

Supplementary Materials for

Molecular ligand modulation of palladium nanocatalysts for highly efficient and robust heterogeneous oxidation of cyclohexenone to phenol

Teng Xue, Zhaoyang Lin, Chin-Yi Chiu, Yongjia Li, Lingyan Ruan, Gongming Wang, Zipeng Zhao, Chain Lee, Xiangfeng Duan, Yu Huang

Published 6 January 2017, *Sci. Adv.* **3**, e1600615 (2017)
DOI: 10.1126/sciadv.1600615

This PDF file includes:

- fig. S1. FTIR spectrum of HB-Pd/C and HB.
- fig. S2. TEM image of large particle formation after homogeneous Pd(TFA)₂-catalyzed reaction.
- fig. S3. Hot filtration test of HB-Pd/C-catalyzed aerobic oxidation reaction.
- fig. S4. XPS spectra of CB-Pd/C before and after reaction in Pd 3d region.
- fig. S5. TEM morphology and size distribution of BB-Pd/C and catalytic behavior.

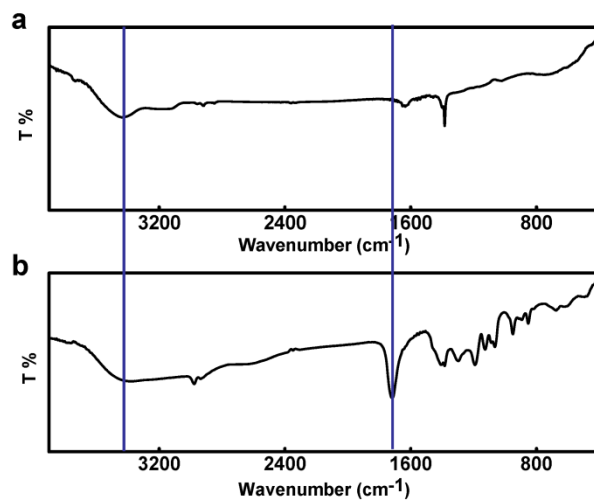


fig. S1. FTIR spectrum of HB-Pd/C and HB. FT-IR spectrum of (a). HB-Pd/C. (b). HB (hydroxyl butyric acid). Compared to HB, $\nu(\text{C}=\text{O})$ at around 1710 cm^{-1} disappeared and a new pair of peaks at around 1635 cm^{-1} showed up in the spectrum of HB-Pd, suggesting the carboxyl groups are the primary binding group to Pd particles. $\nu(-\text{OH})$ also slightly red shifted in HB-Pd, indicating the binding of hydroxyl to the Pd surface is very weak.

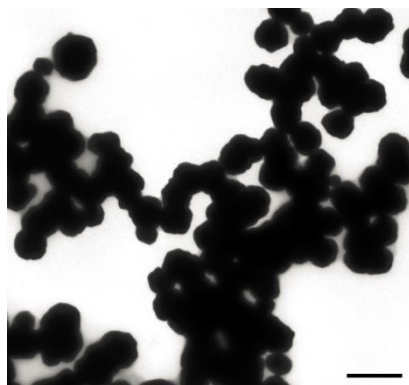


fig. S2. TEM image of large particle formation after homogeneous Pd(TFA)₂-catalyzed reaction. TEM image of large particle formation after homogeneous Pd(TFA)₂ catalyzed reaction. The scale bar is 500 nm.

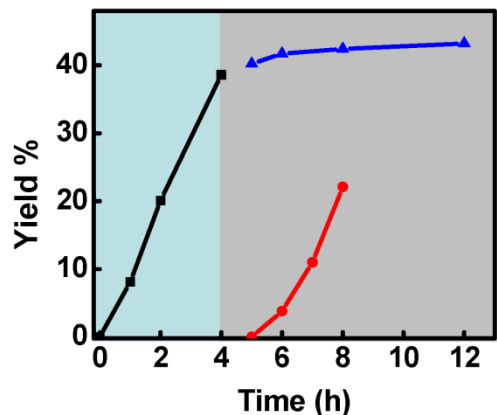


fig. S3. Hot filtration test of HB-Pd/C-catalyzed aerobic oxidation reaction. Hot filtration test of HB-Pd/C catalyzed aerobic oxidation reaction. HB-Pd/C catalyzed reaction was first allowed to run for 4 hours (black line), and then filtered at the reaction temperature (100 °C). The supernatant was gathered back into reaction container and continue reaction (blue line), while the filtered nanoparticles were re-dispersed into fresh DMSO solution with fresh substrate (red line). The results show that the supernatant exhibit nearly no reactivity, while the re-harvested catalysts could catalyze new reaction with nearly the same activity as the original reaction compared at the linear range. The filtration study clearly demonstrates that the reaction is dominated by heterogeneous HB-Pd/C, not homogeneous Pd species that leached into reaction solution.

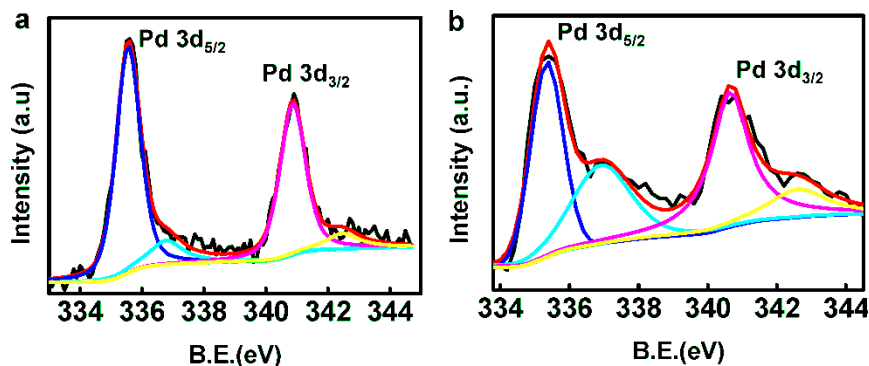


fig. S4. XPS spectra of CB-Pd/C before and after reaction in Pd 3d region. XPS spectra of CB-Pd/C before and after reaction in Pd 3d region. (a) as synthesized, (b) re-harvested after catalytic reaction. Blue lines and pink lines are the simulated results for Pd(0) for Pd 3d_{5/2} and Pd 3d_{3/2}. Green lines and yellow lines are the simulated results for Pd(II) for Pd 3d_{5/2} and Pd 3d_{3/2}. The peak intensities of Pd(II) are much higher after reaction than before reaction.

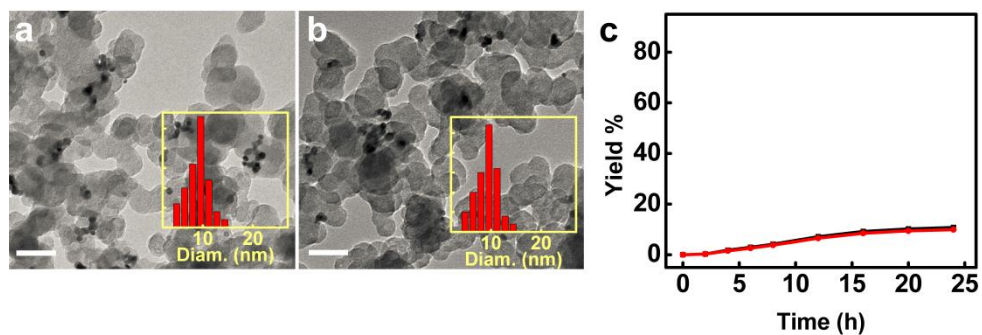


fig. S5. TEM morphology and size distribution of BB-Pd/C and catalytic behavior. TEM morphology and size distribution of BB-Pd/C and catalytic behaviour. (a) TEM morphology and size distribution of the as synthesized BB-Pd/C, (b) TEM morphology and size distribution of BB-Pd/C re-harvested after catalytic reaction. (c) Time dependant reaction profiles of 3-methylcyclohexenone dehydrogenative oxidation. The black red lines represent the reaction profiles catalysed by the fresh and re-harvested catalysts.