. *Anal. Chem.* **92**, 5125-5133 (2020).

8   Terenzi, C., Sederman, A. J., Mantle, M. D. & Gladden, L. F. Enabling high spectral resolution of liquid mixtures in porous media by antidiagonal projections of two-dimensional ^{1}H NMR COSY spectra. *J. Phys. Chem. Lett.* **10**, 5781-5785 (2019).

9   Liu, G., Li, Y. & Jonas, J. Confined geometry effects on reorientational dynamics of molecular liquids in porous silica glasses. *J. Chem. Phys.* **95**, 6892-6901 (1991).

10   Mandic, M., Todic, B., Zivanic, L., Nikacevic, N. & Bukur, D. B. Effects of catalyst activity, particle size and shape, and process conditions on catalyst effectiveness and methane selectivity for Fischer-Tropsch reaction: A modeling study. *Ind. Eng. Chem. Res.* **56**, 2733-2745 (2017).

11   Kliewer, C. E., Soled, S. L. & Kiss, G. Morphological transformations during Fischer-Tropsch synthesis on a titania-supported cobalt catalyst. *Catal. Today* **323**, 233-256 (2019).

12   Papavasileiou, K. D., Peristeras, L. D., Chen, J., van der Laan, G. P., Rudra, I., Kalantar, A. & Economou, I. G. Molecular dynamics simulation of the *n*-octacosane-water mixture confined in hydrophilic and hydrophobic mesopores: The effect of oxygenates. *Fluid Phase Equilib.* **526** (2020).

13   Li, J., He, Y. L., Tan, L., Zhang, P. P., Peng, X. B., Oruganti, A., Yang, G. H., Abe, H., Wang, Y. & Tsubaki, N. Integrated tuneable synthesis of liquid fuels via Fischer-Tropsch technology. *Nat. Catal.* **1**, 787-793 (2018).

14   Gaube, J. & Klein, H. F. Studies on the reaction mechanism of the Fischer-Tropsch synthesis on iron and cobalt. *J. Mol. Catal. A: Chem.* **283**, 60-68 (2008).

15   Gladden, L. F. & Sederman, A. J. Magnetic resonance imaging and velocity mapping in chemical engineering applications. *Annu. Rev. Chem. Biomol. Eng.* **8**, 227-247 (2017).