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Synthesis and stabilization of small Pt nanoparticles on TiO_2 partially masked by SiO_2

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ABSTRACT

Controlling metal nanoparticle size and preserving metal dispersion at elevated temperature remain key challenges in designing new supported metal catalysts. Many methods have been proposed to stabilize metal nanoparticles for catalysis, but the use of specialized equipment or metal precursors can limit the application of these methods for scalable production. Here, we demonstrate a synthesis strategy to improve the dispersion and thermal stability of Pt nanoparticles on an oxide support. A thin SiO_2 coat (< 2 nm) was deposited on TiO_2 through repeated condensation cycles of tetraethyl orthosilicate (TEOS) with or without an organic template on the surface. H_2PtCl_6 was deposited using wetness impregnation, and the samples were dried, calcined, and reduced. The as-synthesized Pt nanoparticles are 1–2 nm by TEM and maintain dispersion $> 45\%$ by CO chemisorption even after prolonged heating at 500 °C, whereas Pt nanoparticles on unmodified TiO_2 are less dispersed ($\sim 33\%$) and their dispersion falls further upon prolonged heating. Ethylene hydrogenation demonstrates that the Pt nanoparticles on modified TiO_2 preserve the catalytic activities of Pt on unmodified TiO_2. The use of wet chemistry-based oxide modification and wetness impregnation makes this strategy a scalable and generalizable synthesis method to prepare other supported metal nanoparticles for catalysis applications.

1. Introduction

Supported metal catalysts are widely used for many energy and chemical production processes [1], and the size of the metal nanoparticles is one of the key factors influencing their total catalytic activity and selectivity. Therefore, the scientific community is continuously searching for methods to control metal particle size during synthesis and reaction [2–4]. In particular, controlling the metal particle size during reaction is challenging since supported metal particles can sinter at the elevated temperatures typical of many catalytic reactions [5,6]. Sintering causes growth of particle size and loss of active metal surface area, and nearly inevitably results in loss of catalytic activity [7,8].

Researchers have developed several different approaches to stabilize supported metal nanoparticles against sintering by adding additional components to the catalyst [5,9–11]. For instance, thermal stability of metal nanoparticles can be enhanced by the introduction of a second, high-melting metal to form bimetallic catalysts [5]. However, the introduction of a second element risks altering the catalytic behavior of the original metal catalyst. Besides alloying routes, several groups have added additional oxide overcoats to stabilize metal particles against sintering. For example, Somorjai and co-workers have reported coating individual, ligand-capped Pt nanoparticles (~ 10 nm) with mesoporous SiO_2 overcoats (~ 20 nm thick) by sol-gel methods at the mg scale, which successfully prevented Pt sintering in high temperature reactions [11]. Stair and co-workers reported enhancements to the thermal stability of a supported Pd catalyst by depositing a thin layer of Al_2O_3 on the as-synthesized Pd catalyst using atomic layer deposition (ALD) [12]. Similarly, Campbell and co-workers developed a thermally stable TiO_2-supported Pt catalyst by overcoating the TiO_2-supported Pt with SiO_2 using a sol-gel method [13]. Especially in this latter case, the second oxide may form a physical barrier to the aggregation of metal nanoparticles, but more importantly, it also creates an energy barrier to sintering due to its weaker interaction with the metal [6,14]. Though these reported procedures all show improved thermal stability of metal nanoparticles, the use of specialized metal

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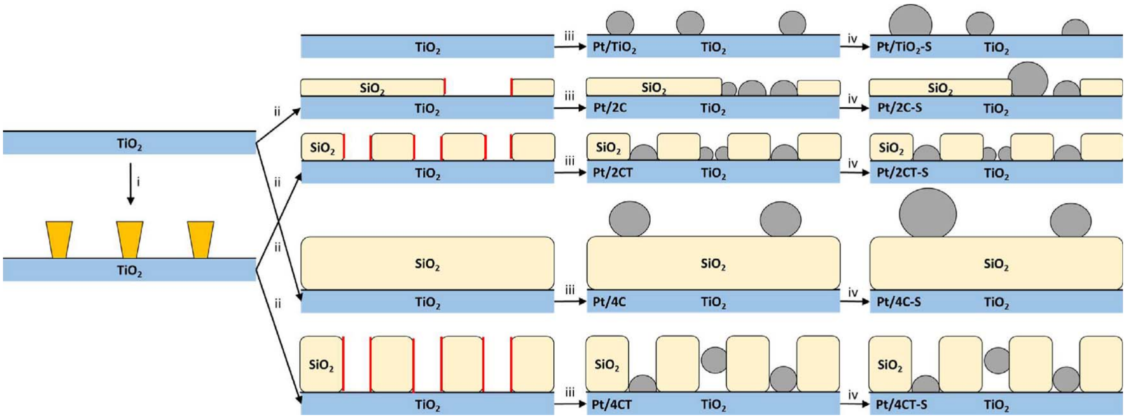

Scheme 1. Procedure for grafting templates, coating the supports, and depositing Pt[a]. [a] Synthesis steps: i. Grafting calixarene template, ii. Overcoating support with SiO_2 by TEOS condensation, iii. Incipient wetness impregnation and reduction of H_2PtCl_6, iv. Additional heat treatment at 500 °C in air. The vertical walls of the nanocavities are new surface area added by overcoat.

nanoparticle syntheses (e.g. ligand-assisted colloidal synthesis) or deposition methods (e.g. ALD) may limit the application of these methods in high volume production of industrially-relevant catalysts. Moreover, relying on an overcoat always introduces the possibility of diffusion limitations or that some of the active metal surface may be covered, negating some of the benefit of the smaller particle sizes.

Here, we report a scalable, wet-chemistry synthesis method to generate metal catalysts with enhanced thermal stability using supported Pt/TiO_2 as a sample system. Supported Pt catalysts are workhorse catalysts in applications including water-gas shift [15,16], aromatics hydrogenation [17–19], and the oxygen reduction reaction in fuel cells [20,21]. TiO_2 particles were first overcoated with a thin SiO_2 layer (< 2 nm) using an optimized Stöber method based on our group's previously reported procedure [22], and then used as supports for synthesizing Pt catalysts by wetness impregnation of H_2PtCl_6. Base-catalyzed sol-gel methods are widely used for large scale production of metal oxides [23], and wetness impregnation is one of the most commonly applied methods for the synthesis of supported metal catalysts [24].

We have previously reported on the size-controlled synthesis of Ag nanoparticles by exploiting photocatalytic deposition onto the exposed TiO_2 domains of a similar, partially-masked SiO_2-TiO_2 material. The current study is not nearly as restricted in scope, and demonstrates that conventional catalyst preparation methods (e.g. wetness impregnation) also result in improved metal dispersion. Both transmission electron microscopy (TEM) and CO chemisorption show that the size and stability of the supported Pt nanoparticles are tuned by the amount of the SiO_2 overcoat and whether an organic template is used to deliberately leave voids in the SiO_2 layer. We also demonstrate that Pt nanoparticles supported on the modified TiO_2 preserve the specific activity (rate per mol surface Pt) of those on unmodified TiO_2 using an ethylene hydrogenation probe reaction. This reaction was run under deliberately coking conditions to demonstrate the accessibility of the Pt surface in the modified materials, and to probe the resistance of the nanoparticles to sintering under the conditions of catalyst regeneration.

2. Experimental

2.1. Synthesis

Organic templates were grafted onto TiO_2 by adapting previously reported procedures [22–26]. TiO_2 (4 g, 20–30 nm primary crystallite size, ~71 m^2/g BET surface area, Degussa P25) was dried under dynamic vacuum overnight at 110 °C. Then, the TiO_2 was dispersed in a solution of p-*tert*-butylcalix[4]arene ('calixarene', 50 mg, $C_{44}H_{56}O_4$, Sigma Aldrich) in 200 ml toluene and heated to reflux overnight, then filtered, washed with 200 ml toluene and 200 ml hexane, and dried under dynamic vacuum.

TiO_2 was coated with SiO_2 using a modified version of the base-catalyzed sol-gel synthesis method some of us reported earlier [22]. TiO_2 (~1 g, modified or unmodified with calixarene) was dispersed in a solution of 182 ml ethanol (200proof) and 27 ml NH_4OH (28–30 wt%) and sonicated for ~30 min. Then, 0.1 ml of tetraethyl orthosilicate (TEOS, 98%, reagent grade, Sigma Aldrich) was added, and the suspension was shaken for at least 1 h. The cycles of sonication and TEOS addition were carried out a total of 1–4 times. Continuous, slow addition of TEOS could be a route to further optimization of the synthesis. After the final cycle, the coated material was filtered and treated under ozone (HG 1500 ozone generator, Ozone Solutions Inc.) at 110 °C for at least 3 h to remove any surface organics or the template molecule. Although not done here, calcination in air could presumably also be used to remove the template, instead of ozone.

Pt was deposited onto TiO_2 supports using incipient wetness impregnation following previously reported procedures [27]. 0.8 g TiO_2 support was dried under dynamic vacuum at 110 °C overnight to remove surface water then impregnated with 2 ml aq. H_2PtCl_6 precursor (~40 mmol, water purified using a Barnstead Nanopure system) and agitated for 48 h, then air dried for ~48 h. After drying, the material was calcined in air for 4 h at 400 °C with a heating rate of 5 °C/min, then reduced in H_2 for 10 h at 450 °C with a heating rate of 5 °C/min under He until the hold temperature was reached. Scheme 1 illustrates the steps to synthesize samples Pt/TiO_2, Pt/2C, Pt/2CT, Pt/4C and Pt/4CT, indicating two or four cycles ('C') of silica deposition, with or without templates ('T'). Some reduced samples were subjected to a second, extended calcination in air at 500 °C for 5 h with heating rate of 10 °C/min to give samples Pt/TiO_2-S, Pt/2C-S, Pt/2CT-S, Pt/4C-S, Pt/4CT-S. The scheme reflects the likelihood that regardless of their initial deposition location, Pt particles will form at and migrate to regions of high cohesive energy on the TiO_2 surface during the reduction pretreatment.

2.2. Characterization

Samples were dried under dynamic vacuum at 110 °C overnight before N_2 physisorption using a Micrometrics ASAP 2010 with specific surface areas calculated using the Brunauer – Emmett – Teller (BET) method. Thermogravimetric analysis (TGA) was carried out using a TA Instruments Q500 under 90%/10% O_2/N_2. Mass loss between 300 °C and 800 °C is assigned to the combustion of the grafted calixarene template and used to calculate the template loading. Pt loading was determined using a Thermo iCap7600 ICP-OES with sample digestion in a mixture of HF and aqua regia (33 vol% of 70 wt% HNO_3 with 66 vol%