Origin of the facet-dependent hydrogenation of olefins catalyzed by Pd nanocrystals: experiment and theory

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Experimental Section

Materials

Pd(acac)$_2$(99%) was purchased from Alfa Aesar, poly(vinylpyrroli-done) (PVP, MW=55000) was purchased from Aldrich. PVP (MW=30000), N,N-dimethylformamide (DMF), NaBr, KBr, FeCl$_3$·6H$_2$O, L-ascorbic acid (AA), PdCl$_2$ and tetrabutylammonium bromide (TBAB) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The water used in all experiments was ultrapure (18.2 MΩ). All reagents were used as received without further purification.

Synthesis of Pd nanosheets

Pd(II) acetylacetonate (Pd(acac)$_2$, 50.0 mg), poly(vinylpyrrolidone) (PVP, MW=30000, 160.0 mg) and TBAB (160 mg) were mixed together with N,N-dimethylformamide (10 mL) and water (2 mL) in a glass pressure vessel. The vessel was then charged with CO to 1 bar, heated from room temperature to 60 ℃ in 0.5 h, and then kept at 60 ℃ for another 2.5 h before it was cooled to room temperature. The dark blue products were precipitated by acetone, separated via centrifugation and further purified by an ethanol-acetone mixture.

Synthesis of Pd nanotetrahedra

Pd(II) acetylacetonate (Pd(acac)$_2$, 10.0 mg), poly(vinylpyrrolidone) (PVP, MW=30000, 40.0 mg) and a DMF solution of FeCl$_3$·6H$_2$O (40μL, 1.35 mg/mL) were mixed together with 10 mL DMF. in a glass pressure vessel. The vessel was pre-heated at 100 ℃ for 10 min and then charged with CO to 1 bar and heated to 140 ℃. After that it was kept at 140 ℃ with stiring for another 3 h before it was cooled to room temperature. The products were precipitated by acetone, separated via centrifugation and further purified by an ethanol-acetone mixture.

Synthesis of Pd nanocubes

In a typical procedure, 8 mL aqueous solution containing poly(vinylpyrroli-done) (PVP, MW= 55 000, 105 mg), L-ascorbic acid (60 mg), KBr (200 mg) were placed in a 20 mL vial, and pre-heated in air under magnetic stirring at 80 ℃ for 10 min. Then 3.0 mL of an aqueous solution containing Na_2PdCl_4 (57 mg) was added into the vial, and kept at 80 ℃ for another 3 h before it was cooled to room temperature. The product was collected by centrifugation and washed with water-acetone mixture.

Catalytic hydrogenation of olefin

The hydrogenation of styrene and trans-stilbene was carried out in a well-stirred glass pressure vessel (48 mL) at 30 ℃. Dispersed in 5 mL ethanol (5 mL DMF for trans-stilbene), 0.05 mg of the catalysts (i.e., Pd sheet and Pd tetrahedron and Pd cube) were mixed with 1 mmol substrate in the pressure vessel. H_2 flow was applied into the vessel for several minutes to remove oxygen. The vessel was then pressurized by 1.0 bar H_2. The reaction was allowed to proceed, and samples were withdrawn at regular intervals, filtered, and analyzed by gas chromatography (GC) with reference to toluene, and further confirming product identity by GC-MS.

Characterizations

TEM studies were performed on a TECNAI F-30 high-resolution transmission electron microscope operating at 300 kV. The samples were prepared by dropping ethanol dispersion of samples onto 300-mesh carbon-coated copper grids and immediately evaporating the solvent. GC analyses were performed with a FuLi 9790II, equipped with a split/splitless injector, a capillary column (KB-5, 30 m×0.32 mm×0.33 μm) and a flame ionization detector.

DFT calculations

First-principles calculations based on density functional theory (DFT) were carried out using the Vienna ab initio simulation package (VASP).[1-2] The valence electrons were described by plane wave basis sets with a cutoff energy of 400 eV, and the core electrons were replaced by the projector augmented wave pseudo- potentials.[3-4] The exchange-correlation functional utilized was the local density approximation with generalized gradient correction, GGA-PBE.[5] Due to the reactant sizes, 6×3 and 3√3×3 unit cell were used to model the Pd{100} and Pd{111} slabs, respectively. The k-points sampling was generated following the Monkhorst-Pack procedure with a 3×3×1 mesh. They covered with different numbers of hydrogen atoms with a four-layer slab and a

vacuum region of 15Å thickness. During structural optimization, the bottom two layers of the slab were fixed at bulk truncated position, while the top two layers and the adsorbates were fully relaxed. All internal structural parameters were relaxed until the Hellman- Feynman forces on each ion were less than 0.03 eV/Å. The minimum energy reaction pathways were calculated using the nudged elastic band (NEB) method. And the final transition state (TS) structures were refined by using a quasi-Newton algorithm until the forces were less than 0.03 eV/Å/ion. Moreover, frequency calculations were performed to confirm that a TS has only one imaginary frequency.

The adsorption energy (ΔE_{ads}) can be defined as:

$$\Delta E_{ads} = E_{Tot} - E_{Olefin} - E_{Pd+nH} \tag{1}$$

where E_{Tot} was the total energy of the whole system, E_{Olefin} was the energy of the styrene or trans-stilbene in the gas phase, and E_{Pd+nH} was the energy of the Pd surfaces covered by n hydrogen atoms. Thus, more negative the energy, more stable the adsorption.

The adsorption energy can be decomposed into three main components, namely, the deformation energy of the molecule $\Delta E_{def}(M)$, the deformation energy of the surface $\Delta E_{def}(S)$, and the interaction energy ΔE_{int}, as shown in Eq. 2:

$$\Delta E_{ads} = \Delta E_{def}(M) + \Delta E_{def}(S) + \Delta E_{int} \tag{2}$$

where $\Delta E_{def}(M)$ and $\Delta E_{def}(S)$ were the energetic costs (always positive) for bringing the molecule and the surface from their equilibrium geometry to the geometry they have in the final system, respectively, and ΔE_{int} was the energy change that occured when the two components in their deformed geometries approached each other.

The stability of the system (ΔE_{Stab}) can be defined as:

$$\Delta E_{Stab} = E_{Tot} - [E_{Olefin} + E_{Pd-slab} + n/2 E_{H2(g)}] \tag{3}$$

Where $E_{Pd-slab}$ stood for the energy of the Pd slab and $E_{H2(g)}$ the energy of a H_2 molecule in the gas phase. The values for ΔE_{Stab} could be used to evaluate the global stability of the whole system with respect to Pd slabs and gaseous olefin and H_2 molecules.

Reference

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2. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169-11186.
3. P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953-17979.
4. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775.
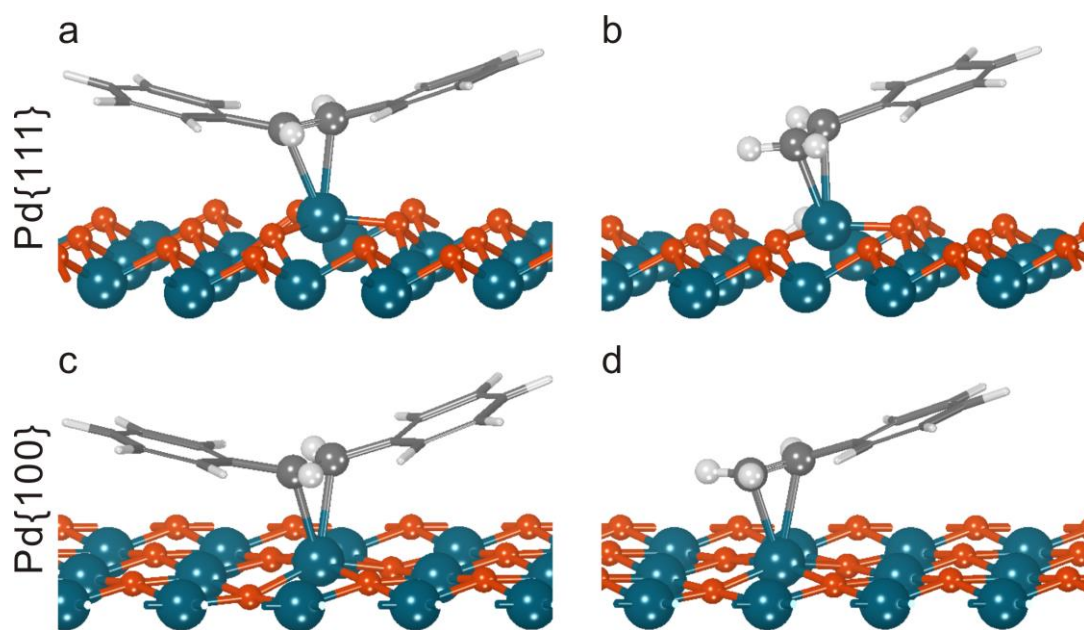5. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

Fig. S1 Optimized geometries of trans-stilbene and styrene adsorption on H atoms pre-saturated Pd{111} surface (a) (b), and Pd{100}surface (c) (d), respectively.
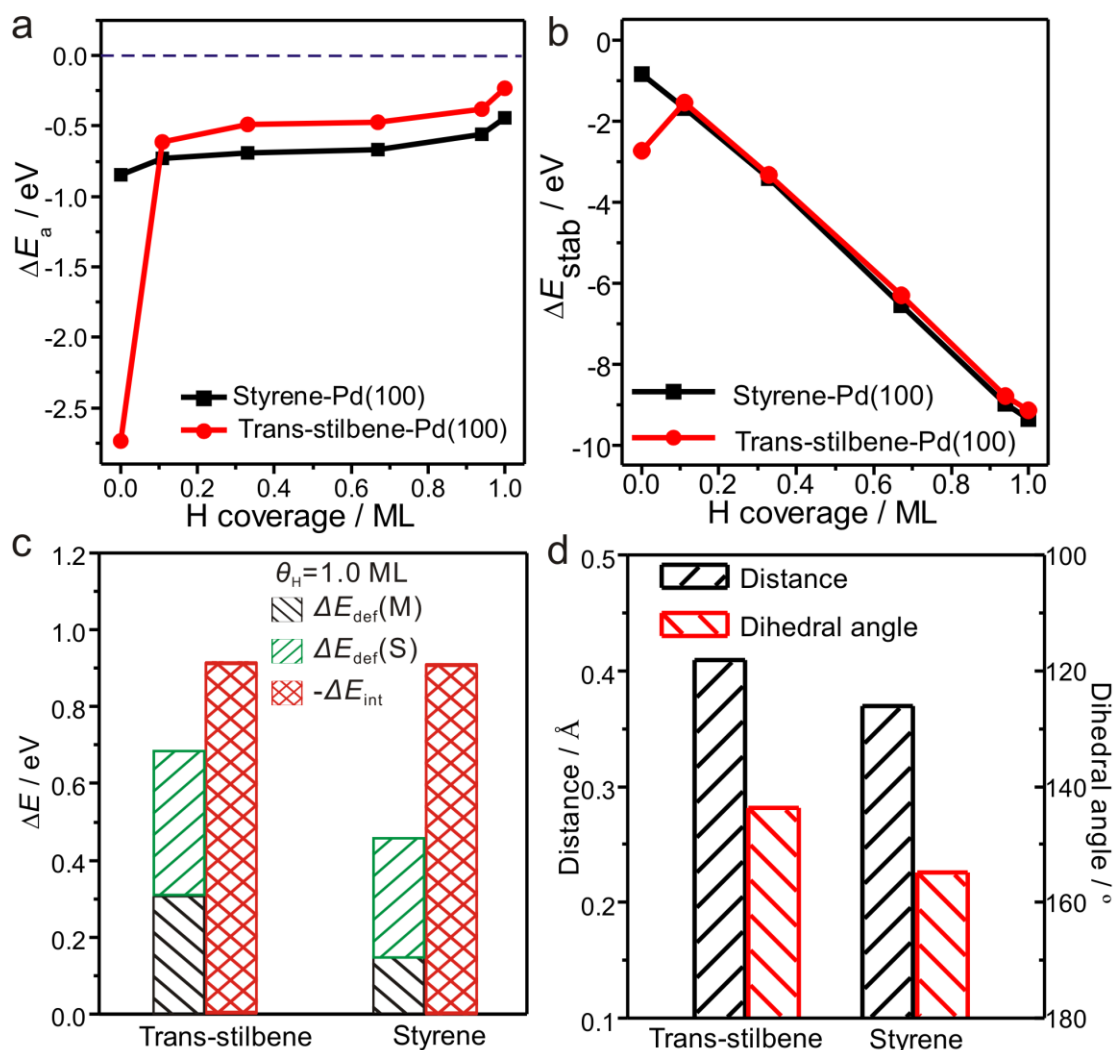
Fig. S2 (a) Adsorption energies of trans-stilbene and styrene interaction with Pd{100} as a function of co-adsorbed atomic hydrogen coverage (θH=0, 0.11, 0.33, 0.67, 0.94, 1.00 ML), (b) the stability of the whole system, (c) Partition of the energies of trans-stilbene and styrene adsorption on H-saturated Pd(100) surfaces and (d) Key geometrical parameters for trans-stilbene and styrene adsorbed on hydrogen-saturated Pd(100) surfaces.
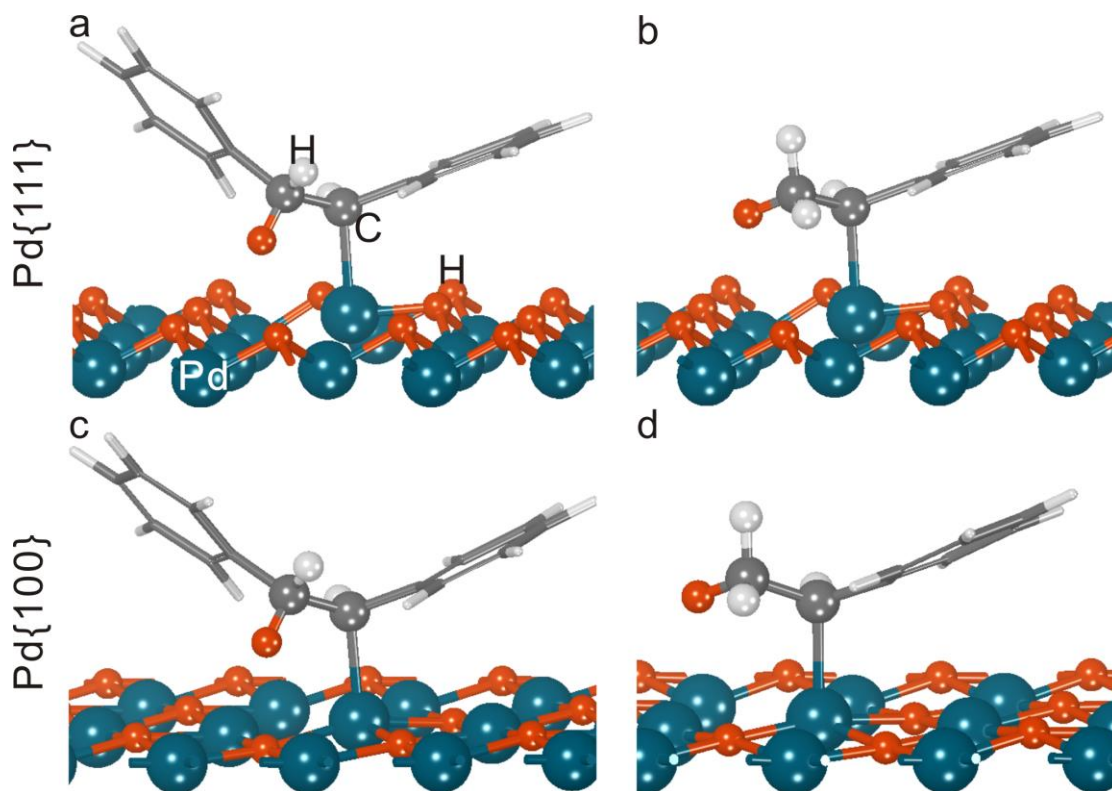
Fig. S3 SHIs on the Pd{111}(a), (b) and Pd{100}(c), (d) surfaces by the first hydrogenation of trans-stilbene and styrene.
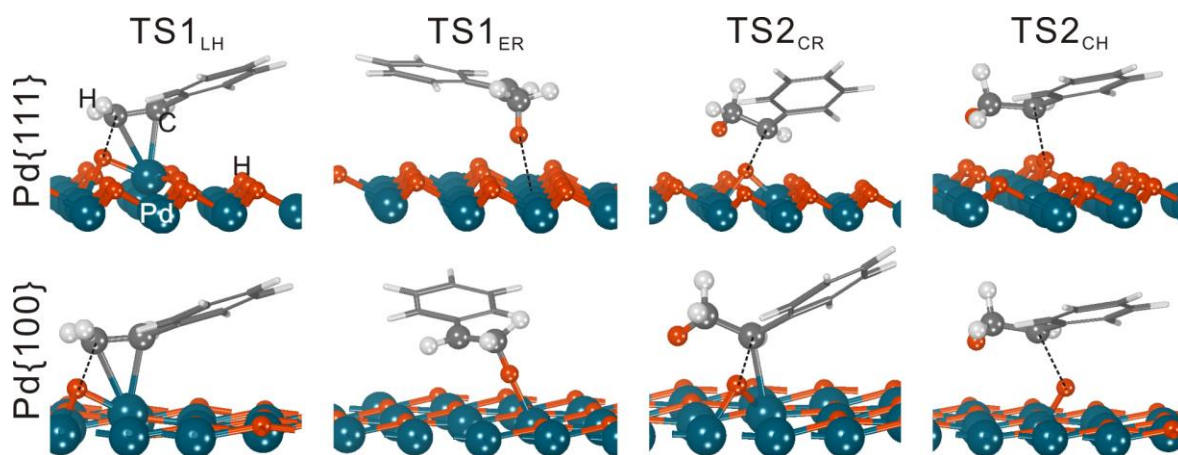
Fig. S4 Transition states of the hydrogenation of styrene adsorption on Pd{111} and Pd{100} surface via LH and ER type mechanisms.