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Site-Dependent Selectivity in Oxidation Reactions on Single Pt Nanoparticles

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Supporting Information

Methods and instruments

Allyl-NHCs synthesis

The allyl-NHCs adduct was synthesized according to a published procedure. *Organometallics* **2016**, *35*, 2980-2986. 1H NMR (400 MHz, DMSO-d6) δ 9.36 (app. s, 1H), 7.87 (d, J = 1.6 Hz, 2H), 5.21 (d, J = 2.6 Hz, 4H), 3.87 (t, J = 2.6 Hz, 2H)

Pt particles preparation and NHCs deposition

Pt particles were prepared by evaporation of metallic Pt film on SiO_2/Si(110) surface, followed by annealing to 923 K for 5 h (hours) under N_2 environment. NHCs activation was carried out in a glove-box. 30 mM solution of allyl-functionalized NHCs in THF was activated using two equivalents of KO^tBu and left for 2 h to ensure carbene formation. The mixture was syringe-filtered and transferred to vials containing the Si-supported Pt NPs. After 12 h of liquid immersion, the functionalized surfaces were intermittently washed with THF and water to remove any unreacted NHCs and base remnants. The samples were then flushed with Ar for 15 min and stored in a glove-box.

Synchrotron-based infrared nanospectroscopy measurements

SINS measurements were performed using synchrotron infrared light (provided by the Advanced Light Source, Lawrence Berkeley National Laboratory) that was focused onto the apex of an oscillating Pt–Si Atomic Force Microscope (AFM) tip (Nanosensors, PtSi-NCH) at frequency ω in a modified commercial AFM (Innova, Bruker). Because the near-field scattered signal depends nonlinearly on the distance between the tip and the sample, the tip oscillation induces higher harmonics ($n\omega$) in the near-field scattered signal. As a result, the near-field signal can be differentiated from the far-field background by detecting the high harmonic frequency 2ω with a lock-in amplifier. A modified commercial FTIR spectrometer (Nicolet 6700, Thermo Scientific) was used to collect the infrared nanospectroscopy signal. Following AFM topography imaging of the surface, infrared nanospectroscopy point measurements were conducted at selected locations of the particles' surface. The Fourier transform of the interferogram provides a complex-valued near-field spectrum. The real (Re(ν), where ν is the wavenumber) and imaginary (Im(ν)) spectra can be represented as spectral amplitude (A(ν)) and phase (φ(ν)). The near-field spectra were reported in the form of a normalized scattering phase (φ(ν) = sample φ(ν) – reference φ(ν)), using the bare Si surface as a reference point.

SINS measurements were conducted at room temperature under nitrogen atmosphere. IR nanospectroscopy measurements were conducted on different sites on the surface of at least 10 particles under each reaction conditions. In these measurements at least 8 out of 10 particles, on average, showed a similar trend in their site-dependent reactivity. In all performed IR nanospectroscopy measurements, it was verified that the AFM tip is positioned either on the center or along the profile of the metallic particles. Therefore, the IR nanospectroscopy signal was mostly induced by molecules that were anchored on the various metal sites with only a minor, if any, contribution from molecules that reside on the metal/metal–oxide interface

<u>X-ray photoelectron spectroscopy measurements</u>

XPS measurements were conducted using an AXIS Ultra XPS instrument (Kratos), with a focused monochromatic Al Kα X-ray (1486.7 eV) source. The X-ray beam was normal to the sample and the photoelectron detector was at 45° off-normal. C1s (binding energy = 284.5 eV) was used as a reference for correction of any charging effects. XPS data analysis was performed using CasaXPS software.

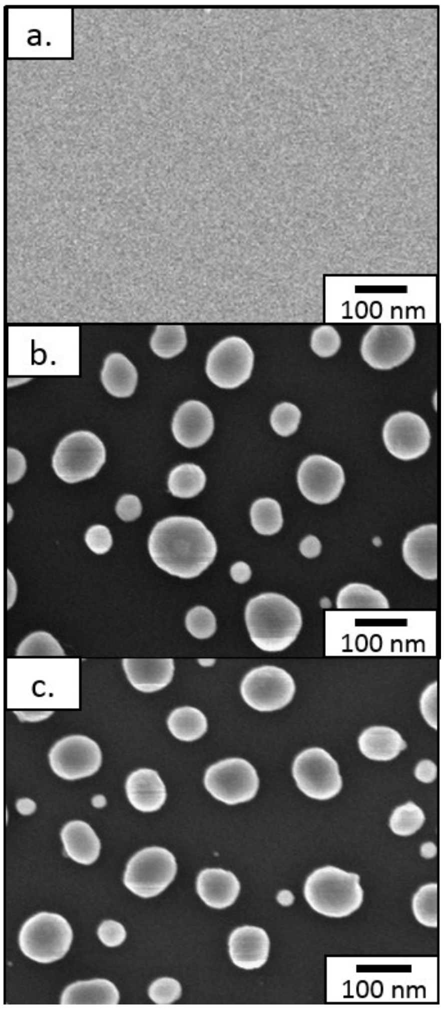

Figure S1. HR-SEM images of 15 nm Pt film on SiO_2/Si(110) before (**a**) and after (**b**) its annealing to 923 K for 5 h. HR-SEM image of Pt particles after NHCs surface anchoring is shown in **c**.

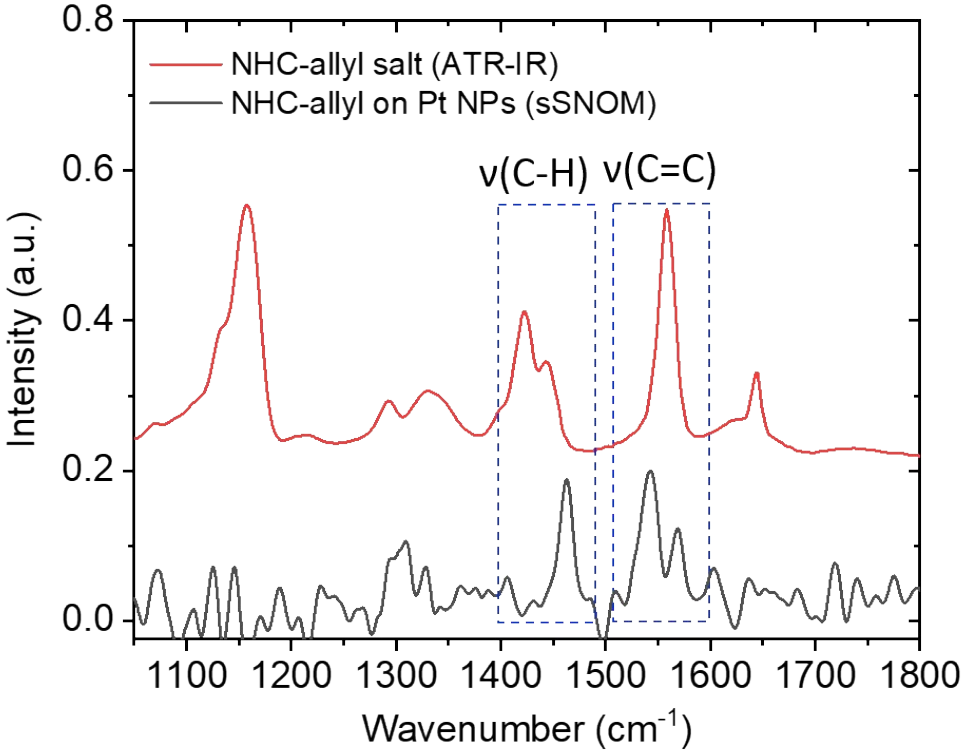

Figure S2. ATR-IR spectrum of allyl-functionalized imidazolium salt (red-colored spectrum) and SINS spectrum of the as-deposited allyl-NHC on Pt nanoparticles (black-colored spectrum).