

Atomistic Description of Active Surface Sites by ^{195}Pt DNP SENS

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The determination of surface structures with atomic-level precision remains a fundamental challenge in surface chemistry and heterogeneous catalysis. We have recently shown that by leveraging the tremendous increase of the NMR sensitivity induced by Dynamic Nuclear Polarization (DNP) for surface species, the three-dimensional structure of surface sites could be fully resolved. We demonstrated this approach on an organometallic Pt-NHC complex anchored on an amorphous silica surface. Quantitative ^{13}C - ^{15}N and ^{29}Si - ^{15}N internuclear distances measured by DNP enhanced NMR spectroscopy in combination with EXAFS data that provided distances between the Pt and surface O atoms, yielded a well-defined conformation folded towards the surface [1].

Here, we show that the presence of stabilizing noncovalent interactions between Pt and surface oxygen atoms is confirmed by DNP surface enhanced ^{195}Pt NMR spectroscopy. Broadband adiabatic inversion (BRAIN) cross-polarization (CP) and WURST Carr-Purcell Meiboom-Gill (CPMG) schemes were implemented in combination with the step-wise variable offset cumulative spectrum (VOCS) acquisition method [2] to acquire sensitive static ^{195}Pt NMR spectra (Figure). The experimental ^{195}Pt CSA tensor parameters were then confronted with DFT calculated values obtained on model structures in order to get new insight into the environment of the Pt atom. DFT calculations of the CSA tensors performed on a series of molecular Pt complexes show an excellent agreement between experimental and calculated values, and highlight the sensitivity of the Pt CSA tensor parameters to different coordination ligands. For the surface complex, the calculations show clear evidence for the presence of an oxygen atom in the coordination sphere of platinum, thus corroborating several previously results suggesting the existence of surface-ligand interactions that stabilize active species in immobilized catalysts.

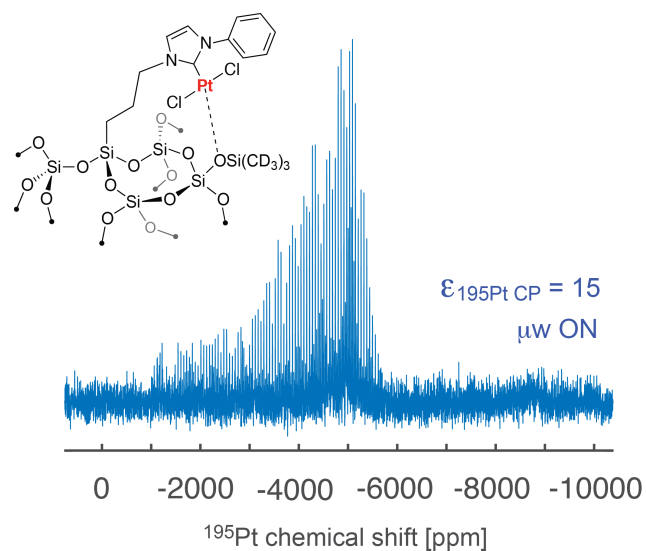


Figure: Ultrawideline DNP enhanced ^{195}Pt spectrum of the Pt-NHC surface supported complex.

[1] P. Berruyer, M. Lelli, M. P. Conley, D. L. Silverio, C. M. Widdifield, G. Siddiqi, D. Gajan, A. Lesage, C. Copéret, L. Emsley, Three-Dimensional Structure Determination of Surface Sites. *J. Am. Chem. Soc.* **2017**, *139*, 849–855.

[2] Schurko, R. W. Ultra-Wideline Solid-State NMR Spectroscopy. *Acc. Chem. Res.* **2013**, *46* (9), 1985–1995.