IChemE Andrew Fellowship Final Report

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1) Introduction

This report summarises the work carried out between 2020-2024 with the financial support of the Andrew Fellowship. The context and objectives of the research are presented, and key achievements are highlighted to demonstrate how the original objectives were met.

The objective of this research was to develop Nuclear Magnetic Resonance (NMR) methods to study the adsorption and mass transport of molecules of interest within heterogeneous catalytic systems. NMR relaxation measurements are sensitive to the motions of molecules and can be used to explore how adsorption at the catalyst surface alters these dynamics. Ratios of the spin-lattice (T_1) and spin-spin (T_2) relaxation time constants have emerged in recent years as a non-invasive tool for probing adsorption properties within porous materials[1–3]. However, these measurements provide a snapshot of complex molecular dynamics and cannot always be interpreted straightforwardly. A key objective of this fellowship was to explore the applicability of variable frequency relaxation measurements, specifically fast field cycling (FFC) NMR, to catalytic systems. The research aimed to characterise and quantify the dynamics of liquids at catalyst surfaces, and to explore how co-imbibition affected adsorption and liquid phase behaviour within catalyst pores.

Mass transport of molecules within porous catalysts can be measured using Pulsed Field Gradient (PFG) NMR, which allows a direct measurement of the tortuosity of porous catalytic materials. A second theme of the fellowship was to extend the PFG NMR methodology to the catalyst synthesis process, and to explore how different formulations affect the transport properties of the final catalyst.

2) Achievements

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

(1)   Ward-Williams, J.; Korb, J.-P.; Rozing, L.; Sederman, A. J.; Mantle, M. D.; Gladden, L. F. Characterizing Solid–Liquid Interactions in a Mesoporous Catalyst Support Using Variable-Temperature Fast Field Cycling NMR. *The Journal of Physical Chemistry C* **2021**, *125*, 8767–8778.

(2)   Ward-Williams, J. A.; Karsten, V.; Guédon, C. M.; Baart, T. A.; Munnik, P.; Sederman, A. J.; Mantle, M. D.; Zheng, Q.; Gladden, L. F. Extending NMR Tortuosity Measurements to Paramagnetic Catalyst Materials Through the Use of Low Field NMR. *Chemistry–Methods* **2022**, *2*, e202200025.

(3)   Elgersma, S. V; Ward-Williams, J. A.; Zheng, Q.; Sederman, A. J.; Mantle, M. D.; Guédon, C. M.; Gladden, L. F. Investigating the Coupling between Transport and Reaction within a Catalyst Pellet Using Operando Magnetic Resonance Spectroscopic Imaging. *Catal Today* **2024**, *430*, 114497.

(4)   Ward-Williams, J. A.; Guédon, C. M.; Mantle, M. D.; Sederman, A. J.; Gladden, L. F. Insights into Molecular Accessibility in Catalyst and Sorbent Materials Using NMR Porosity Measurements. *React. Chem. Eng.* **2024**, *9*, 1320–1324.

2.1)   Characterising molecular interaction strength with an oxide surface

The dynamics of molecules at the solid-liquid interface depend on the nature of the surface interactions. Figure 1 shows the spin-lattice relaxation rate, $R_1 = 1/T_1$, for seven different liquids imbibed within the same γ-alumina extrudates. The highest measured field strengths are comparable to the field strengths used in conventional fixed field relaxometry studies, and at these field strengths the ordering of the relaxation rates was ambiguous. As the frequency was reduced, the relaxation experiments probed motions occurring on longer timescales and became more sensitive to surface diffusion processes. At low field strengths, the order of R_1 values correlated well with the polarity of the adsorbate, which was used as an indicator of surface interaction strength for adsorption on a hydrophilic surface. Variable-temperature FFC NMR measurements were used to further classify the type of surface interaction, with the imbibed liquids being grouped as nonpolar, polar aprotic, and polar protic adsorbates. Working in collaboration with Professor Jean-Pierre Korb (Université Sorbonne, France), each group of adsorbates was fitted with models that described the underlying molecular dynamics, and surface correlation times and diffusion coefficients were extracted to quantify the adsorption dynamics.[4] For example, the non-polar species were shown to have surface diffusion coefficients between 5-7 times smaller than their corresponding bulk diffusion coefficients. For each class of adsorbate, the assumptions and limitations of the modelling processes were discussed.[4]

For methanol, it was possible to resolve the dynamics of the alkyl and hydroxyl group (see figure 1), which showed relaxation rates that differed by up to a factor of 10. The relaxation behaviour of the alkyl group was consistent with a strong and directional binding at the alumina surface, whilst the relaxation behaviour of the hydroxyl group was consistent with an exchange process between the methanol hydroxyl and surface hydroxyl groups. The observation of functionality specific dynamics is important for

understanding and modelling of pore scale dynamics, in particular for water, where exchange effects are not trivial to separate from whole molecule dynamics.
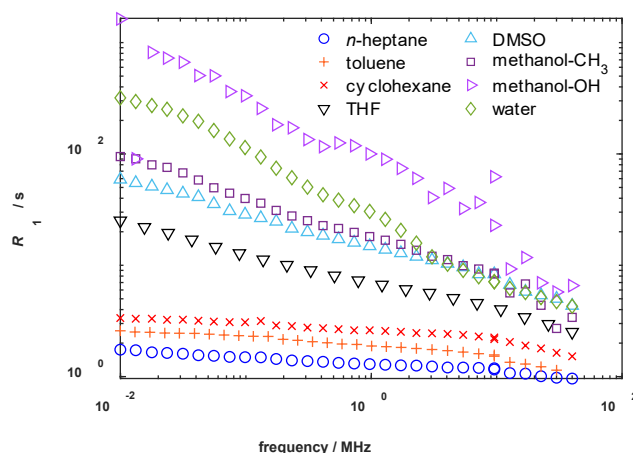

Figure 1: The FFC NMR dispersion curves for seven different liquids imbibed within γ-alumina.

2.2)   Phase behaviour of water-ethanol mixtures within silica pores

Understanding the competitive adsorption at solid-fluid interfaces is key to controlling the properties of a wide range of sorptive and catalytic materials. By exploiting the unique surface sensitivity of NMR relaxation measurements, fixed field (T_1-T_2) and fast field cycling (FFC) NMR relaxation measurements were used to probe the microphase separation and liquid structuring that occurs for mixtures of water and ethanol imbibed within a series of well-controlled silica materials with pore sizes ranging from 5-38 nm. Clear differences were observed between the relaxation behaviour of liquid mixtures imbibed within the as-received small pore silicas (<17 nm) and the larger pore silicas (>21 nm), with the former showing a mixed water-ethanol surface phase that was influenced by the intra-particle compositions and the latter showing a strong microphase separation which resulted in a surface adsorbed layer that was dominated by water regardless of the intra-pellet composition. The surface hydroxyl density of the small pore silicas (1.3-1.5 nm^{-2}) was much lower than that of the large pore silicas 4.5-5.4 nm^{-2}). Surface modifications of the smallest (5 nm) and largest (38 nm) pore silicas were carried out through rehydroxylation and silylation procedures respectively to separate the effects of surface chemistry from pore size. Figure 2 shows the fast component of the renormalised FFC dispersion profiles for water-ethanol mixtures before and after rehydroxylation. After rehydroxylation, the hydroxyl density increased to 6.0 nm^{-2} and the normalized NMRD profiles of single component water adsorption and water-ethanol binary mixture adsorption in Q6 collapsed onto a single master curve, consistent with a microphase separation occuring and water dominating the pore surface. The surface chemistry, in particular the surface hydroxyl density, was shown to be the dominant factor defining the competitive adsorption and phase behaviour within

silica pores. Competitve adsorption and phase separation processes will influence access of molecules to active sites at catalyst surfaces and therefore have important implications for the understanding and tuning catalytic activity and selectivity in micro and mesoporous materials.
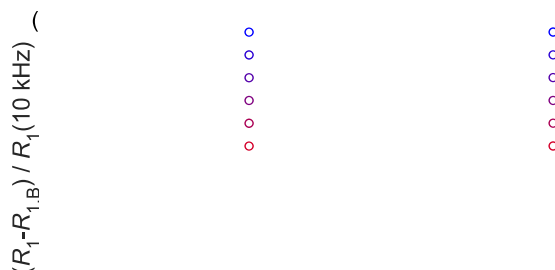

Figure 2: The renormalized NMRD profiles of the fast-relaxing component of water-ethanol binary liquid mixtures imbibed within (a) as-received Q6 silica and (b) rehydroxylated Q6 silica. For each NMRD profile the mol% of intra-pellet water is given.

2.3) Tortuosity Measurements of Paramagnetic Catalyst Materials

Internal mass transport limitations can have a strong influence on the reactant distribution within a catalyst pellet,[5,6] which can control the activity and selectivity of chemical reactions. The characterisation of this internal mass transport can be achieved through measurements of the catalyst tortuosity, but few techniques exist to measure tortuosity. Pulsed Field Gradient (PFG) NMR methods allow direct measurements of tortuosity as:[7]

$$\tau = D_{\mathrm{b}}/D_{\mathrm{p}} ,$$

where D_{b} and D_{p} are the PFG NMR diffusion coefficients of a non-interacting liquid in the bulk and confined within the pore space respectively. During the Fellowship, it was shown that by transitioning the relaxation analysis from high field (300 MHz) to low field (2 MHz) it was possible to overcome limitations due to short signal lifetimes (T_2) and extend NMR tortuosity measurements to catalytic materials containing paramagnetic species.[8] Ten catalyst extrudates were studied; three titanias, two titanias with 1 wt.% MnO_2, two oxidized 20 wt.% Co_3O_4/TiO_2 catalysts, and three aluminas. At high field strengths the samples containing even small quantities of paramagnetic materials (1 wt.% MnO_2) were unmeasurable. By transitioning to a low magnetic field strength, the T_2 limitations were overcome and the PFG NMR measurement became simple for all catalyst materials up to the maximum tested loading of 20 wt.% Co_3O_4. Figure 3 shows a comparison of the tortuosity measured by PFG NMR and the value estimate from a standard correlation based on the catalyst porosity, ε. The titania samples were well-

approximated by the correlation (1/ε) for all formulations, but the aluminas had measured porosities up to 70% larger than the expected values. Notably addition of 20 wt.% Co_3O_4 through incipient wetness impregnation onto Ti-I increased the tortuosity by 0.46 (an increase of 28%) and it was found that co-mulling of titania and Co_3O_4 phases produced a 20 wt.% Co_3O_4 catalyst with a tortuosity of just 1.59. For these materials, the structure of the support structure was the dominant factor in determining the tortuosity. By transitioning this analysis to low magnetic field strengths, the approach shows great applicability to diamagnetic or paramagnetic catalyst system during synthesis, operation, or during post-mortem characterisation.
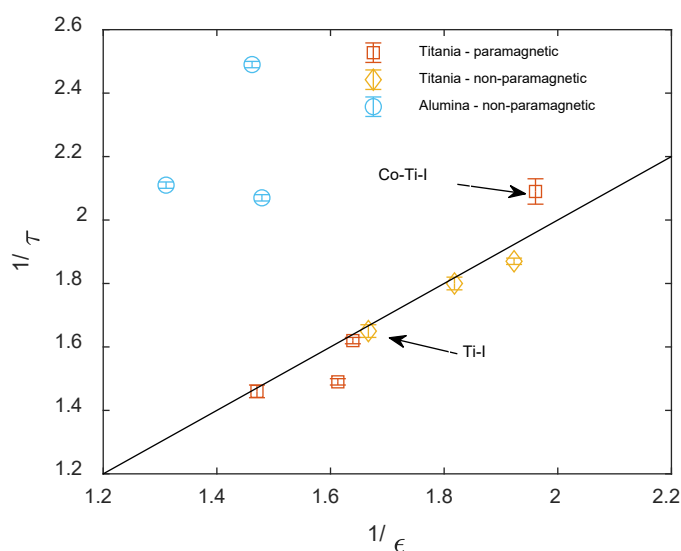

Figure 3. The tortuosity measured by PFG NMR for 7 titania and 3 alumina catalyst materials compared to the tortuosity estimated from a standard correlation based on the porosity, ε, of the material. A line of y=x is shown as a guide to the eye.

The standard PFG tortuosity characterisation assumes a homogeneous (or quasi-homogeneous) catalyst formulation. Inhomogeneity in catalytic materials may be introduced during synthesis (e.g. egg-shell, egg-yolk or other asymmetric metal distributions) or arise as a result of reaction or deactivation processes. By coupling relaxation and diffusion measurements with MRI imaging techniques, it is possible to map variations at the pellet-scale and to understand the influence the heterogeneity has on the physical properties of the system. Figure 4a shows the T_2 map (xy plane) of decane imbibed within a 1 wt.% $Cu(NO_3)_2/Al_2O_3$ catalyst, prepared by incipient wetness impregnation of a cylindrical γ-alumina extrudate. Decane in contact with paramagnetic Cu^{2+} ions showed enhanced relaxation rates relative to decane adsorbed on the bare alumina. An egg-shell metal distribution was observed, with a highly symmetrical metal loading. By taking the radial average of the T_2-map (figure 4b), the egg-shell thickness was estimated as 0.44 mm, consistent with a visual inspection of the catalyst after impregnation. By coupling the pellet scale MRI approach with PFG measurements, a tortuosity map and

corresponding radial average tortuosity were obtained (figure 4c-d). Tortuosity values measured within the egg-shell region were approximately 3% larger than tortuosity values measured at the catalyst core. This observation was consistent with a weak, but non-negligible, increase in the tortuosity of catalytic materials when loading metals through incipient wetness impregnation. The images obtained in this study were measured at high magnetic field strengths, but this approach could theoretically be performed at low magnetic field strengths to mitigate the signal lifetime issues associated with measuring paramagnetic catalyst species.
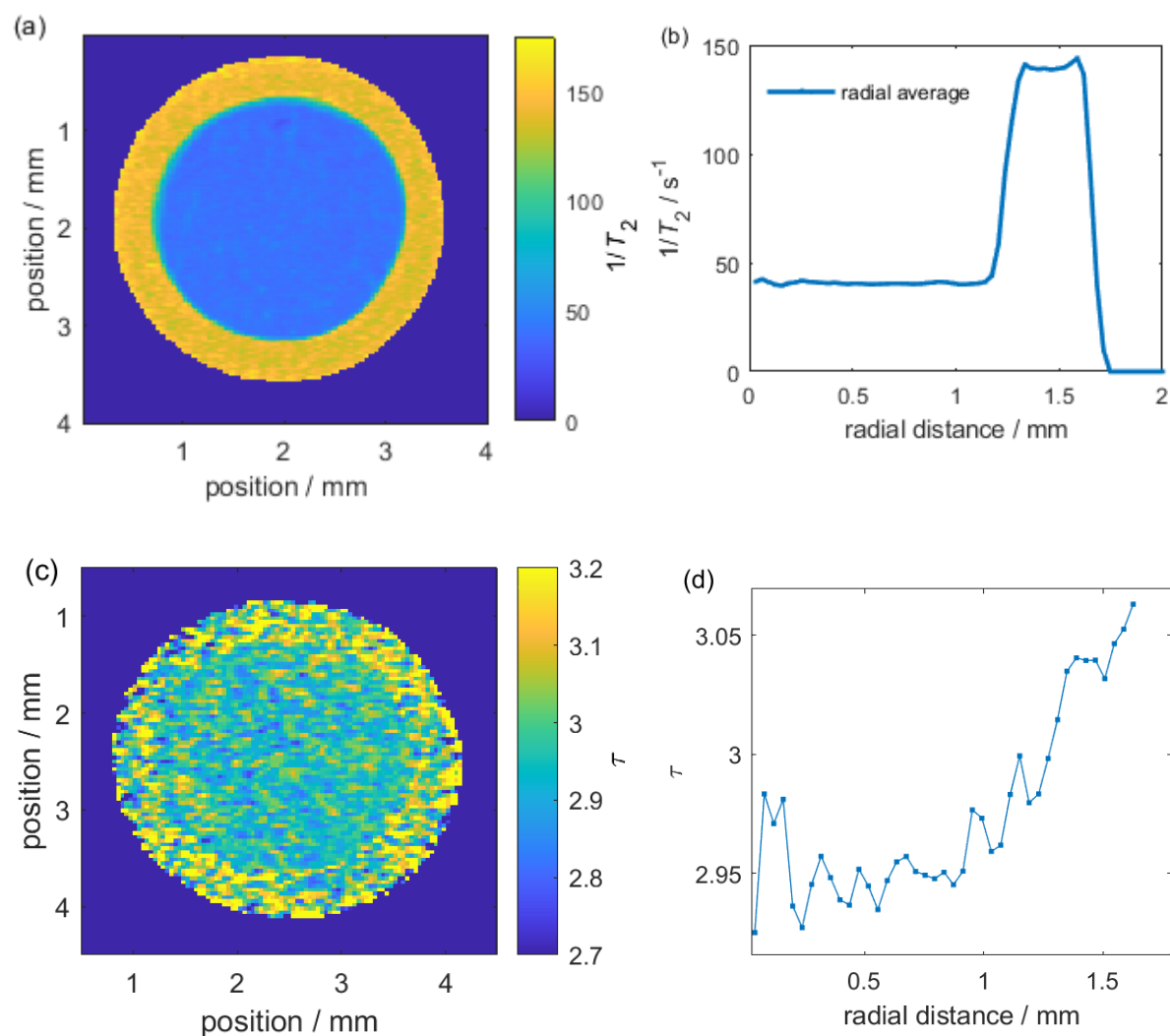

Figure 4: The (a) T_2 and (c) tortuosity maps obtained for decane imbibed within a 1 wt.% Cu/(NO$_3$)$_2$/Al$_2$O$_3$ egg-shell catalyst. In each case the cylindrical catalyst supports were oriented in the z direction and an xy map is shown. The radial average (b) T_2 and (d) tortuosity were calculated for comparison.

3) Conclusion

In conclusion, fast field cycling NMR has been demonstrated as a powerful characterisation tool for understanding and quantifying dynamic processes occurring at

solid-liquid interfaces in porous catalytic materials. In particular, detailed information about competitive adsorption and liquid phase behaviour can be extracted from the measurements, and frameworks for understanding multicomponent systems were developed. The observation of the microphase separation of ethanol-water mixtures within silica pores is one of the few experimental studies to demonstrate this effect and has important implications for how reactants and other species access catalytically active sites at the pore surface.

Measurements of mass transport within catalytic systems were achieved through PFG NMR methods. By transitioning the analysis to low magnetic field strengths, it was possible to extend the measurement capability to paramagnetic catalytic materials and make direct measurements of the tortuosity a routine process. The importance of these direct measurements was shown when comparing the measured tortuosity of different materials to the values obtained from standard porosity correlations. For the titanias, the correlation was shown to be a good approximation, but for the aluminas the correlation underestimated the tortuosity by up to 70%. Loading metals onto the catalyst supports was shown to have a modest effect on the mass transport properties of the system, and is likely to be more significant for hierarchical or microporous materials. The low field PFG tortuosity measurements have great potential for use during the rational optimisation of transport properties when designing catalysts and for quantifying transport changes through the catalyst lifetime.

4) References

1   D. Weber, J. Mitchell, J. McGregor and L. F. Gladden, *The Journal of Physical Chemistry C*, 2009, **113**, 6610–6615.

2   C. D'Agostino, J. Mitchell, M. D. Mantle and L. F. Gladden, *Chemistry*, 2014, **20**, 13009–13015.

3   N. Robinson, C. Robertson, L. F. Gladden, S. J. Jenkins and C. D'Agostino, *ChemPhysChem*, 2018, **19**, 2472–2479.

4   J. Ward-Williams, J.-P. Korb, L. Rozing, A. J. Sederman, M. D. Mantle and L. F. Gladden, *The Journal of Physical Chemistry C*, 2021, **125**, 8767–8778.

5   M. E. Davis and R. J. Davis, *Fundamentals of chemical reaction engineering*, McGraw-Hill, New York, 2013.

6   R. Klaewkla, M. Arend and W. F. Hoelderich, *A Review of Mass Transfer Controlling the Reaction Rate in Heterogeneous Catalytic Systems*, INTECH Open Access Publisher, 2011.

7   M. P. Hollewand and L. F. Gladden, *Chemical Engineering Science*, 1995, **50**, 309–326.

8   Ward-Williams, J. A., V. Karsten, C. M. Guédon, T. A. Baart, P. Munnik, M. D. Sederman, A. J., Mantle, Q. Zheng and L. F. Gladden, *Chemistry Methods*.