

Supplementary Information

for

**Following the temperature-induced activation of carbon-supported
trigonal Pd₃ nanoclusters for catalysis**

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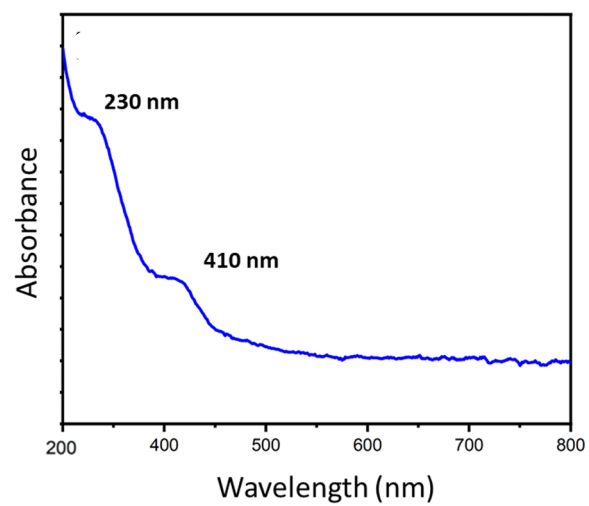


Fig S1. UV-Visible spectra of Pd₃ NCs in ethanol after a week.

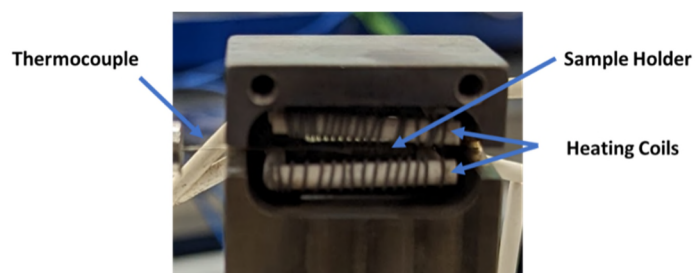


Fig S2. High-temperature furnace setup used for *in-situ* dPDF studies.

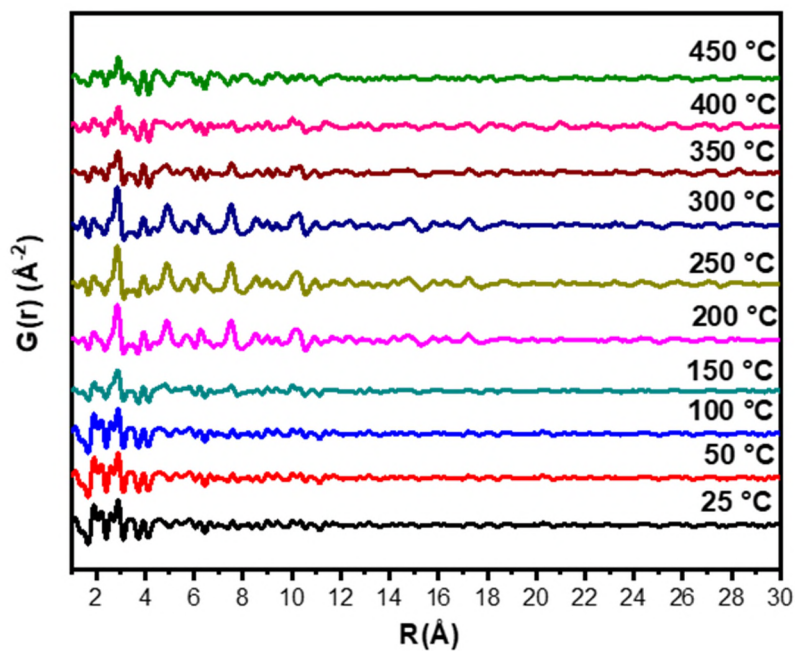


Fig S3. Long distance dPDF plots, $G(r)$ of $\text{Pd}_3@C$ upon *in-situ* heating.

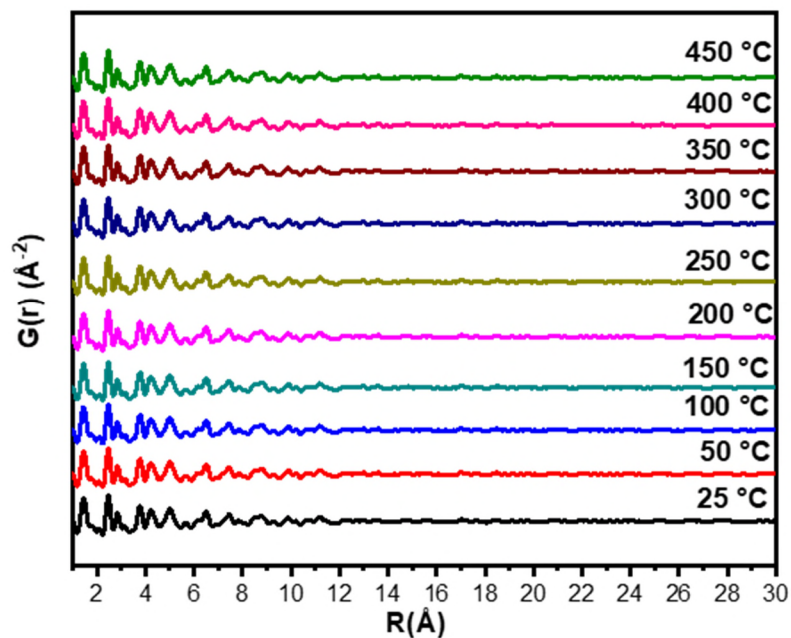


Fig S4. PDF plots, $G(r)$ of carbon support upon *in-situ* heating.

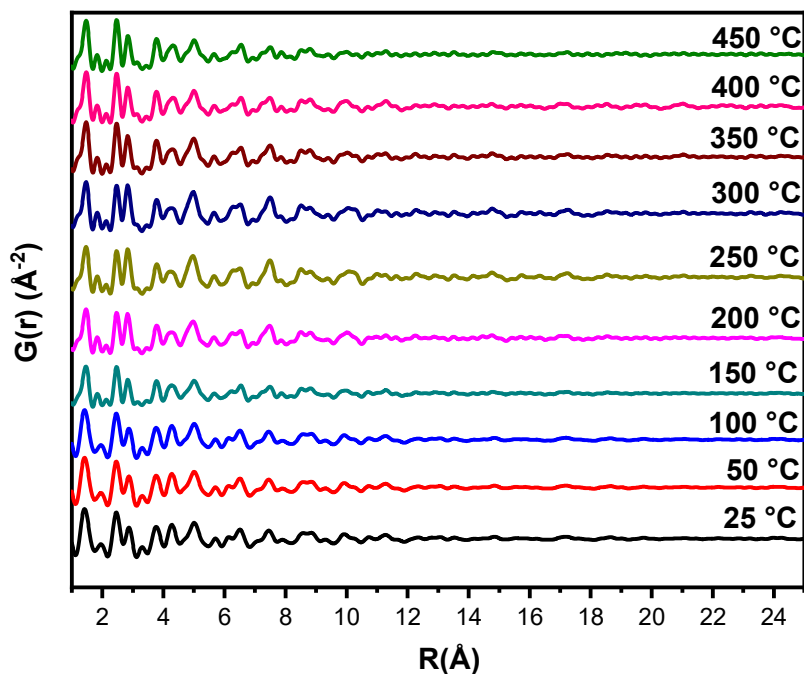


Fig S5. PDF plots, $G(r)$ of Pd₃@C upon in-situ heating.

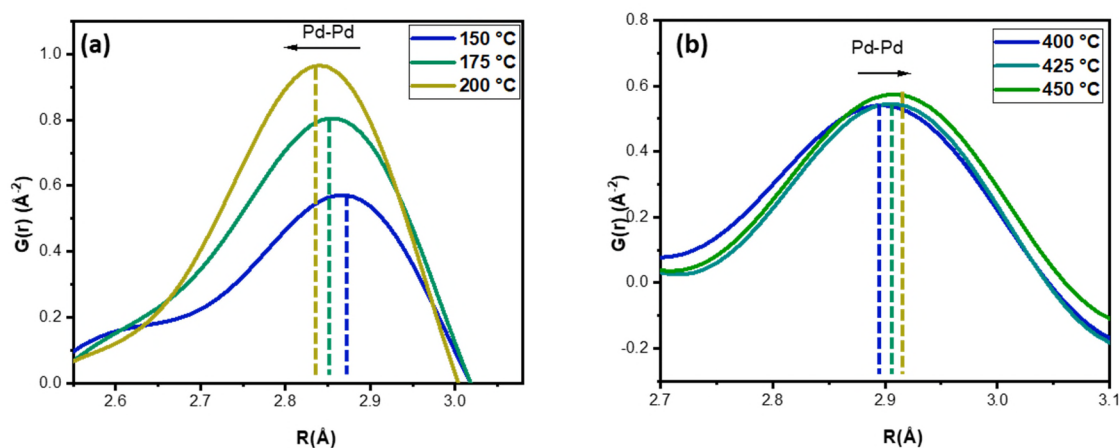


Fig S6. Overlay of in-situ dPDFs, $G(r)$ of Pd₃@C collected at different temperatures: (a) to visualize the decrease in Pd-Pd bond length upon in-situ heating at 150-250 °C; (b) to visualize the increase in the Pd-Pd bond length and the intensity of Pd-Pd peak during transition of temperature from 400 to 450 °C.

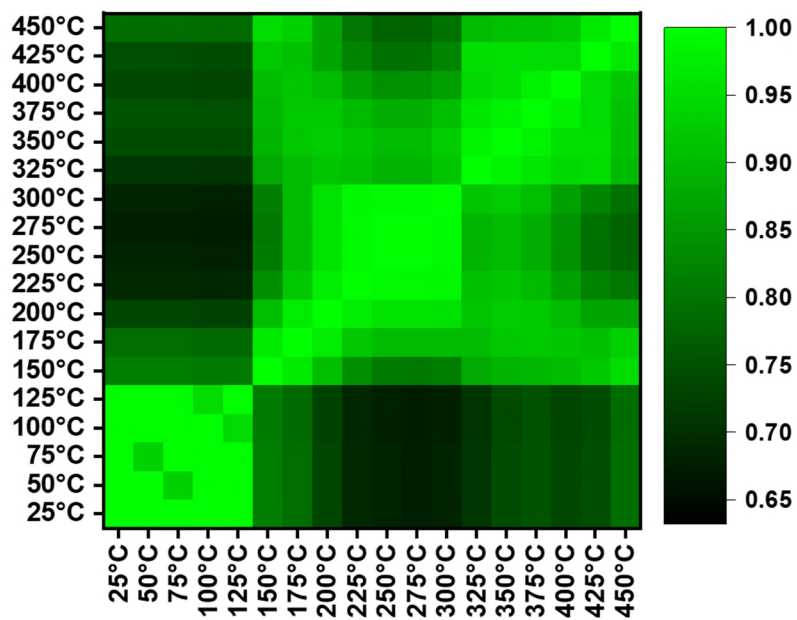


Fig S7. Heatmap of the Pearson correlation matrix analysis of the dPDF G(r) a R range 1.5-25 Å of Pd₃@C system upon in-situ heating.

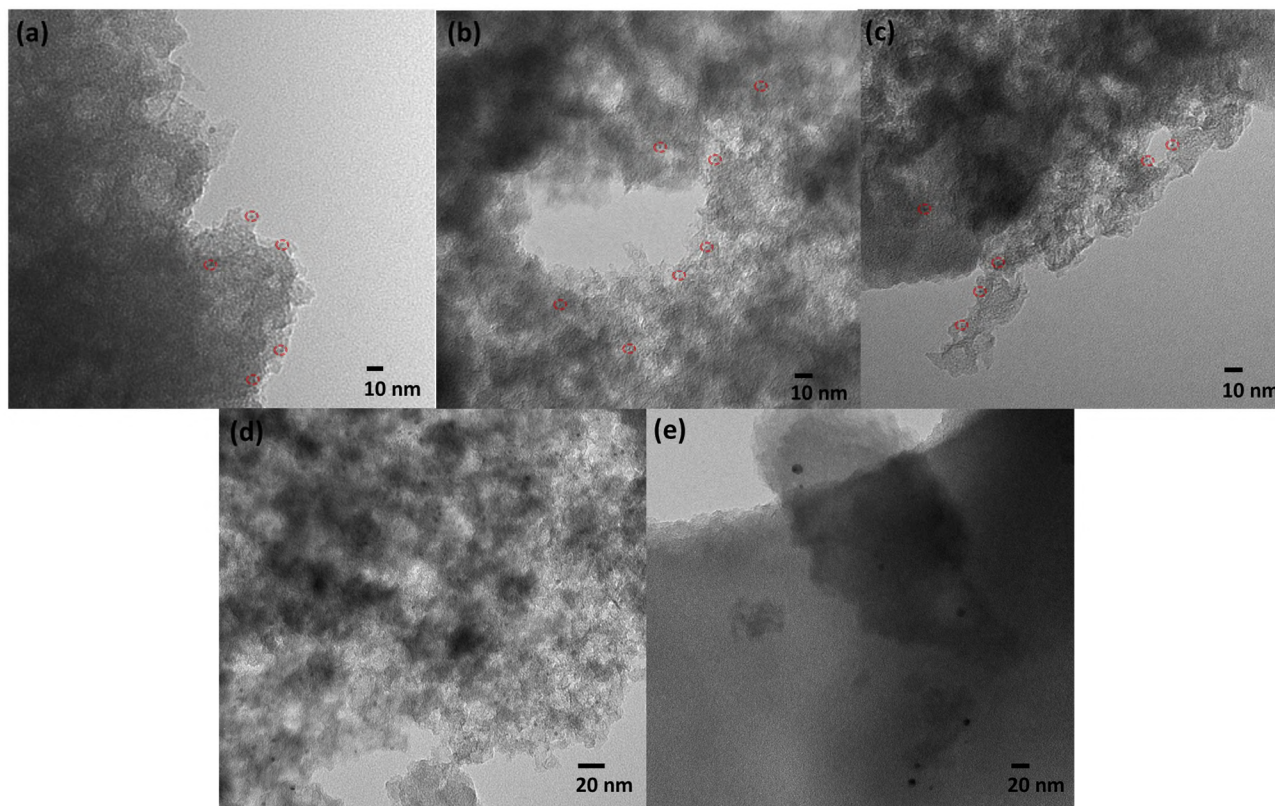


Fig S8. TEM images of: (a) $Pd_3@C$; (b) $Pd_3@C-150$; (c) $Pd_3@C-200$; (d) $Pd_3@C-250$; (e) $Pd_3@C-350$. Red circles are drawn in (a), (b), and (c) around some of the Pd NCs for ease in visibility.

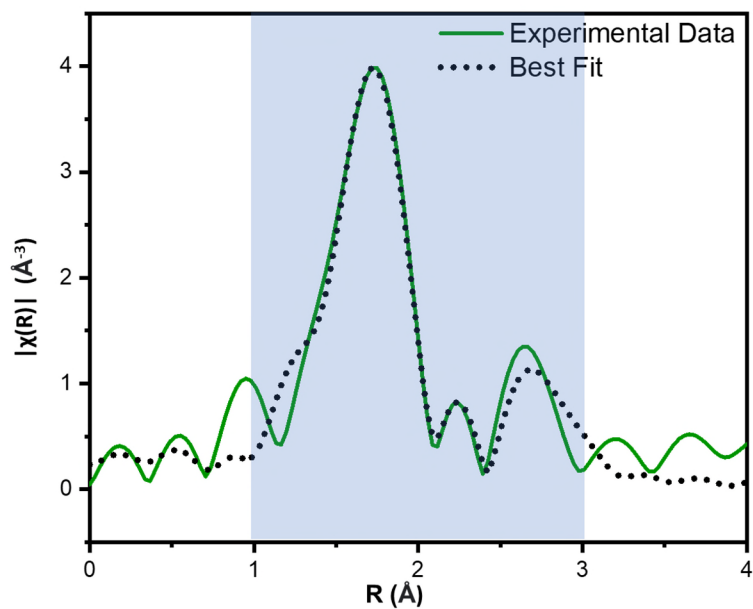


Fig S9. Experimental data of the Fourier transformed EXAFS and calculated theoretical best fit for Pd₃@C. The shaded region represents the fitting region.

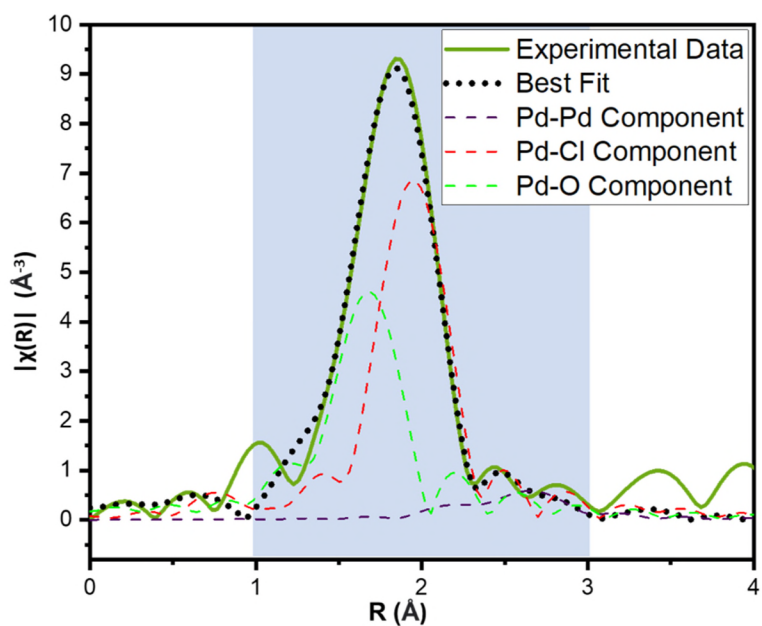


Fig S10. Experimental data of the Fourier transformed EXAFS and calculated theoretical best fit for Pd₃@C-150. The shaded region represents the fitting region.

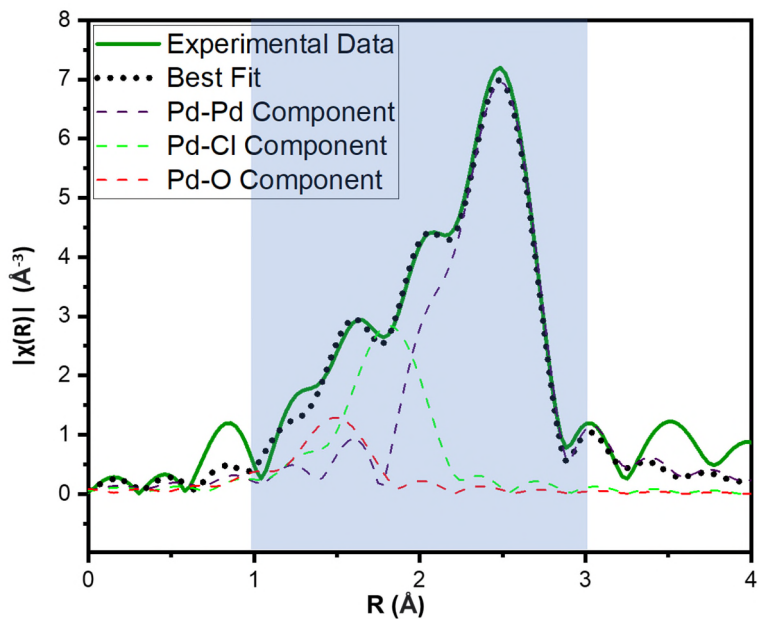


Fig S11. Experimental data of the Fourier transformed EXAFS and calculated theoretical best fit for Pd₃@C-200. The shaded region represents the fitting region.

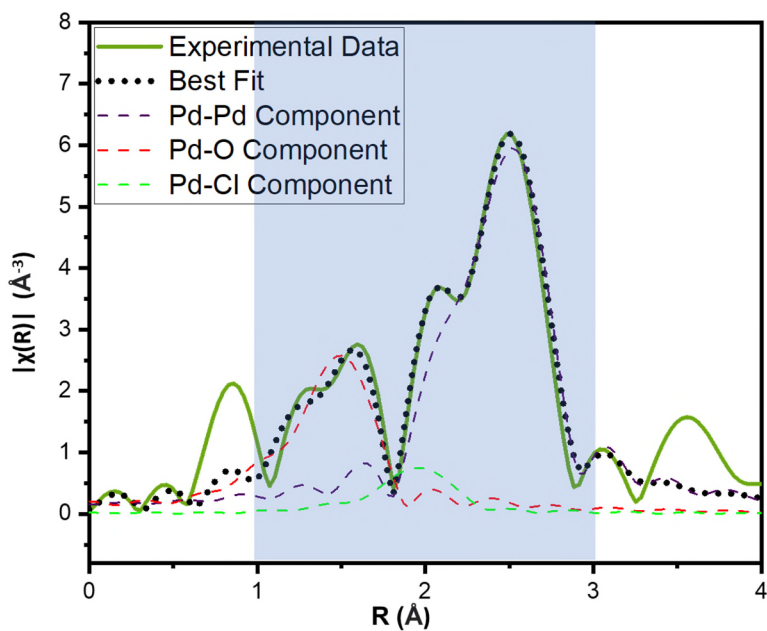


Fig S12. Experimental data of the Fourier transformed EXAFS and calculated theoretical best fit for Pd₃@C-250. The shaded region represents the fitting region.

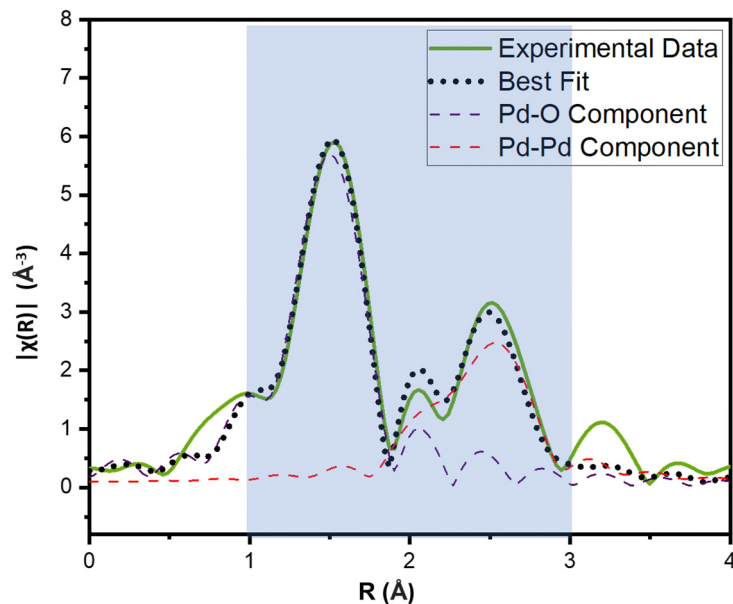


Fig S13. Experimental data of the Fourier transformed EXAFS and calculated theoretical best fit for Pd₃@C-350. The shaded region represents the fitting region.

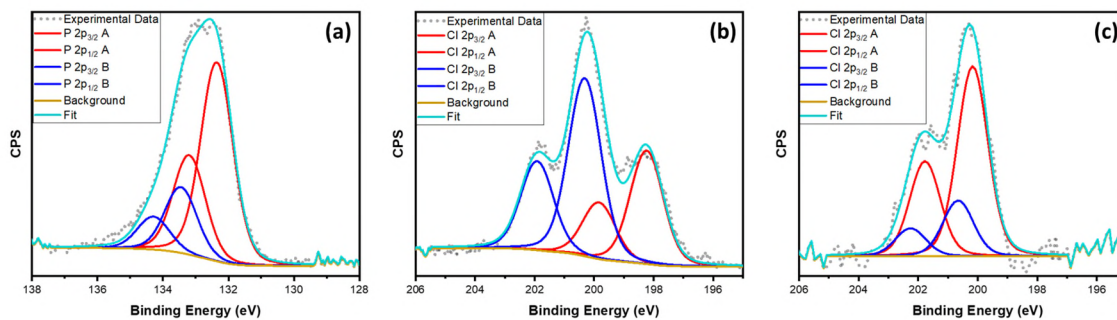


Fig S14. (a) XPS P 2p spectra of Pd₃@C, (b) XPS Cl 2p spectra of Pd₃@C, and (c) XPS Cl 2p spectra of Pd₃@C-150; A and B represents two different atoms in distinct electronic environments.

S1. Validation of Leaching

To show the quenching in the leaching of Pd clusters after activation, we have performed a hot filtration test on the cross-coupling reaction between 4-bromophenol and phenylboronic acid.¹ In this test, two cross-coupling reactions using Pd₃@C and Pd₃@C-150 as catalysts were carried out. For the test, 1 mmol of 4-bromophenol, 1.5 mmol of phenyl boronic acid, and 2 mmol of K₂CO₃ were dissolved in 5 mL of 4:1 DMF:H₂O mixture. Thereafter, 50 mg of the catalysts were added to the reaction mixture followed by refluxing. After 3 hours from the start of the catalytic reaction, some of the reaction mixture was filtered using a 0.2 μm PTFE syringe filter, and the filtrate was further refluxed in a new flask for 3 more hours. Thereafter, the NMR of the reaction mixture was taken before filtration and 3 hours after filtration. The results of hot filtration tests are shown below in Table S1.

Table S1. Summarization of hot filtration test Results for the cross-coupling between 4-bromophenol and phenylboronic acid.

Catalyst	Conversion Before Filtration (At 3 hours)	Conversion After Filtration (At 6 hours)
Pd ₃ @C	47.9%	92.5%
Pd ₃ @C-150	52.6%	58.2%

This test shows that in the case of Pd₃@C, the catalytic process did not stop even after filtration. However, in the case of Pd₃@C-150, the catalytic process slowed down significantly. This implies that in the case of Pd₃@C, the Pd clusters are soluble inside the reaction mixture (homogeneous mixture) due to the leaching from the carbon support. As the strong metal-support interaction between Pd and carbon is stronger in the case of Pd₃@C-150, the majority of the Pd clusters were present on the surface of carbon and acting as heterogeneous catalysts. The small increase in the conversion in the case of Pd₃@C-150 after filtration may be due to the leaching of Pd(II) ions due to oxidative addition of 4-bromophenol to the Pd clusters.

Reference:

1. G.K. Rao, A. Kumar, B. Kumar, D. Kumar and A.K. Singh, *Dalt. Trans.*, **2012**, *41*, 1931–1937.