Bonding Network Connectivity of Mesoporous Silica Encapsulated Pt & PtSn Nanoparticles: Structural Characterization by Dynamic Nuclear Polarization-Enhanced Si-29 2D MAS NMR

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Introduction

Mesoporous silica shell encapsulated Pt ($Pt@mSiO_2$) and Pt-Sn ($PtSn@mSiO_2$) nanoparticles are an emerging class of heterogeneous catalysts with superior phase purity and crystalline order, uniform particle size, stability and longevity compared to conventional metal oxide-supported metal nanoparticles. We utilize DNP-enhanced Si-29 2D NMR to elucidate bonding connectivity and structure of the silica shell.

Experimental

2D ^{29}Si $SR26_4^{11}$ double-quantum NMR was performed on $PtSn@mSiO_2$ (impregnated with AMUPol) at 100 K at a MAS speed of 4000 Hz with continuous microwave irradiation at 6.4 W. A 3 μs 90° ^{1}H excitation pulse was applied followed by a ramped CP pulse on the ^{1}H channel with a contact time of 3.7 ms. For the $SR26_4^{11}$ sequence, the duration of 90° ^{29}Si excitation and recoupling pulse was 5 μs and 9.61 ms (nutation frequency is 6.5 times the rotor frequency), respectively. The TPPI method in which all pulses prior to the t_1 evolution are given phase shifts in increments of 45° as t_1 is incremented. cwLg13 and SPINAL64 (83 kHz) were used for proton decoupling during ^{29}Si recoupling and acquisition.

Results and Discussion

The dipolar coupling of 160 Hz delivers ~1% polarization transfer efficiency when a recoupling time of 2.6 ms is employed in the pulse sequence. The internuclear distance between nearest unbonded ^{29}Si nuclei is ~5 Å, and thus the coherence transfer between unbonded Si sites can be safely neglected. The transfer efficiency is further reduced by transverse relaxation. The dephasing time in the $PtSn@mSiO_2$ NPs was measured to be 4 ms in a spin-echo experiment, which is significantly shortened by the impregnated radicals. Therefore, the 2D correlation experiments probe only the ^{29}Si spin pairs bonded via one oxygen atom. In the figure above, the isotropic chemical shift of ^{29}Si is shown on the horizontal axis (single quantum coherence) and the sum of the isotropic chemical shifts is shown on the vertical axis (double quantum coherence). The signals in the spectrum reflect only the bonded ^{29}Si spin pairs. The spectral slices at -193 ppm (Q^2+Q^3), -204 ppm (Q^3+Q^3) and -213 ppm (Q^3+Q^4) are shown in Fig. 1B.

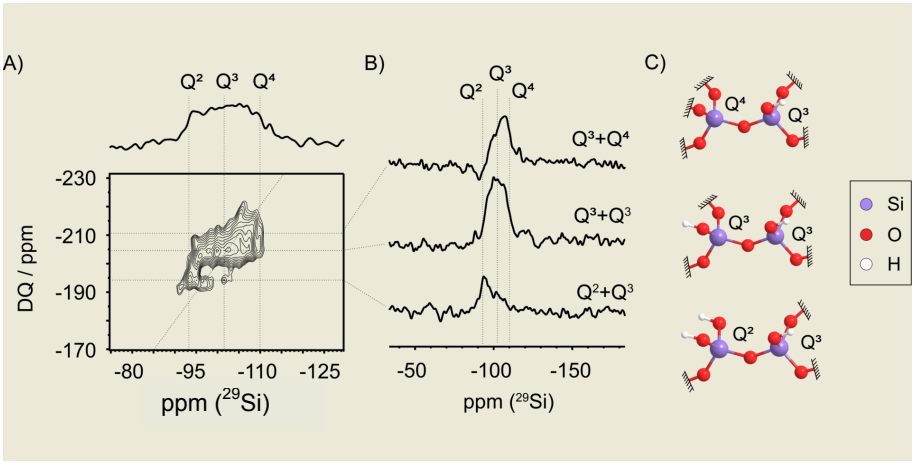

Figure 1. (A) 2D double quantum (DQ) - single quantum (SQ) spectrum. The sum of th 1D projection along the SQ dimension is shown at the top panel. (B) 1D projection along the SQ dimension at -193 ppm, -204 ppm and -213

Conclusions

The gain in ^{29}Si NMR sensitivity afforded by CP DNP allowed us to probe the connectivity among the Q^x sites in the $PtSn@mSiO_2$ catalyst using a 2D $SR26_4^{11}$ ^{29}Si-^{29}Si homonuclear correlation experiment. This would have been impractical by conventional MAS NMR using natural abundant ^{29}Si (4.9%) for our samples. The spectra demonstrate Q^2 - Q^3, Q^3-Q^3 and Q^3 - Q^4 bonding linkages.

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