Design and Synthesis of Supported Single Atom Catalysts through Surface Organometallic Chemistry and Atomic Layer Deposition

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Introduction
The design and synthesis of supported metal particles with controllable size and high dispersity has long been the frontier of heterogeneous catalyst research [1]. While preparation methods of supporting metal particles within the nanometer range has been extensively reported, comparatively less is known about the fabrication of supported subnanometer particles or single metal atoms [2]. Fabrication of supported metal catalysts within this regime of size (< 1 nm) are considerably more challenging due to the aggregation of surface metal species and the difficulty in achieving high dispersity. We combine the used of surface organometallic chemistry and atomic layer deposition [3] techniques to engineer highly dispersed metal species (Pd/Pt) on oxide supports with well-defined synthetic steps.

Materials and Methods
The corresponding metal precursors were prepared according to published literature reports [4]. For Pd/SiO₂, solution phase grafting of the Pd precursor was done by slowly adding a dilute toluene solution of the Pd complex to a slurry of SiO₂ (Silicycle S10040M, S.A. ~100 m²/g) suspended in toluene under inert atmosphere. This pre-catalyst was then washed with additional toluene and taken to dryness. A thin layer of Al₂O₃ was deposited between the chemisorbed species by ALD at 50°C before the catalyst was calcined at 400°C under O₂ for 4 hours and then reduced at 300°C with H₂ (5% in N₂). Catalysts with different supports or with Pt were prepared in a similar fashion. Solution phase ¹H and ³¹P NMR experiments were carried out to confirm the grafting of the metal precursor to the support. Removal of the ligand was monitored by solid state ³¹P NMR experiments. Adsorption of CO to the catalyst was studied by diffuse reflectance infrared fourier transform spectroscopy (DRIFTS).

Results and Discussion
Scheme 1 illustrates the overall synthetic approach to create atomically dispersed metal sites on the surface of the support. Solution phase NMR experiments confirmed that the metal complex had chemisorbed to the support through protonolysis with surface –OH groups by monitoring the disappearance of the ligand’s characteristic ¹H and ³¹P signal’s once the support is added to the solution.

Solid state ³¹P NMR (Figure 1.A) shows that once adsorbed, the metal complex maintains its ligand structure until calcination forms possible surface phosphate species. DRIFTS spectra of CO adsorption on the catalyst (Figure 1.B) shows an intense linear CO adsorption peak with exceptionally high intensity compared to the bridging peak, indicating atomically isolated Pd sites on the surface of the support.

Figure 1. A) Solid state ³¹P NMR spectra of (1) supported catalyst without ALD coatings, (2) supported catalyst with 10 cycles of ALD coatings and (3) ALD coated catalyst after calcination (* denotes spinning sidebands). B) DRIFTS spectra of CO adsorption on Pd/SiO₂.

Significance
Our current results with Pd/Pt imply that this chemisorption based grafting method can be extended to deliver a variety of metals to different supports creating subnanometer species with fabrication steps that can be characterized by appropriate analytical techniques. This strategy of combining surface organometallic chemistry and ALD to rationally design and synthesize catalysts with such potential generality has not been shown in the literature. We believe that this methodology will open opportunities to create new catalysts at the subnanometer scale.

References