

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).^{1,2} The projector augmented wave method was used to describe the interaction between ions and electrons.^{3,4} We used the generalized gradient approximation (GGA) with Perdew–Burke–Ernzerhof (PBE) formulism to treat exchange–correlation interaction,⁵ and van der Waals (vdW) interactions were considered by using the DFT-D3 developed by Grimme.⁶ The structures were relaxed until the forces on all unconstrained atoms were ≤ 0.08 eV/Å. All surfaces were modeled by two layered slabs separated by at least 15 Å of vacuum. A p(5×5) 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 1×1×1 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 state⁷ and the transition path was optimized until the forces acting to the path were converged typically to ≤ 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

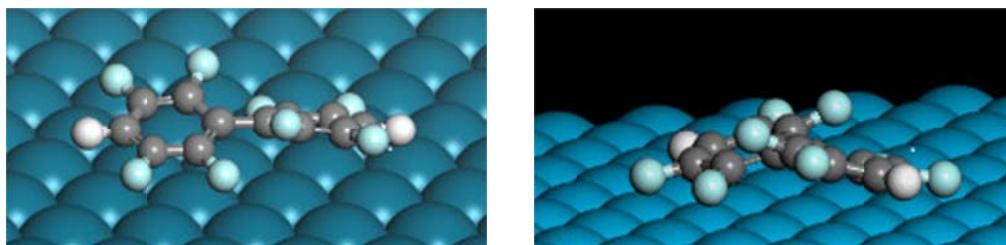


Figure S1. Different views of the final state (FS) in Fig. 6b

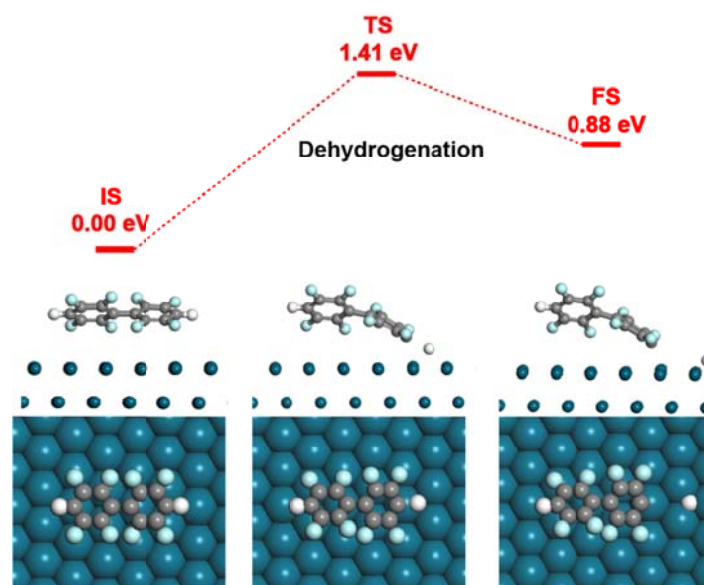


Figure S2. DFT-calculated energy diagrams for dehydrogenation of the dimer of 1,2,4,5-tetrafluorobenzene on Pd(111).

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:

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