

Vapor Phase Conversion of Pt Nanoparticles into Pt-Sn Bimetallic Nanoparticles

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Bimetallic nanoparticles (BMNPs) offer interesting size and composition-dependent properties. Pt-Sn BMNPs are particularly important in the field of catalysis, highlighted by their widespread industrial use for propylene production. They are widely accepted as a model system in fundamental studies of structure-performance relationships. ALD has proven successful in preparing catalytic systems with fine control over nanoparticle sizes and compositions, but the creation of non-noble metal-containing alloys often requires a high temperature reduction step¹. Here, we report the vapour phase conversion of Pt NPs into Pt-Sn BMNPs based on the selective decomposition of tetrakis(dimethylamido)tin (TDMASn), a common Sn ALD precursor, on Pt, which induces a solid-state reaction of metallic Sn with Pt to form BMNPs at low temperature.

The decomposition of ALD precursors is often mainly considered a temperature dependent property. However, TDMASn provides an example where the precursor decomposition is also a substrate dependent property. We found that TDMASn selectively decomposes on Pt in a temperature range of 150-300°C, whereas no decomposition was observed on other substrates like SiO₂, Al₂O₃ and TiN (**Fig. 1a**). The decomposition of TDMASn on Pt thin films led to the formation of different Pt-Sn alloys (**Fig. 1b**). The exposure of ALD-grown Pt NPs (**Fig. 2a**) to TDMASn pulses resulted in their conversion to Pt-Sn BMNPs, but the conversion process induced extensive particle ripening, leading to large and non-uniform particle sizes, undesired for catalytic applications (**Fig. 2c**). Interestingly, the conversion process could be improved by using an alternating pulsing sequence of TDMASn and H₂ exposures. The introduction of H₂ substantially aids in retaining the small NP sizes of the original Pt NPs (**Fig. 2b**). *In situ* mass spectrometry data during this process showed the removal of organic ligands during the H₂ pulse. The Sn uptake was monitored by *in situ* X-ray fluorescence (XRF), revealing saturation of the Sn incorporation in the Pt NPs as a function of the number of TDMASn-H₂ conversion cycles (**Fig. 3a**). Moreover, the amount of inserted Sn can be controlled via the deposition temperature. PtSn versus Pt₃Sn is accomplished by varying the deposition temperature during this process from 150°C-250°C (**Fig. 3b**). Finally, we confirmed

the compatibility of this method with high surface area supports by the successful conversion of a mesoporous Pt/SiO₂ catalyst.

1. Ramachandran et al., *RSC advances* **2017**, 7 (33), 20201-20205.

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