A comparison study of the structural thermostability of SiO$_2$ supported Au@Pt and Au@Pd core-shell nanoparticles

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EXPERIMENTAL

A. Catalyst synthesis

**Chemicals and Materials.** Tetrachloroauric acid (HAuCl₄·4H₂O, >99%), ammonium hydroxide (NH₃·H₂O, 26~28 wt%), tetraethyl orthosilicate (C₈H₁₂O₈Si, 99%) and ethanol (>99.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Palladium hexafluoroacetylacetate (Pd(hfac)₂, >97%) was purchased from Sigma-Aldrich and trimethyl(methylcyclo-pentadienyl) platinum (IV) (MeCpPtMe₃, >99%) was purchased from Strem Chemicals. All gases including ultrahigh purity N₂ (99.999%), Ar (99.999%) and O₂ (99.999%), and the mixtures of 10% O₂, 10% H₂, and 10% CO in Ar (or He) were all provided by Nanjing Special Gases. All chemicals were used as received without further purification.

**Synthesis of SiO₂ support.** SiO₂ spheres were prepared by the Stöber method¹. Typically, 17.8 mL tetraethyl orthosilicate (TEOS), 5.4 mL NH₃·H₂O, 358 mL C₂H₅OH and 30 mL H₂O were added into a 500 mL beaker, then the solution mixtures were vigorously stirred at 25 °C for 24 h. After that, the colloid was centrifuged and washed by ethanol for several times and dried at 70 °C overnight. Finally, the obtained material was calcined at 700 °C under 10% O₂/Ar at a flow rate of 40 mL·min⁻¹ for 5 h in a tube furnace to get the sphere SiO₂ support.

**Synthesis of Au/SiO₂ catalyst.** An Au/SiO₂ catalyst was prepared using the deposition–precipitation (DP) method². Here 2 mL HAuCl₄ aqueous solution (0.0485 M), 1.0 g spherical SiO₂ and 150 mL deionized water were co-added into a three-necked bottle and mixed for 30 min under vigorous stirring at 65 °C, and ammonia was used to adjust the pH value between 9 and 10. Then, the system was continued vigorously stirred for another 12 h. The suspension was then centrifuged and washed with deionized water for several times and dried at 80 °C overnight. Finally, the resulting material was calcined at 300 °C in 10% O₂/Ar at a flow rate of 40 mL·min⁻¹ for 2 h to obtain the Au/SiO₂ catalyst.
Synthesis of Au@Pt/SiO$_2$ catalyst. Precisely synthesis of Au@Pt/SiO$_2$ bimetallic catalyst was performed by selective deposition of Pt on Au NPs via ALD. Typically, Pt ALD was carried out on the Au/SiO$_2$ sample at 150 °C in a viscous flow reactor (ALD-V401-PRO, ACME (Beijing) Technology) using MeCpPtMe$_3$ and ultrahigh purity O$_2$ (99.999%) as precursors. Ultrahigh purity N$_2$ (99.999%) was used as a carrier gas at a flow rate of 200 mL/min. The MeCpPtMe$_3$ precursor container was heated to 65 °C to get a sufficient vapor pressure. The reaction chamber was heated to 150 °C, and the inlet manifolds were held at 110 °C to avoid precursor condensation. The timing sequence was 30, 200, 10 and 200 sec for MeCpPtMe$_3$ exposure, N$_2$ purge, O$_2$ exposure and N$_2$ purge, respectively. An Au@Pt/SiO$_2$ core-shell bimetallic catalyst with a Pt shell thickness of 2.5 monolayers was fabricated by selectively depositing Pt onto Au/SiO$_2$ catalyst for 8 cycles. As a control experiment, Pt ALD was also applied on the bare SiO$_2$ support with several ALD cycles under the same condition to verify the selective Pt ALD on Au NPs.

Synthesis of Au@Pd/SiO$_2$ catalysts. Similar to the procedure above, an Au@Pd/SiO$_2$ catalyst was also synthesized by selectively depositing Pd onto the Au/SiO$_2$ sample using Pd ALD. Here Pd ALD was carried out on the same ALD reactor at 150 °C for 8 cycles. The Pd(hfac)$_2$ precursor was heated to 65 °C to achieve a sufficient vapor pressure and purity H$_2$ was used as the reductant. The timing sequence was 60, 200, 20, and 200 s for Pd(hfac)$_2$ exposure, N$_2$ purge, H$_2$ exposure, and N$_2$ purge, respectively. An Au@Pd/SiO$_2$ core-shell bimetallic catalyst with a Pd shell thickness of 2.3 MLs was fabricated by selectively depositing Pd onto Au/SiO$_2$ catalyst for 8 cycles. As a control experiment, Pd ALD was also applied on the bare SiO$_2$ support with several ALD cycles under the same condition to verify the selective Pd ALD on Au NPs.

B. Characterizations

Morphology and composition. Transmission electron microscope (TEM) measurements were performed on a JEM-2100F instrument operated at 200 kV to characterize the morphology of these catalysts. Elemental mapping using energy-dispersive spectroscopy (EDS) was performed on the same equipment. Scanning
transmission electron microscope (STEM) characterization of Au@Pd/SiO₂ and Au@Pt/SiO₂ bimetallic catalysts with an atomic resolution was carried out on an aberration-corrected high-angle annular dark-field STEM (HAADF-STEM) instrument at 200 kV (JEM-ARM200F, University of Science and Technology of China). The contents of the resulting bimetallic catalysts were determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) by dissolving these samples into hot aqua regia. X-ray diffraction (XRD) patterns of these samples were collected on a Rigaku/Max-3A X-ray diffractometer with Cu Kα radiation (λ = 1.54178 Å), where the operation voltage and current were maintained at 40 kV and 200 mA, respectively. The data was recorded over 2θ ranges of 20-80°.

**In-situ DRIFTS CO chemisorption measurements.** (Diffuse reflectance infrared Fourier transform spectroscopy) DRIFTS CO chemisorption measurements were performed on a Nicolet iS10 spectrometer equipped with a mercury-cadmium-telluride (MCT) detector and a low-temperature reaction cell (Praying Mantis Harrick). After loading a sample into the cell, it was first calcined in 10% O₂/Ar at 150 °C for 0.5 h followed by a reduction in 10% H₂/Ar at different temperatures (150, 250, 350, 450 and 550 °C) for another 1 h. After cooling the sample to room temperature under a continuous flow of Ar, a background spectrum was collected. Subsequently, the sample was exposed to 10% CO/Ar at a flow rate of 25 mL/min for about 0.5 h until saturation. Next, the sample was purged with Ar at a flow rate of 25 mL/min for another 0.5 h to remove the gas-phase CO, and then the DRIFT spectrum was collected with 256 scans at a resolution of 4 cm⁻¹.

**Metal dispersion measurements.** The Pd or Pt dispersions of Au@Pd/SiO₂ and Au@Pt/SiO₂ bimetallic catalysts were determined by CO pulse chemisorption, which were conducted on a Micromeritics AutoChem II chemisorption instrument. After loading a sample, the catalyst was first calcined in 10% O₂/He at 150 °C and then reduced in 10% H₂/He at different temperatures (150, 250, 350, 450 and 550 °C) for 1 h, respectively. Then, the catalysts were cooled to room temperature in He, and CO pulses were introduced to the catalyst surface using 10% CO/He until saturation. The
amount of chemisorbed CO was calibrated by using a thermal conductivity detector. For Pd dispersion calculations, a stoichiometry of CO : Pd of 1 : 1 was assumed for Au@Pd/SiO$_2$ catalyst reduced under 550 °C due to the high ratios of linear to bridge-bonded CO in the DRIFTS CO spectra, while a stoichiometry of CO : Pd of 1 : 1.5 was applied to Au@Pd/SiO$_2$ catalyst reduced at other temperatures, according to literature$^3$-$^5$. For Pt dispersion calculations, a stoichiometry of CO : Pt of 1 : 1 was assumed for Au@Pt/SiO$_2$ catalyst with different reduction temperatures$^6$. 
References

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