

Hydrogen bonding network disruption in nanoporous catalyst supports probed by PFG-NMR diffusometry and NMR relaxometry

Carmine D'Agostino, Lynn F. Gladden and Mick D. Mantle

Department of Chemical Engineering and Biotechnology, University of Cambridge,
Pembroke Street, Cambridge, CB2 3RA, UK, E-Mail: cd419@cam.ac.uk

1. Introduction

Pulsed field gradient nuclear magnetic resonance (PFG-NMR) has been applied to study molecular self-diffusion of several classes of organic compounds within different inorganic supports (TiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and SiO_2) commonly used in heterogeneous catalysis to assess the effect of chemical functionality on the effective self-diffusion coefficient of the probe compound within the pore space [1]. A new parameter, ξ , the PFG-NMR interaction parameter, is introduced and is defined as the ratio of the PFG-NMR derived free bulk liquid self-diffusivity to that measured within the pore space. Such a ratio is reminiscent of the tortuosity factor [2], τ , but it is theoretically different [3]. True tortuosity values of porous media from PFG-NMR measurements can only be calculated when the small liquid-phase probe molecules (such as liquid alkanes) do not interact with the solid phase. In contrast, diffusion measurements of polar liquids with chemical functionalities yield values of the self-diffusivity ratio that reflect the physico-chemical interactions between the probe molecules themselves and their interaction with the surrounding pore space (see Figure 1).

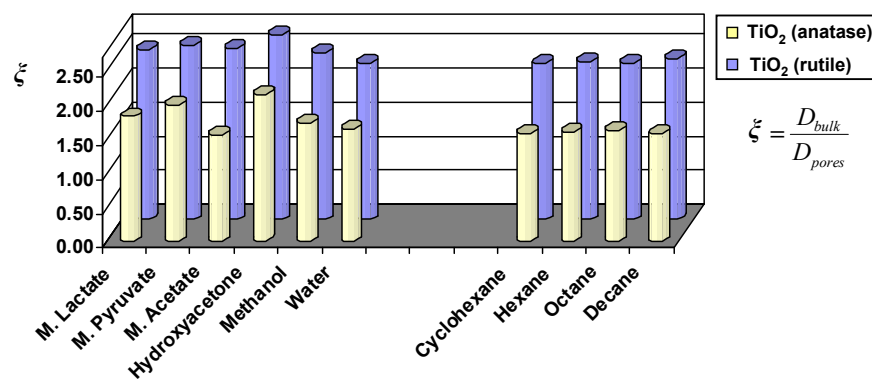


Figure 1. Values of the PFG interaction parameter, ξ , for several molecules in two different TiO_2 supports. The ξ -values are independent of the chemical compound when alkanes are the probe molecules.

2. Hydrogen bonding network disruption in nanoporous supports

The tortuosity of each porous support, τ , was obtained for a number of different alkanes as shown in Figure 1. Its value was then taken as a reference and compared with the PFG interaction parameter values, ξ , obtained by using molecules with different functional groups, giving a normalized value of such parameter, ξ_N . Mono-alcohols give values of the normalized PFG interaction parameter, ξ_N , slightly higher than one, which is indicative of a slightly reduced diffusivity. Substantially higher ξ_N -values are observed for carbonyl compounds and are indicative of a *reduced restricted diffusion* that reflects the physical interaction of the carbonyl compounds with the solid porous medium. Polyols, on the other hand, exhibit a very interesting behavior in terms of molecular self-diffusion within the supports studied and actually show an *enhanced restricted diffusivity* relatively to their theoretical value, i.e., the free liquid self-diffusivity reduced by the true tortuosity factor of the porous support. The effect becomes even more pronounced when glycerol is the guest molecule. In particular, glycerol shows a highly enhanced diffusivity in all supports and its diffusion coefficient in γ - Al_2O_3 is even higher than the diffusivity of the free bulk liquid, which is a quite remarkable result. The experimental findings suggest that the dynamic hydrogen bonding network of the polyols is disrupted or broken down to some extent by the porous medium, which results in an enhanced self-diffusion coefficient. Spin-lattice (T_1) relaxation measurements on free bulk liquids and liquids imbibed in support materials were also performed to elucidate further the molecular dynamics of the probe molecule within the pore space. Polyols imbibed in porous supports experience only a slight drop of their T_1 value compared to the free bulk liquid, whereas carbonyl compounds show much larger deviations.

3. Conclusions

The overall experimental results strongly suggest that the enhanced rate of diffusion of polyols in porous supports, as well as their enhanced rate of tumbling motion, is caused by a disruption of the extensive hydrogen bonding network characterising these kinds of compounds, which results in an enhanced self-diffusion coefficient relative to one in which the hydrogen bonding network remained intact inside the porous media. This work shows that NMR techniques are very useful in characterizing structural properties of porous media and give a new and fascinating insight into the diffusive motion of functional organic compounds in porous media.

4. References

- [1] Hollewand, M. P. and Gladden, L. F., "Transport heterogeneity in porous pellets. 1. PGSE NMR studies", *Chemical Engineering Science* **50**, 309-326, (1995).
- [2] Barrie, P. J., "Characterization of porous media using NMR methods", *Annual Reports on NMR Spectroscopy* **41**, 265-316, (2000).
- [3] Mantle, M. D., Enache, D. I., Nowicka, E., Davies, S. P., Edwards, J. K., D'Agostino, C., Mascarenhas, D. P., Durham, L., Sankar, M., Knight, D. W., Gladden, L. F., Taylor, S. H. and Hutchings, G. J., "Pulsed-field gradient NMR spectroscopic studies of alcohols in supported gold catalysts", *Journal of Physical Chemistry C* **115**, 1073-1079, (2011).