

Controlling catalytic selectivity on metal nanoparticles by direct photoexcitation of adsorbate-metal bonds

Matthew J. Kale,¹ Talin Avanesian,¹ Hongliang Xin,² Jun Yan³ and Phillip Christopher^{1,*}

¹University of California, Riverside, Riverside, CA 92521 (USA)

²Virginia Tech University, Blacksburg, VA, 24061

³Colorado School of Mines, Golden, CO, 80401

*Christopher@engr.ucr.edu

Introduction

Branching ratios of competing reaction pathways in thermal driven heterogeneous catalysis on metal surfaces are determined by inherent linear scaling relationships between adsorption energies and activation barriers for elementary reaction steps, limiting control of reaction selectivity [1]. Significant effort has been placed on utilizing visible photon excitation of adsorbate covered metal surfaces for enabling reactivity channels that cannot be achieved using solely thermal excitations, through ultrafast electronic energy transfer [2]. These photon driven reactions typically occur through a substrate mediated photoexcitation process, where photons absorbed by excitations between metal electronic states create hot electrons that inelastically scatter through unpopulated adsorbate orbitals, thereby depositing vibrational energy into adsorbates or adsorbate-metal bonds. Because photon absorption is dominated by electronic transitions between bulk metal electronic states, wavelength dependent cross-sections for all reaction channels follow absorption spectra of the metals. Similarity between the wavelength dependences of competing reaction channels dictates that control of reaction selectivity cannot be achieved by varying photon excitation wavelength, as typically done in molecular photochemistry. Here, we show that strong chemisorption bonds formed between CO and Pt metal surfaces can be activated with visible photons to drive catalysis through direct, resonant photoexcitation of hybridized Pt-CO states [3]. This bond activation mechanism allows for control of selectivity in preferential CO oxidation in an H₂ rich atmosphere through photon induced targeted activation of Pt-CO bonds.

Materials and Methods

We investigated photocatalytic CO, H₂ and preferential CO oxidation by O₂ on Pt nanoparticles of various sizes, supported on chemically and optically inert α -Al₂O₃. Reactions were performed in a continuous flow isothermal packed bed reactor, which allowed for specular catalyst illumination and temperature control. Continuous wave illumination was used to drive photocatalysis with a maximum photon flux of ~ 240 mW/cm² for wavelength dependent measurements. Photocatalytic activity was quantified by subtracting the background thermal reaction rate from the reaction rate under illumination. Quantum yields (QY) were calculated by normalizing the photocatalytic rate to the photon flux. *In-situ* diffuse reflectance (DR) spectroscopy was used to measure the impact of adsorbates on the Pt UV-Vis absorption spectrum. Linear-response time dependent density functional theory (Ir-TDDFT) calculations were used to theoretically analyze electronic transitions localized at adsorbate metal bonds.

Results and Discussion

Figure 1(a) shows the measured QY for CO oxidation (rate controlled by the activation of Pt-CO bonds) as a function of photoexcitation wavelength over Pt nanoparticles of varying size. The smallest nanoparticles exhibited a wavelength dependent QY that resonantly deviates from the Pt catalyst absorbance spectrum at 450 nm. This deviation

suggests that uniquely on small Pt nanoparticles, photon driven CO oxidation at 450 nm was not occurring through a substrate mediated photoexcitation mechanism. However, it was observed that in H₂ oxidation (rate controlled by the activation of Pt-O bonds) the wavelength dependent QY followed the Pt absorption spectrum for all sizes (data not shown). The results suggest that a more effective, adsorbate-specific, channel of transferring 450 nm photon energy into the activation of Pt-CO bond exists uniquely on small Pt particles. In Figure 1(b) it is shown that this unique energy transfer process could be used to significantly enhance selectivity towards CO₂ in the preferential oxidation of CO in a H₂ rich environment (PROX), through photoexcitation of small Pt particles with resonant 450 nm photons.

We hypothesized that direct photoexcitation of electronic transitions involving hybridized Pt and CO states could destabilize the CO molecule and were responsible for the observed resonant QY behavior and enhanced PROX selectivity on small particles. Using Ir-TDDFT calculations and *in-situ* DR UV-Vis measurements we substantiated this hypothesis. It was shown that the addition of CO to Pt surfaces induces a resonant electron-transition in the visible photon energy regime, Figure 1(c). The involved electron energies suggest a transition from hybridized Pt-CO orbitals (formed due to back donation from Pt 5d states into CO 2 π^* states) into hybridized antibonding Pt-CO orbitals (formed through donation of CO 5 σ states into Pt 6sp). Direct photoexcitation of the proposed transition could destabilize the Pt-CO bond and are consistent with facilitating photocatalytic CO oxidation and promoting PROX selectivity. On the other hand, no such electronic transitions were identified for the Pt-O bond.

Significance

This is the first example of a heterogeneous catalytic process being driven by direct photoexcitation of adsorbate-metal bonds. These results open new avenues to control reaction selectivity on sub 5-nm catalytic particles, whereby the energy of a photon flux can be specifically funneled into the breaking and making of targeted chemical bonds.

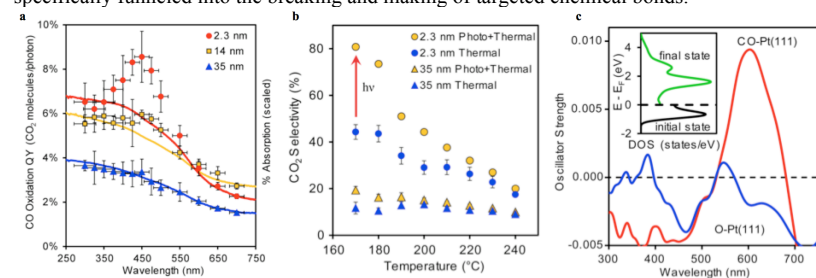


Figure 1. (a) CO Oxidation QY vs. photon wavelength over various sizes of Pt nanoparticles. (b) The impact of 450 nm photons on selectivity in PROX vs. temperature for 2.3 and 35 nm Pt particles. (c) Ir-TDDFT calculated impact of CO and O on Pt absorption spectrum. Inset shows electron energies involved in resonant transitions localized at hybridized Pt-CO states.

References

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