

Sum Frequency Generation Vibrational Spectroscopy of 1,3-Butadiene Hydrogenation on 4 nm Pt@SiO₂, Pd@SiO₂, and Rh@SiO₂ Core-Shell Catalysts

Supporting Information

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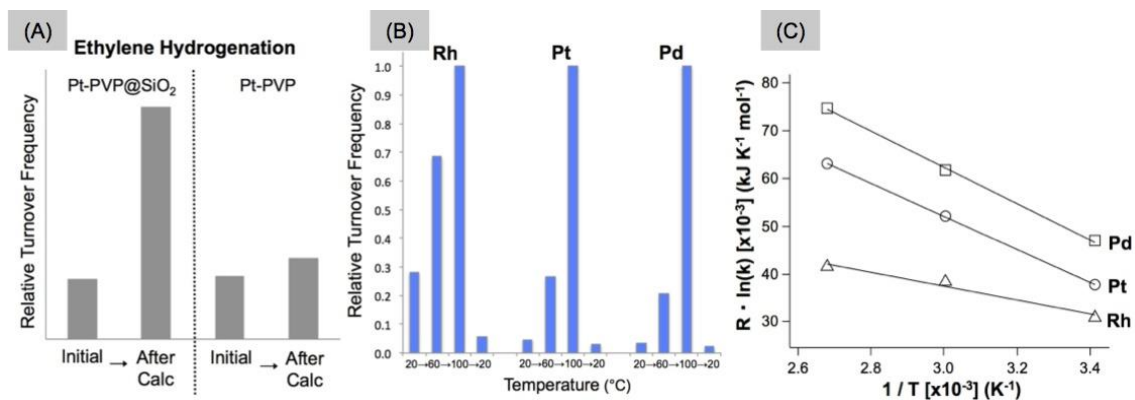


Figure S1: (A) Ethylene hydrogenation (normalized to the initial untreated sample) on Pt-PVP@SiO₂ and Pt-PVP before and after calcination at 350 °C for 10 min. (B) Relative turnover of 1,3-BD hydrogenation (normalized to 100 °C) for Rh@SiO₂, Pt@SiO₂, and Pd@SiO₂. Deactivation is calculated by comparing 20 °C before and after reactions at 60 and 100 °C. (C) Arrhenius plot for Rh@SiO₂, Pt@SiO₂, and Pd@SiO₂. Because of C accumulation on Rh@SiO₂ there is deactivation and deviation from Arrhenius behavior.

Experimental Methods

NP Synthesis and Core-shell Encapsulation. All synthesis was performed under Ar atmosphere with 29,000 MW polyvinylpyrrolidone (PVP, Sigma-Aldrich) and ethylene glycol (EG, Sigma-Aldrich) solvent. 3.7 ± 0.7 nm Pt-PVP NPs were prepared by combining 20 mL of EG, 100 mg of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (1.9×10^{-4} mol, Sigma-Aldrich), and 440 mg of PVP (4×10^{-3} mol) in a 50 mL three-neck round bottom flask.¹ The flask was sealed and residual air was evacuated by three cycles of vacuum pumping followed by an Ar purge. 3.8 ± 0.8 nm Pd-PVP were prepared by combining 10 mL of EG, 70 mg of PdCl_3 (1.0×10^{-4} mol, Sigma-Aldrich), and 220 mg of PVP (2×10^{-3} mol) in a 25 mL round bottom flask. The synthesis of Pt and Pd was carried out at 165 °C with vigorous stirring in Ar flow for 25 min. Continuing for longer times did not increase the size of the NPs. 4.1 ± 1.2 nm Rh-PVP NPs were synthesized with 0.657 g (1×10^{-4} mol) of rhodium(II)trifluoroacetate dimer [$\text{Rh}_2(\text{TFA})_4$] (i.e., 2×10^{-4} mol per Rh atom, Sigma-Aldrich) and 220 mg of PVP (2×10^{-3} mol) in 10 mL EG heated to 110 °C for 10 min and then to 165 °C for 1.5 h.²

When the solution returned to room temperature after synthesis, 100 mL of acetone was added to the solution and the NPs were precipitated by centrifugation (VWR Clinical 50, 4000 rpm) for ~10 min. The NPs (black precipitate) were then redispersed in ethanol (10-20 mL) and precipitated with hexane (40-80 mL) at least three times to wash away excess PVP.

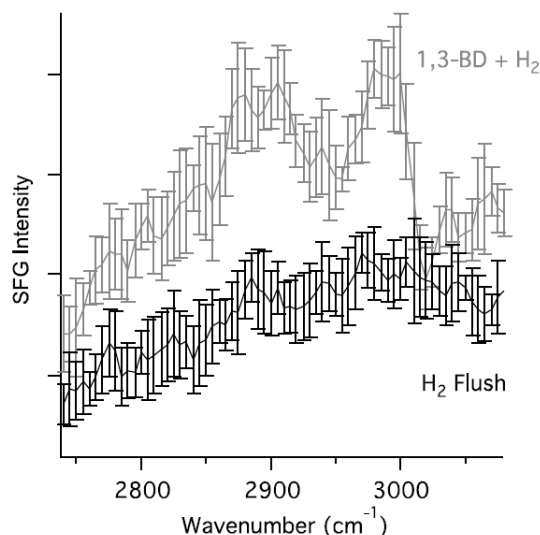
Core-shell NPs were synthesized by dissolving 100-300 μL of Pt-PVP, Pd-PVP or Rh-PVP and 5-10 μL of tetraethyl orthosilicate (TEOS) with 15 mL of ethanol in a 20 mL glass scintillation vial.^{3,4} Subsequently, 2.25 mL of ammonium hydroxide ($\text{NH}_3/\text{H}_2\text{O}$) was added drop-wise while the mixture was stirred for 5 min. After all $\text{NH}_3/\text{H}_2\text{O}$ was added, the mixture was left in the sonicator for 2 h. To achieve the thinnest shell while ensuring complete encapsulation of all NPs, the ratio of NP to TEOS was adjusted. To separate the $\text{Pt}@\text{SiO}_2$ NPs from the synthesis mixture, ~6 mL of acetone and ~22 mL of hexane were combined and centrifuged (4000 rpm) for 10 min. Pt-PVP@ SiO_2 were washed two additional times by dissolution in ~2 mL of ethanol, precipitation in ~12 mL of hexane, and centrifugation. Before Langmuir-Blodgett (LB) film deposition, Pt-PVP@ SiO_2 NPs were dissolved in 300 μL of EtOH and 300 μL of CHCl_3 and sonicated for ~1 h or until dissolved.

Langmuir-Blodgett Film Deposition. LB films were deposited on the SiO_2 prism by submersion in a water sub-phase followed by addition of the NP solution drop-wise to the surface.⁵ After the surface pressure increased to 10-20 mN/m, the film was allowed to rest for 30 min in order for the solvents to evaporate. The film was then compressed at a rate of 5 mm/min to the maximum compression (> 30 mN/m) such that any additional compression would create multilayers. To increase the signal intensity in the SFG experiments, two LB monolayers were deposited onto the fused SiO_2 prism by again submersing the prism and repeating compression.

Calcination. To remove the PVP, the NPs were placed into a tube furnace (Lindberg Blue M) at 350 °C for 10 min. SFG experiments in the aliphatic and aromatic stretching range confirmed the removal of PVP (Figure 3), resulting in a flat baseline in H_2 before introducing the reaction mixture.

1,3-Butadiene Hydrogenation Reactions. 1,3-BD hydrogenation was performed in a batch reactor equipped with a capacitance manometer pressure gauge (MKS Baratron), a recirculating pump (Senior Aerospace MB-21), a turbomolecular pump (Pfeiffer) and a rotary oil pump. Pt@SiO₂, Pd@SiO₂ or Rh@SiO₂ catalysts were loaded with 10× sand dilution into ¼-inch-diameter stainless steel tubing with glass wool. The conversion was assessed using a gas chromatograph (Agilent 6890) equipped with a flame ionization detector and Supelco I-2809-U 23% SP-1700 packed column. Prior to each reaction, the chamber was evacuated down to 10⁻⁴ Torr with a turbomolecular pump. Selectivity was calculated with total conversion <20%. Blank experiments indicated negligible background activity. To test the background of the SFG spectra for 20 Torr 1,3-BD, blank experiments were performed with a clean SiO₂ prism. These experiments show a =CH₂(s) stretch at 2995 cm⁻¹ and no other features. This peak is noted as a spectator in Figures 6, 7, and 8. Kinetic and SFG experiments were performed in 760 Torr total pressure using Ar background with 20 Torr 1,3-BD and 100 Torr H₂, unless otherwise indicated.

Sum Frequency Generation Vibrational Spectroscopy. SFG experiments were performed with a mode-locked Nd:YAG dye laser (Continuum Leopard D-20) with 1064 nm fundamental output, 20 Hz repetition rate and 20 ps pulse width. A frequency doubling crystal was used to generate a 532 nm visible (VIS) beam from the fundamental beam. An optical parametric generator/amplifier produced tunable infrared (IR) in the range 2680–3180 cm⁻¹, corresponding to the stretching modes of aliphatic and aromatic groups. Visible and infrared beams of ~220 μJ power were spatially and temporally overlapped at the base of a polished fused silica equilateral (60°) prism (ISP Optics) at angles of 63° and 48°, respectively, from the surface normal to achieve total internal reflection. All of the experiments were performed in *ppp* polarization combination. SFG photons were detected by a photomultiplier tube with a gated boxcar integrator. Each data point represents the average SFG photon output of at least 480 shots collected for each frequency. Pd@SiO₂ (Figure 7 in main text) has the lowest intensity signal during reaction (1,3-BD + H₂) compared to the background (H₂ Flush). The raw data are shown below (no offset) with error bars equal to +/- one standard deviation.



The intensity of the SFG signal I_{SFG} is given by

$$I_{SFG} = |\chi_{NR}^{(2)} + \chi_R^{(2)}|^2 I_{IR} I_{VIS} = \left| \chi_{NR}^{(2)} + \sum \frac{A_q}{\omega_{IR} - \omega_q + i\Gamma_q} \right|^2 I_{IR} I_{VIS}$$

where $\chi_{NR}^{(2)}$ is the nonresonant second-order susceptibility, $\chi_R^{(2)}$ is the resonant second order susceptibility, and A_q , ω_{IR} , ω_q , and Γ_q are the amplitude, scanning IR frequency, q^{th} resonant vibrational frequency of the adsorbates and line width, respectively.⁶⁻⁹ In SFG peak assignments “p” indicated perturbation from the metal surface and “FR” denotes Fermi resonance.

Transmission Electron Microscopy. NPs were supported on Cu grids (Electron Microscopy Sciences) and imaged using a JEOL 2100 microscope operated at 200 kV.

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