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Probing Longer-Range Co-operative Effects in Vapour Adsorption and Solid Melting Within Mesoporous Solids Using NMR Relaxometry and Cryodiffusometry

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1. Introduction

In order to improve catalyst activity and selectivity for diffusion-limited reactions within porous heterogeneous catalysts it is necessary to understand the inter-relationship between pore structure and mass transport. In particular, an accurate knowledge of the pellet pore size distribution is essential. However, current techniques for analysing nitrogen adsorption isotherms (such as the BJH and NLDFT methods), and cryoporometry melting curves, make unfounded assumptions concerning the thermodynamic independence of differently-sized pores within complex pore networks.

Hence, potential pore-pore interaction effects leading to co-operative cascades of advanced adsorption, or advanced melting, in sorption and cryoporometry experiments respectively, are not taken into account. For example when analysing gas adsorption data, a potential discrepancy of a factor of two, between estimated and actual pore sizes, would be anticipated from employing the wrong meniscus geometry in the Kelvin equation. In order to obtain accurate pore size distributions these effects must be assessed and accounted for. In this work, partially saturated mesoporous sol-gel silica pellets were used as a model catalyst to investigate co-operative adsorption and melting effects by using nuclear magnetic resonance (NMR) relaxometry and cryodiffusometry techniques.

2. Preliminary findings and discussion

It has been shown that conventional analysis techniques for gas adsorption data are likely to lead to highly inaccurate pore size distributions due to advanced adsorption effects. Corresponding advanced melting effects have also been observed in cryoporometry melting curves, and, hence, pore size distributions obtained by the conventional version of this technique are also likely to be inaccurate. Hence, these findings are likely to have serious implications for attempts to implement intelligent design of heterogeneous catalysts.

In this study, water vapor was adsorbed on a mesoporous sol-gel silica material, at relative pressures across the capillary condensation region of the isotherm. For this, silica pellets were left to equilibrate, at 294K, above salt solutions, offering different saturation pressures.

The spin-spin relaxation time (T_2) of the condensed liquid phase has been measured and the relaxation has been found to increase with relative pressure, as might be anticipated due to capillary condensation in increasing pore sizes. NMR cryoporometry freezing and melting curves were also obtained for the adsorbed phase. Pulsed Field Gradient (PFG) NMR has been used to probe the self-diffusivity of the molten adsorbed phase at various saturation levels and molten volume fractions. The apparent self-

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diffusivity of the condensed water has been used to probe the inter-connectivity and spatial extent of adsorbed ganglia. Freeze/thaw 'mini scanning loops' along the melting process, for the different saturated systems, along with T_2 relaxation experiments was used to investigate the distribution of the molten fractions in the pores and their connectivity.

According to the conventional view, in a homogeneous, random pore structure it would be expected that adsorption would occur sporadically and pervasively throughout the pore network, such that, initially, adsorbate ganglia would be limited in spatial extent, and adsorption would be confined to the smallest pores. However, if advanced adsorption were occurring the adsorbed ganglia might be expected to be of larger spatial extent and consist of both large and small pores. PFG NMR data was assessed to determine whether fully, partially restricted, or free, diffusion was present, and the appropriate model was then used to determine the typical ganglion size.

If advanced melting were occurring then cryoporometry melting curves for the adsorbed phase would also be expected to steeper than expected. Observations of the changes in the steepness of the cryoporometry melting curves and the change of the melting point depression, as the partial pressure was increased, suggest that advanced melting effects are occurring and provide additional information about the filling process of water in the porous media. Scanning loops observed at the same molten fraction, are not congruent for the different saturation levels. Their steepness/shape, in conjunction to T_2 values obtained, indicate a different spatial distribution of water in the porous network implying that advanced melting phenomena is occurring in a different extent.

3. Conclusions

Advanced melting phenomena and pore connectivity over the capillary condensation region has been studied, for partially saturated systems. Preliminary findings suggest that advanced melting occurs on solid melting and this has to be taken into account while investigating pore size distribution and pore connectivity using cryoporometry technique. The morphology of the absorbed water ganglia for the various saturation levels changes and further work is currently in progress for the assessment of ganglia connectivity and tortuosity.

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