Despite the tremendous importance of catalysis for all types of chemistry and biochemistry, there is still a huge gap in detailed knowledge of the processes and reaction intermediates on the surfaces of the catalysts or inside. The combination of conventional and Dynamic Nuclear Polarization (DNP) enhanced solid-state NMR spectroscopy, x-ray diffraction, electron microscopy, chemical modelling and quantum chemical calculations, often loosely summarized as NMR crystallography, has evolved into one of the most powerful characterization tools to fill this gap and study solid catalysts and chemical processes on their surface or the active center of an enzyme. These techniques give an unprecedented view in the chemistry of immobilized homogeneous transition metal catalysts, supported e.g. on silica or crystalline nanocellulose (CNC) or polymer based core shell structures as carriers or reactants and reaction intermediates on transition metal nanoparticles (MNPs). The contribution presents recent examples from our group about solid-state NMR spectroscopic characterizations of mono- or binuclear Rhodium, Ruthenium and Iridium catalysts and a Nickel containing enzyme. The focus is set to the immobilization of Wilkinson’s type catalyst and the dirhodium-acetate dimer (Rh2ac4). These are linked covalently to high-surface silica or crystalline nanocellulose support materials, employing amine, phosphine, pyridyl or carboxyl functions on the surface of the support materials or mesoporous silica supports. Combinations of 13C-, 15N-, 29Si- and 31P- CP MAS, J-resolved 31P-MAS and HETCOR solid-state NMR techniques are employed to monitor the preparation of the catalyst. Moreover, by DNP enhanced solid-state NMR it is feasible to detect different carboxyl and amine binding sites in natural abundance at a fast time scale. The interpretation of the experimental chemical shift values for different binding sites is corroborated by quantum chemical calculations on dirhodium model complexes. Finally results on the mode-of-action of Nickel super-oxide dismutase employing a combination of selective 13C, 15N and 19F isotope labelling, REDOR-NMR and quantum chemical modelling are presented, which reveal the position of the substrate in the active center of the enzyme.

**Keywords:** Solid-state NMR, REDOR, DNP