A Solid State NMR Study of the Local Mobility of Water and Water Induced Dynamics of Linkers on Silica Surface

A thesis submitted
in partial fulfilment for the award of the degree of

Doctor of Philosophy

in

Physics

by

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March 2021

Abstract

Materials with hybrid organic-inorganic interface, large void pore volume, high surface area per unit volume, and broad pore size distribution, are used in diverse applications like molecular transport, surface catalysis, bio-mineralization etc., where water is the most widely used solvent. In the work presented here, we have employed proton and deuterium solid state magic angle spinning (MAS) NMR to investigate the distribution of water on silica surface and water induced dynamics of functionalized silica materials. Our study contributes to the understanding of surface binding, pore filling, and local dynamics in mesoporous hybrid materials.

In the first part of the work, we have employed existing solid state NMR techniques to investigate the distribution of water molecules near the pore surface of PMO_E. Proton MAS NMR spectra of PMO_E acquired at different hydration levels are analysed and interpreted in terms of water clusters of various sizes and distributions of water layers on the pore surface. Based on the analysis, a possible pore filling mechanism is proposed. For PMO_E, the proton spectral analysis suggests that both radial and axial filling mechanisms play a significant role in the hydration process. Formation of larger clusters at lower hydration suggests that the pores of PMO_E are getting filled with water at lower hydration levels than those of SBA-15. The challenges faced while analysing ^1H MAS NMR spectra of PMO_E are addressed.

Correlation between dynamics induced by a few water molecules/nm^2 on SBA-15 amine-functionalized linkers and the resultant possible molecular conformations is the main focus of the study in the second part of the work presented here. Two widely used mesoporous hybrid materials with amine functionalization are used in the study. The diamines tethered at the end group of GPTMS and MATMS are deuterated. By analysing deuterium and proton MAS NMR spectra acquired at different temperatures and various hydration levels, dynamics of the linkers and its dependence on temperature is investigated. Effective quadrupolar parameters calculated from deuterium MAS NMR spectra were indicative of molecular dynamics induced by a few water molecules within the proximity of the grafted linkers. *A-priori* molecular dynamic simulations were performed to (i) derive possible molecular conformations associated with dynamics, (ii) to understand the connection between the length of the linker and dynamics, and (iii) to understand the restriction on dynamics due to steric hindrance generated by double bonds. The effective quadrupolar parameters calculated from the MD simulations were consistent with those obtained from deuterium MAS NMR analysis.