A nanoscale insight into C-C coupling on cobalt nanoparticles

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Experimental Methods

All STM imaging was performed at 5 K with an ultra-high vacuum (UHV) low temperature scanning tunnelling microscope (LT-STM, Omicron Nanotechnology). The Cu(111) crystal (MaTeCK) was prepared in the preparation chamber (P = 2 × 10⁻¹⁰ mbar) by cycles of Ar⁺ (~1 kV/20 μA) sputtering for 30 min followed by annealing to ~1000 K. The sample was then transferred to the separate STM chamber (P ≤ 1 × 10⁻¹¹ mbar) where it was cooled to 5 K in the scanning stage. To deposit Co, the clean sample was first warmed to room temperature in the STM chamber, and then transferred to the preparation chamber where Co was deposited with a flux between 0.02 and 0.10 ML min⁻¹ by use of an electron beam evaporator (EFM3, Focus GmbH). The resulting Co nanoparticles covered 25–35% of the Cu surface. Following Co deposition, the sample was immediately transferred back to the pre-cooled STM scanning stage (~5 min) to prevent intermixing of Co and Cu.

Bromobenzene (Sigma-Aldrich >99.5%) and benzylbromide (Sigma-Aldrich 98%), which were purified by cycles of freeze/pump/thaw, were deposited onto the cold Co/Cu(111) sample through a high-precision leak valve. The sample was annealed to temperatures <300 K by removing the sample from the STM stage for a calibrated period of time. Annealing to >300 K required moving the sample to the preparation chamber, where resistive heating was carried out on the sample manipulator. All temperatures are given within ±20 K. The sample was allowed to cool ~45 minutes following every anneal to assure that scanning was conducted at 5 K. Imaging was performed with an etched W tip with tunnelling currents between 100-500 pA and voltages between ±50 and ±300 mV. dI/dV spectra were recorded using a lock-in amplifier, which modulated the bias voltage with a frequency of 1000 Hz and an amplitude of 10-14 mV. The I(V) curves were acquired simultaneously with the dI/dV(V). The spectra were taken in a rotation between all of the surface species, not consecutively over one species, to ensure that any changes within the STM tip state would be apparent. All of the individual spectra were averaged to provide the final measurement (~6 sweeps).
STM image and dI/dV spectra of the reaction intermediates of bromobenzene and the Ullmann coupling product, biphenyl, on a Co nanoparticle. Bromobenzene dissociates into Br atoms (blue circle) and Ph species (green circle), and couples to form biphenyl (purple circle). dI/dV spectroscopy was performed on each of these surface species, as well as the surface metals (red and black X for copper and cobalt, respectively). The biphenyl and the single phenyl species have a different density of states above the Fermi level (~0.2 V) that allows them to be distinguished. Scale bar = 4 nm.

STM images showing the ordered network of Br atoms and phenyl groups that forms at high coverage on the Co nanoparticle surfaces. The phenyl molecules appear as dimmer protrusions in the matrix of brighter round features, which are the Br atoms. Scale bar = 3 nm.