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CO oxidation on PtSn nanoparticle catalysts occurs at the interface of Pt and Sn oxide domains formed under reaction conditions

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ABSTRACT

The barrier to CO oxidation on Pt catalysts is the strongly bound adsorbed CO, which inhibits O_2 adsorption and hinders CO_2 formation. Using reaction studies and *in situ* X-ray spectroscopy with colloidally prepared, monodisperse ~2 nm Pt and PtSn nanoparticle catalysts, we show that the addition of Sn to Pt provides distinctly different reaction sites and a more efficient reaction mechanism for CO oxidation compared to pure Pt catalysts. To probe the influence of Sn, we intentionally poisoned the Pt component of the nanoparticle catalysts using a CO-rich atmosphere. With a reaction environment comprised of 100 Torr CO and 40 Torr O_2 and a temperature range between 200 and 300 °C, Pt and PtSn catalysts exhibited activation barriers for CO_2 formation of 133 kJ/mol and 35 kJ/mol, respectively. While pure Sn is readily oxidized and is not active for CO oxidation, the addition of Sn to Pt provides an active site for O_2 adsorption that is important when Pt is covered with CO. Sn oxide was identified as the active Sn species under reaction conditions by *in situ* ambient pressure X-ray photoelectron spectroscopy measurements. While chemical signatures of Pt and Sn indicated intermixed metallic components under reducing conditions, Pt and Sn were found to reversibly separate into isolated domains of Pt and oxidic Sn on the nanoparticle surface under reaction conditions of 100 mTorr CO and 40 mTorr O_2 between temperatures of 200–275 °C. Under these conditions, PtSn catalysts exhibited apparent reaction orders in O_2 for CO_2 production that were 0.5 and lower with increasing partial pressures. These reaction orders contrast the first-order dependence in O_2 known for pure Pt. The differences in activation barriers, non-first-order dependence in O_2, and the presence of a partially oxidized Sn indicate that the enhanced activity is due to a reaction mechanism that occurs at a Pt/Sn oxide interface present at the nanoparticle surface.

1. Introduction

CO poisons Pt surfaces and prevents the formation of CO_2 by inhibiting O_2 adsorption. While pure Sn becomes readily oxidized in the presence of O_2 and does not react with CO, the rate of CO oxidation can be improved by incorporating Sn into Pt catalysts [1–6]. The barrier to understanding the mechanism of CO oxidation on PtSn, and even pure Pt catalysts, is knowledge of the structure and chemical environment of the surface and the nature of the catalytic active phase. The key in determining the true active phase of the catalyst is monitoring the atomic- and molecular-level details of surface atoms and reactants on the surface of the catalyst as the reaction proceeds. Nanoparticle catalysts can undergo significant structural and compositional changes that depend on the temperature and gas atmosphere during pre-treatment, reaction, and post-treatment [7–9]. Often, prenatal and postmortem spectroscopic characterization studies are used to understand the nature of the catalytic active phase. This approach often leads to diverse conclusions because the catalyst surface changes with different treatments and when samples are transferred from reactor to characterization tool. In order to make definitive conclusions about the catalyst's active phase using spectroscopic tools, the catalyst must be studied under reaction conditions.

Catalysts that are used industrially and commonly for laboratory kinetic reaction studies present challenges for atomic-level spectroscopic investigations because the porous supports

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attenuate signal and the active catalyst is polydisperse in size and composition. In order to observe changes in catalyst surfaces under reaction conditions, nanoparticle catalysts should not be embedded deep within pores of the support material. An effective method that allows for both reaction studies and spectroscopic observation under reaction conditions is deposition of colloidally prepared nanoparticles onto two-dimensional supports such as Si wafers [10,11]. Understanding how structure and composition of catalysts correlate with catalytic activity and selectivity requires ensembles of nanoparticles that have monodisperse size, shape, and composition distributions. Achieving monodispersity in size and composition is challenging when creating nanoparticles with incipient impregnation methods used in industry (i.e., reducing the metal precursors directly onto a mesoporous or microporous supports such as silica or alumina) due to uncontrolled mixing of the precursors at the liquid–solid interface, or from sequential reduction of multiple elements. However, an alternative synthesis approach that provides control over nanoparticle size and composition is inorganic colloidal synthesis [12,13].

In this work, we use ambient pressure X-ray photoelectron spectroscopy (APXPS) [14,15] to monitor the chemical composition and electronic environment of well-defined, colloidally prepared PtSn nanoparticle catalysts under various gas atmospheres. PtSn catalysts exhibit dynamic segregation with an intermixed Pt–Sn phase under reducing conditions and separated metallic Pt and oxidic Sn domains under CO oxidation reaction atmospheres. By intentionally poisoning the Pt surface sites with CO, we show that the enhanced activity displayed by PtSn catalysts is due to the presence of Sn, which allows for O_2 adsorption and dissociation and a Pt/Sn oxide interface where SnO is reduced by CO. An alternative and more facile reaction mechanism at the interface is confirmed by measurements of the effective activation barriers and reaction rate dependencies with respect to O_2 and CO.

2. Experimental methods and materials

2.1. Materials

Hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$, 99%), tin chloride ($SnCl_2$, 98%), tin(II) acetate ($Sn(C_2H_3O_2)_2$, 99%), poly(vinylpyrrolidone) (PVP, MW = 29,000/55,000 amu), ethylene glycol (reagent grade), hydrochloric acid (HCl, 2 M), sodium hydroxide (NaOH, 99.9%), sodium borohydride ($NaBH_4$, 99.9%), acetone (99%), tetraorthosilicate (99.9%), and ammonium hydroxide (99.9%) were manufactured by Sigma Aldrich. 1,5-pentanediol (95%), ethanol (100%), and hexane (99.9%) were manufactured by Fluka, KOPTEC, and BDH, respectively. Oxygen (5.0 UHP), carbon monoxide (5.0 UHP), and helium were purchased from Praxair. Polished Si(100) wafers were purchased from Addison Engineering. To minimize Fe or Ni carbonyls in the reactant gases, CO was stored in an Al cylinder and was passed through Cu tubing heated to 300 °C immediately before the reactor inlet.

2.2. Nanoparticle synthesis

Pt, PtSn, and Sn nanoparticles were prepared using inorganic colloidal methods as described previously with a PVP capping ligand [10,16,17]. The syntheses can be conducted using different initial amounts of precursors as long as the relative ratios remain constant. Polyhedral platinum nanoparticles of 2 nm average diameter were prepared by mixing 10 mL of ethylene glycol, 100 mg of $H_2PtCl_6{\cdot}6H_2O$ (1.9×10^{-4} mol), and 5 mL of a 0.5 M NaOH solution (0.1 g) in a 25-mL three-neck round-bottom flask. The flask was sealed with septa, and the residual air atmosphere was evacuated by three cycles of vacuum pumping followed by an Ar purge. The synthesis was conducted at 160 °C with vigorous stirring in Ar flow for 2 h. After the colloid returned to room temperature, 20.3 mg of PVP (0.18 mol) was added followed by vigorous stirring for 20 min. Finally, 100 mL of acetone was added to the solution, and the particles were precipitated by centrifugation at 4000 rpm (VWR Clinical 50) for ~10 min. Further washing with ethanol and hexane was performed three times to remove residual molecular fragments from the particle surface. These nanoparticles, as well as the PtSn and Sn nanoparticles, were stored in ethanol under refrigeration before their use in kinetic and spectroscopic studies.

Polyhedral PtSn nanoparticles of 2.2 nm average diameter were prepared by mixing 10 mL of ethylene glycol, 28 mg of $H_2PtCl_6{\cdot}6H_2O$ (7×10^{-5} mol), 13 mg of $SnCl_2$ (7×10^{-5} mol), and 111 mg of PVP (1×10^{-3} mol) in a 25-mL three-neck round-bottom flask. The synthesis was conducted at 160 °C with vigorous stirring in Ar flow for 2 h. After the colloid returned to room temperature, 40 mL of acetone was added to the solution and the particles were precipitated by centrifugation and washed with the same procedure used for the Pt nanoparticles.

To synthesize polyhedral Sn nanoparticles of 6 nm average diameter, 0.14 g of $Sn(OAc)_2$ (6×10^{-4} mol) and 1.7 g of PVP (1.5×10^{-2} mol) were loaded into a 100-mL three-neck round-bottom flask in a glove box. After adding 20 mL of dried 1,5-pentanediol into the precursor solution, the flask was evacuated by vacuum pumping followed by an Ar purge and heating to 100 °C with vigorous stirring. A reducing agent, which was prepared by dissolving 0.23 g of $NaBH_4$ in 60 mL of dried 1,5-pentanediol, was quickly injected into the precursor solution, and the reaction was maintained at 100 °C for 15 min. After cooling to room temperature, acetone was added to the solution and the nanoparticle solids were precipitated by centrifugation and washed with the same procedure used for the Pt nanoparticles.

2.3. Preparation of silica encapsulated Pt and PtSn nanoparticles for reaction studies

For the reaction studies, the Pt and PtSn nanoparticle catalysts were encapsulated in a porous silica shell to eliminate sintering during the long-term high-temperature experiments [18]. The nanoparticles were encapsulated in a SiO_2 shell using a modified sonication-assisted Stöber method with PVP as a pore structuring agent [19,20]. To prepare the shell surrounding the nanoparticles, a 50 μL aliquot of the as-prepared colloid was mixed by sonication (Branson, 3510) with 15 mL of ethanol in a 20 mL scintillation vial. While the mixture remained in the sonication bath, 2 ± 1 μL of TEOS was added (the total amount varied depending on the concentration of the nanoparticle solution). Following ~30 s of continued sonication, 2.25 mL of NH_3OH was added drop-wise over a period of 5 min. The solution was left in the sonication bath for 2 h. The ~21 mL solution of core–shell nanoparticles was washed with 21 mL of a 50:50 mixture of acetone and hexane and was precipitated by centrifugation for 10 min.

2.4. Catalyst sample preparation (Langmuir–Blodgett film deposition)

For kinetic and spectroscopic studies, nanoparticles were supported on two-dimensional surfaces. The use of a two-dimensional support differs from common catalytic studies that use high surface area materials (e.g., silica, alumina, or carbon) as catalyst supports. Surface-sensitive X-ray spectroscopy only probes the particles at the exterior of the high surface area three-dimensional supports. For kinetic studies, SiO_2-encapsulated Pt or PtSn nanoparticles were deposited onto a Si(100) wafer using a Langmuir–Blodgett trough (Kibron, MTX). For spectroscopic studies, the Pt or PtSn nanoparticles were supported on Au-coated Si wafers. Both supports exhibited negligible activity for CO oxidation.