Supporting Information

The Effect of External Magnetic Fields on the Catalytic Activity of Pd Nanoparticles in Suzuki Cross-Coupling Reactions

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Theoretical calculations:

The Vienna AB-initio Simulation Package (VASP) code has been used for our calculations[1, 2]. This code solves the Kohn-Sham equations of density functional theory (DFT) using a plane-wave basis set and the projector augmented wave (PAW) method[3]. The exchange and correlation effects were calculated by the generalized gradient approximation in the formulation of Perdew-Wang-91[4]. To ensure the accuracy of the calculated results, the cutoff energy was set to 400 eV for the plane-wave expansion of the electronic wave function. All structures were optimized with a convergence criterion of 1×10-5eV for the energy and 0.01eV/Å for the forces. Brillouin-zone integration was performed with 5 × 5 × 1 Monkhorst-Pack grid. A system of 3 × 3 slab with four layers was employed to model the Pd (111) surface and the vacuum layer was set to 20 Å. During geometry optimization the bottom two layers of Pd atoms were fixed, while the top two layers of Pd atoms along with bromobenzene were allowed to relax. The adsorption energy of the bromobenzene molecule on the metal substrate is calculated as follows:

$$E_{ads}=E_{slab+molecule}-E_{slab}-E_{molecule} \quad (1)$$

where E_{ads} is the adsorption energy, $E_{slab+molecule}$ represents the total energy after bromobenzene molecule adsorbed on the Pd(111) surfaces, $E_{molecule}$ is the energy of an isolated bromobenzene molecule and E_{slab} was the total energy of the slab. By our definition, the more negative adsorption energy signified stronger binding between the molecule and the metal surfaces.

Table S1. The yield of the diphenyl of Suzuki reactions catalyzed by Pd@$Co_3[Co(CN)_6]_2$ nanoparticles at 30 °C with different strength of MFs and the yield of production at the absence of MFs.

Times/h	2	4	6	8	10	12	24
0 T	13%	19%	25%	29%	32%	35%	44%
0.1 T	15%	23%	31%	35%	38%	40%	49%
0.25 T	16%	31%	37%	40%	42%	45%	54%
0.5 T	17%	32%	40%	45%	50%	54%	65%

Table S2. The yield of the diphenyl of Suzuki reactions catalyzed by Pd@$Co_3[Co(CN)_6]_2$ nanoparticles at 45 °C with a strength of MFs of 0.5T and the yield of production at the absence of MFs.

Times/h	2	4	6	8	10	12	24
0.5 T	45%	60%	66%	70%	74%	76%	83%
0 T	34%	51%	55%	60%	64%	66%	75%

Table S3. The yield of the diphenyl of Suzuki reactions catalyzed by Pd@$Co_3[Co(CN)_6]_2$ nanoparticles at 60 °C with a strength of MFs of 0.5T and the yield of production at the absence of MFs.

Times/h	2	4	6	8	10	12	24
0.5 T	69%	73%	75%	77%	78%	79%	85%
0 T	67%	70%	73%	76%	78%	79%	85%

Table S4. The yield of the diphenyl of Suzuki reactions catalyzed by Pd particles (the $Co_3[Co(CN)_6]_2$ is removed by acid treatment) at 30 °C with a 0.5T MF and without MF applied.

Times/h	2	4	6	8	10	12	24
0.5 T	18%	32%	41%	46%	51%	55%	66%
0 T	14%	20%	25%	29%	32%	35%	45%

Table S5. Adsorption Energies (eV) of bromobenzene molecules on the various adsorption sites of the Pd (111) surface.

Energy	Top	Bridge	Eads
Eads	-0.12eV	-0.19 eV	-1.07 eV

Table S6. Adsorption Energies (eV) of borbenzene on the Bri30 Site of Pd (111) with and without MFs.

Energy	Emolecular	Eslab	Eslab+molecular	Eads
No-MFs	-74.11 eV	-176.83 eV	-252.01 eV	-1.07 eV
MFs	-74.11 eV	-176.84 eV	-252.07 eV	-1.12 eV

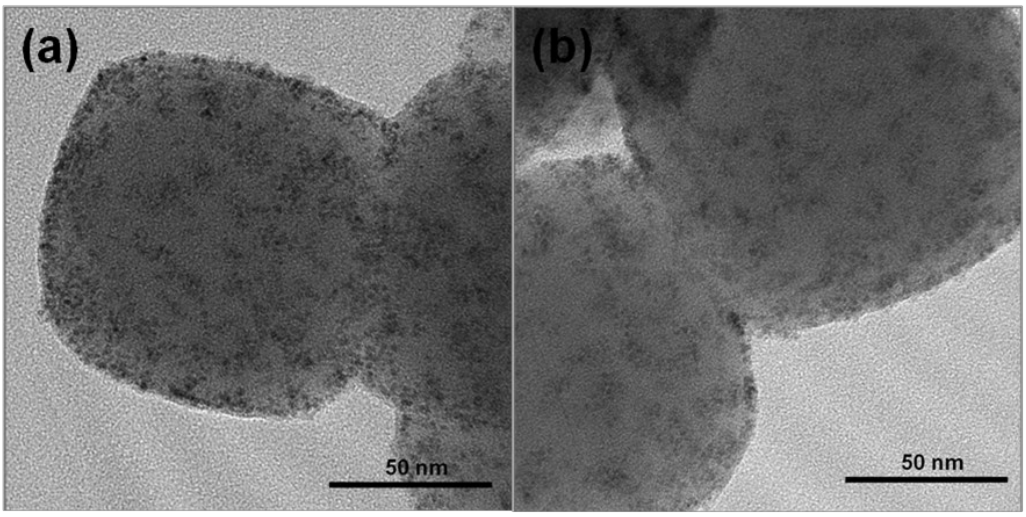

Figure S1. (a, b) HRTEM image of $Pd@Co_3[Co(CN)_6]_2$ nanoparticles. From it 100 Pd particles are randomly selected and measure their sizes, and its corresponding cumulative grain size distribution is obtained.

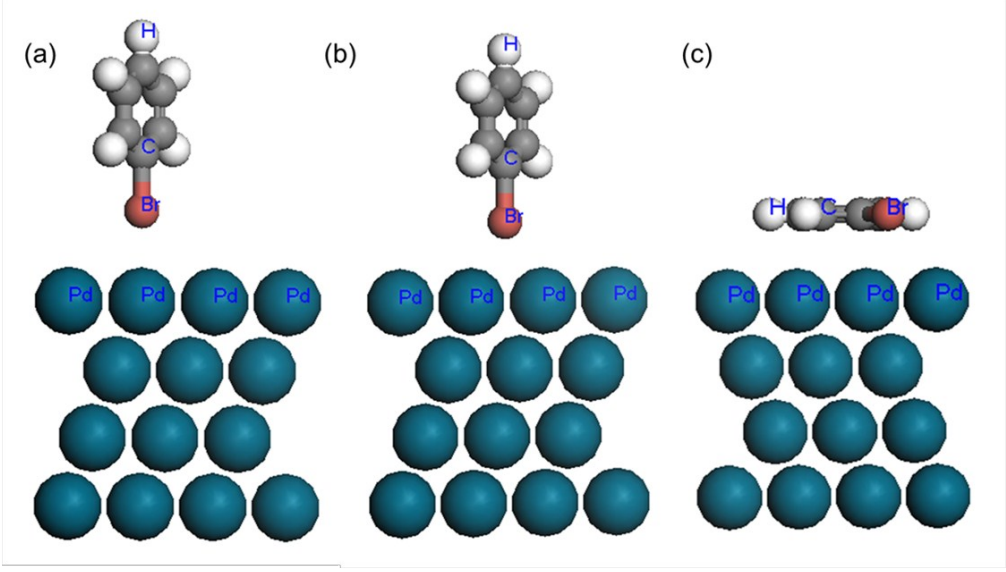

Figure S2. (a) The top site; (b) bridge site; and (c) the parallel adsorption geometry of brobenzene molecule absorbed on Pd (111) for different adsorption configurations before geometry optimizations.

Removing $Co_3[Co(CN)_6]_2$ from $Pd@Co_3[Co(CN)_6]_2$ by acid treatment: Firstly, 3 mg $Pd@Co_3[Co(CN)_6]_2$ nanoparticles were treated with superfluous 6 mol/L hydrochloric acid (HCl) at 60 °C for 12 h to remove $Co_3[Co(CN)_6]_2$ support. The precipitate was further washed with deionized water four times, filtered and dried at 60 °C for 12 h to yield black powder (Pd particles). Then the black powder were added to 20 mL alcohol solution which contains the reactants for Suzuki cross-coupling reactions. The yield of diphenyl catalyzed by Pd particles at 30 °C with a 0.5T MF applied and without MF applied was measured at different times.

REFERENCES

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