Dehydrogenative homocoupling of tetrafluorobenzene on Pd(111) via para-selective C-H activation

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Supporting Information

1. General procedure for the calculation
2. Reagent source
3. Dehydrogenation energy and the side view of the Dimer
4. General procedure for the ToF-SIMS measurement
1. General procedure for the calculation

The calculations were carried out in the framework of DFT by using the Vienna Ab Initio Simulation Package (VASP).\textsuperscript{1,2} The projector augmented wave method was used to describe the interaction between ions and electrons.\textsuperscript{3,4} We used the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) formulism to treat exchange–correlation interaction,\textsuperscript{5} and van der Waals (vdW) interactions were considered by using the DFT-D3 developed by Grimme.\textsuperscript{6} The structures were relaxed until the forces on all unconstrained atoms were $\leq 0.08$ eV/Å. All surfaces were modeled by two layered slabs separated by at least 15 Å of vacuum. A $p(5\times5)$ surface unit cell for Pd(111) was used for C-H reaction. Calculated lattice constants of 3.90 Å for Pd was used All calculations were done with a $1\times1\times1$ k-point sampling and a 400 eV kinetic energy cutoff. Transition-state calculations according to the nudged elastic band. The climbing-image nudged elastic band was applied to locate the transition state\textsuperscript{7} and the transition path was optimized until the forces acting to the path were converged typically to $\leq 0.08$ eV/Å.

2. Reagent source

1,2,4,5-Tetrafluorobenzene was bought from ALDRICH company (purity $\geq 99\%$)

3. Different views of the final state (FS) in Fig. 6b and dehydrogenation of the dimer of 1,2,4,5-tetrafluorobenzene

\textbf{Figure S1.} Different views of the final state (FS) in Fig. 6b
4. General procedure for the ToF-SIMS measurement

ToF-SIMS experiments were performed using a ToF-SIMS V spectrometer (IONTOF GmbH, Münster, Germany). A pulsed 30 keV Bi⁺ ion beam was used as the primary ion beam for all measurements. The analysis area was 500×500 µm. Target current was 1 pA. All data were obtained and analyzed using the IONTOF instrument software. Negative mass spectra were calibrated using C⁺, CH⁺, CH₂⁻ and C₂⁻ peaks.

References: