Controlling Metal Nanoparticle Dispersion with Partially Overcoated Supports

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Introduction

Supported metal catalysts are widely used in many industries. The catalytic activity of supported metal catalyst is highly dependent on the particle size of metals on the support. The catalysis community is continuously searching for ways of preparing highly dispersed supported metal catalysts. Though controlling particle size in synthesis stage is important, preserving particle size at elevated temperature remains another unsolved challenge. Several approaches have been attempted to enhance the thermal stability of supported metal catalysts, including exotic routes such as overcoating a second oxide on top of the catalyst particle.[1]

Recently, our group has successfully developed an approach that creates a sieving layer of one oxide (e.g. SiO2 or Al2O3, <2 nm) that partially coats (10-50% coverage) a primary oxide particle, leaving only small domains uncovered. This is accomplished by first grafting the supports with sacrificial templates, then partially overcoating the surface with a second oxide and finally removing the templates.[2] By using a similar approach, we synthesized TiO2 with partial SiO2 overcoats, and the modified TiO2 support was backfilled with Ag nanoparticles using photodeposition of AgNO3.[3] This approach controls the resulting Ag nanoparticle size and improves the thermal stability by creating spatially-restricted islands of strong metal-support interaction.

Materials and Methods

Partially overcoated TiO2 particles were synthesized by drying TiO2 (P25) at 110°C, dispersing in anhydrous toluene to which was added a template molecule such as tert-butyl calix[n]arene, and the suspension brought to reflux. Template density was controlled by the amount added to the reaction solution. The resulting modified particles were vacuum filtered, washed and dried. The modified TiO2 was redispersed in ethanol, then NH4OH and limiting amounts of tetraethyl orthosilicate (TEOS) were added. The suspension was shaken 1 hr to deposit ‘one cycle’ of SiO2 on the TiO2 surface. The process was typically repeated 3-8 times. Finally, the overcoated sample was heated in air to 325°C for 1 h and treated in ozone at 110°C for 2 h to remove the template.

Ag was deposited by suspension of the modified TiO2 particles in ethanol with dissolved AgNO3 followed by UV illumination (365 nm) of the degassed solution for 5-120 s. The resulting materials were filtered and washed. Select samples were heated in He at 450°C for 3hrs to study sintering behavior. The Ag-loaded samples were characterized by Transmission Electron Microscopy (TEM) and Extended X-Ray Absorption Fine Structure (EXAFS) analysis and the Advanced Photon Source. The weight loading of Ag was determined using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES).

Results and Discussion

Photoreduction conditions were optimized to an illumination time of 30s, a Ag+ concentration of 0.5mM, and 50mg/L TiO2 nanoparticles. These conditions give a base-case deposition of ~1 wt% Ag and 4.7 nm diameter nanoparticles on unmodified TiO2 supports (by TEM). (Figure 1a). On the partially overcoated supports, the resulting Ag nanoparticles are 2.9 ± 0.6 nm at 1.5 wt%, regardless of the template surface density (Figure 1b). In addition to controlling the particle size deposited, the SiO2 overcoat provides additional Ag+ adsorption sites, providing a rare example of higher dispersion at higher loading. Furthermore, the Ag nanoparticle size is preserved after heat treatment for deposition into the partially overcoated samples, while the Ag particles on unmodified TiO2 experience severe sintering. (Figure 1c vs. 1d) EXAFS analysis complemented TEM, showing 5±1 nm Ag nanoparticles on modified TiO2 vs. 7±1 nm on unmodified TiO2. After sintering, EXAFS is consistent with a significant growth on unmodified TiO2, while the Ag nanoparticles on the partially overcoated TiO2 actually decrease slightly to 4±1 nm. As has been seen for TiO2 on SiO2, isolated islands of TiO2 improve the sintering resistance of the Ag nanoparticles.[4]

Figure 1. Representative TEM images of (from left) a) Ag/TiO2, b) Ag/SiO2-TiO2 c) sintered Ag/TiO2, d) sintered Ag/SiO2-TiO2. Few, large Ag nanoparticles are present in 1c (circled).

Significance

This presentation demonstrates the feasibility of using partially-covered domains on TiO2 to control nanoparticle deposition methods relevant for the synthesis of supported metal catalysts. This backfilling strategy synthesizes thermally-stable and highly-dispersed uniform supported metal nanoparticles at both the synthesis and use stage. Further applications will be discussed.

References