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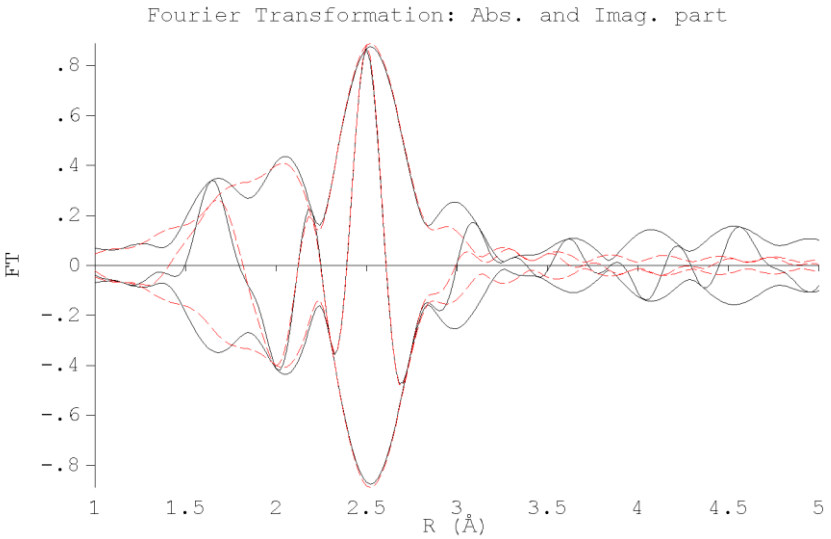
Supporting information

In order to detect the presence of Pd-C shell, the Fourier transform spectra were first fitted at a full range at R= 1.0 – 5.0 Å, with and without the Pd-C shell. After that the fitting range was decreased to R= 1.5 –2.3 Å where the contribution of the Pd-C shell manifests itself. At this range the contribution of the Pd-Pd shell(s) was fixed and only the parameters of the Pd-C shell optimized. A further improvement in the fit quality occurred. Due to the different R-ranges used during fitting, the improvement in the fitting cannot be judged by comparing the goodness of fit. The Pd-C shell is always detected in the presence of 1-pentyne, in presence and absence of hydrogen. The Pd-C contribution in the Pd/SiO_2 -10.5 is very small relative to the Pd-Pd contribution and the parameters have large error.

(a)

(b)



(c)

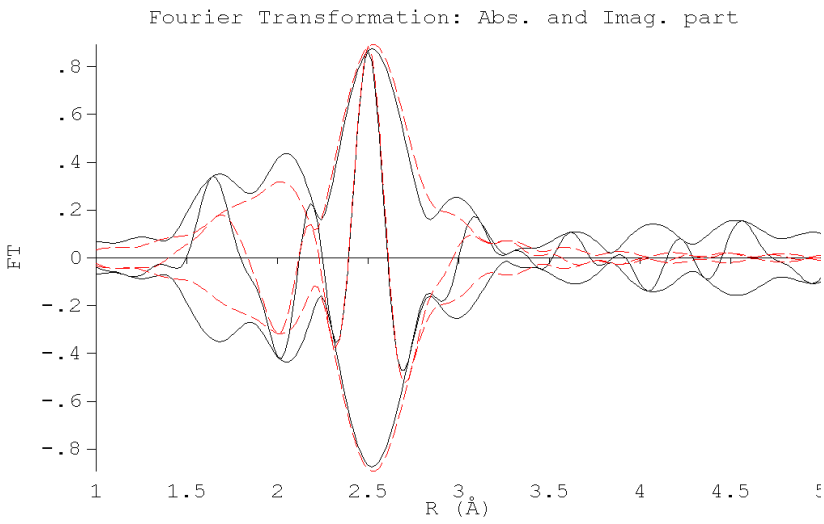


Figure S1. The fitting of Pd K edge spectra of Pd/SiO_2 -2.8 at 40°C in 1-pentyne (a) with the Pd-C shell at long fitting range (b) with the Pd-C shell at short fitting range and (c) without the Pd-C shell.

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Table S1. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2 -2.8 at, 40°C in 1-pentyne with and without the Pd-C shell.

	Scat. pair	CN	R (Å)	DWF (10^{-3}Å^2)	ΔE_0 (eV)
With Pd-C shell	Pd	8.0	2.76	4.5	4.2
	C(Long range fit)	1.3	2.23	11.7	-5.0
	C(Short range fit)	1.6	2.16	9.7	0.9
Without Pd-C shell	Pd	8.6	2.76	4.5	4.5

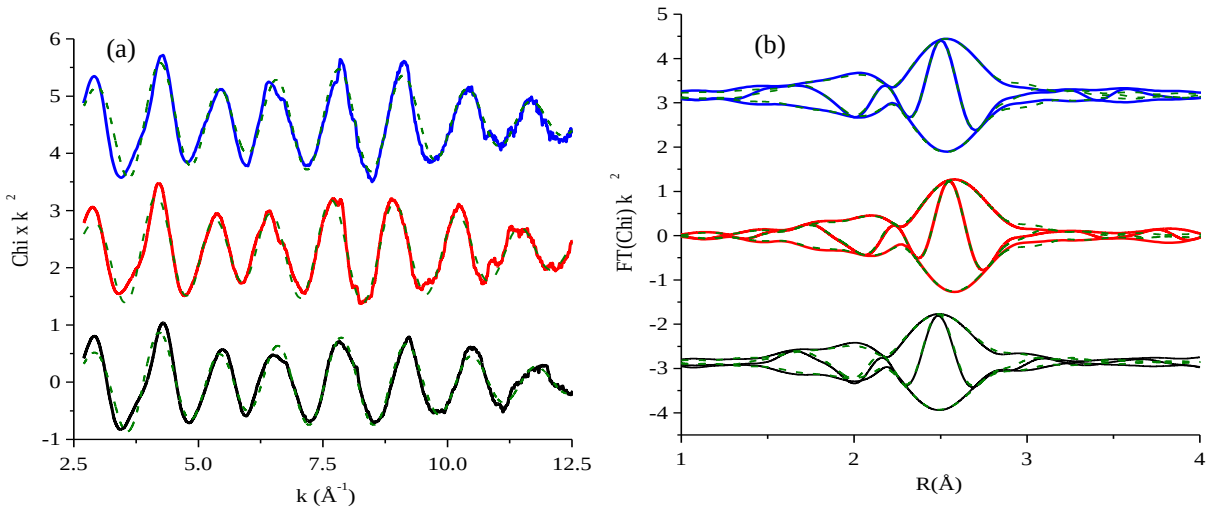
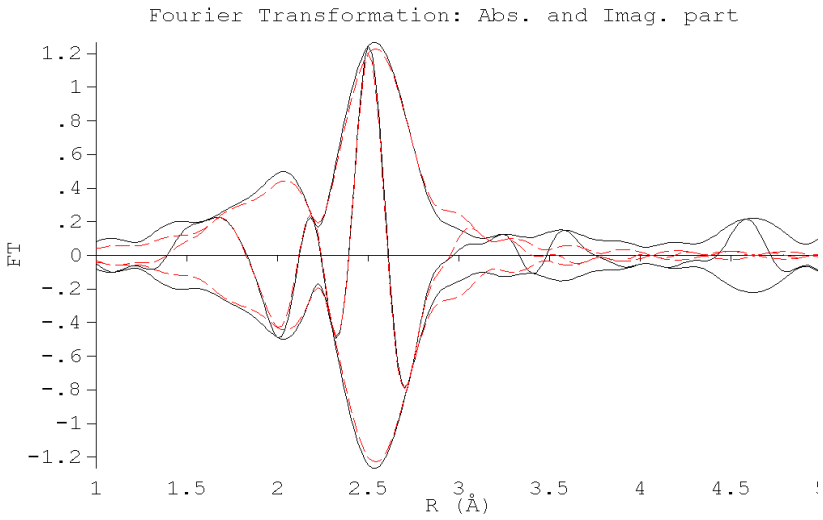


Figure S2. Pd K edge XANES of Pd/SiO_2-10.5 at 150 °C in H_2 (black), 40 °C in H_2 (red), and in 1-pentyne (blue). (a) Chi-functions and (b) the fitted Fourier transforms. The fitting is shown as green dashed lines.

(a)



(b)

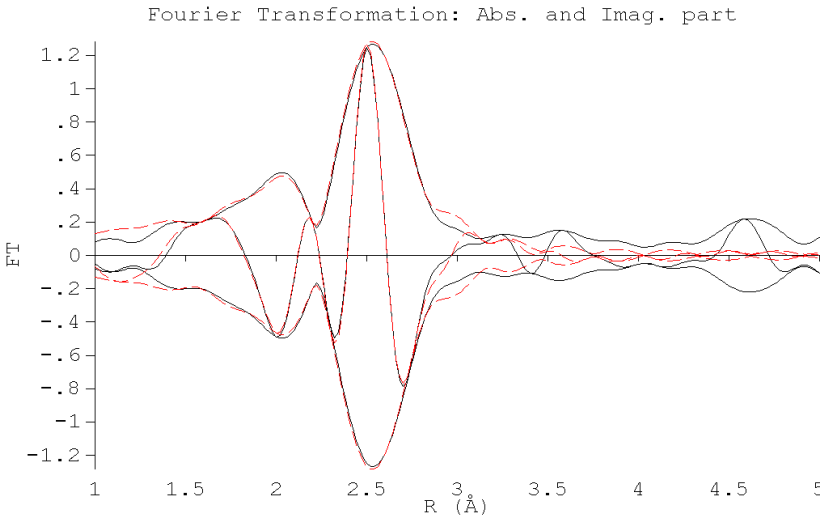


Figure S3. The fitting of Pd K edge spectra of Pd/SiO_2-10.5 at 40°C in 1-pentyne (a) without the Pd-C shell, and (b) with the Pd-C shell using the shorter fitting range in R-space.

Table S2. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2-10.5 at 40°C in 1-pentyne, with and without the Pd-C shell.

	Scat. pair	CN	R (Å)	DWF (10^{-3}Å^2)	ΔE_0 (eV)
Without Pd-C shell	Pd	11.6	2.77	4.0	4.0
With Pd-C shell	Pd	11.6	2.77	4.0	4.0
	C	2.1	1.94	21.4	11.5

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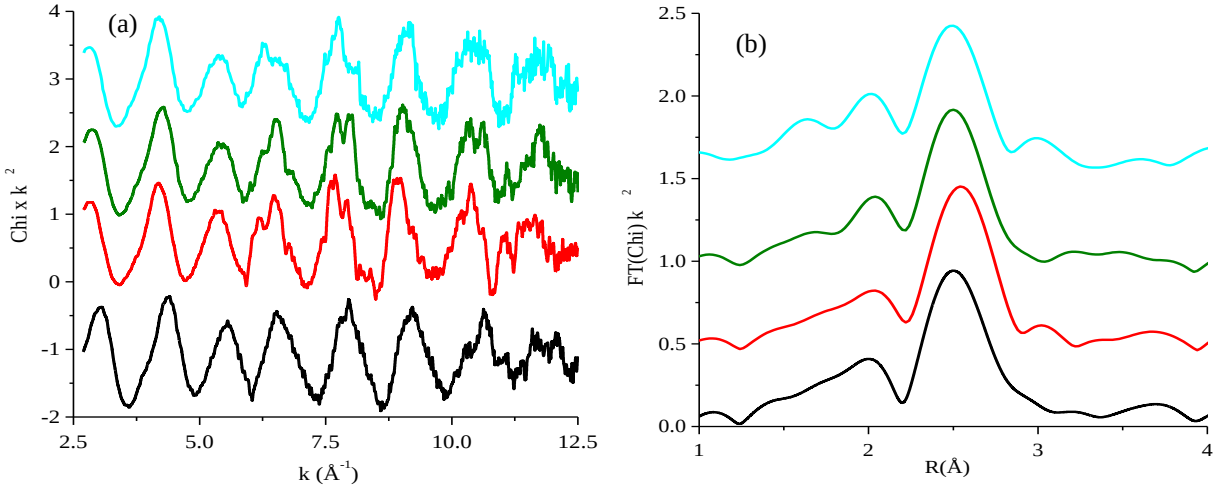
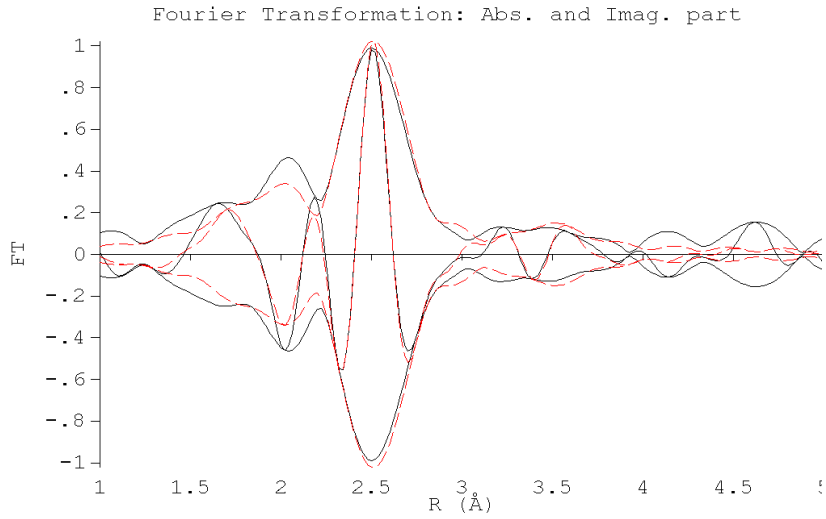


Figure S4. Pd K edge XANES of Pd/SiO_2-2.8 at 150 °C in H_2 (black), 40 °C in H_2 (red), during reaction at 40 °C at a gas flow of 24.5 (green) and 57.1 mL/min (cyan). (a) Chi-functions and (b) Fourier transforms.

(a)



(b)

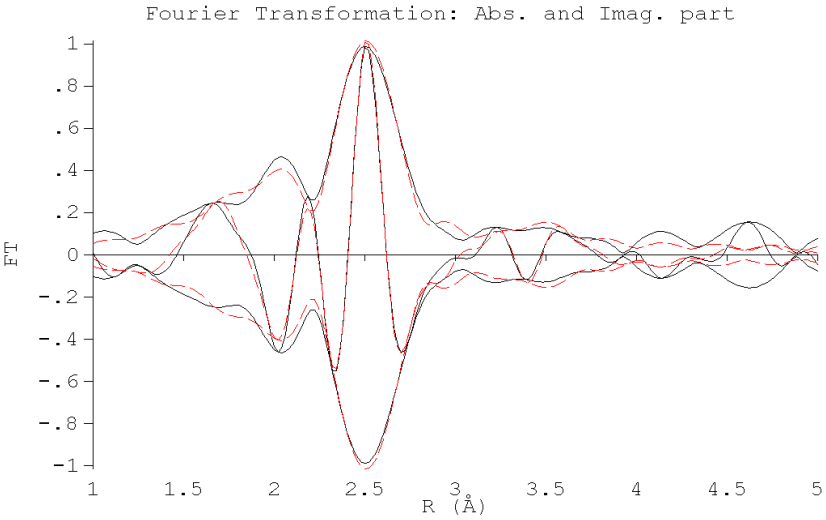


Figure S5. The fitting of Pd K edge spectra of Pd/SiO_2 -2.8 during reactions at 40 ^oC (flow =24.5 mL/min), without the Pd-C shell, and (b) with the Pd-C shell using the shorter fitting range in R-space.

Table S3. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2 -2.8 during reactions at 40 ^oC (flow =24.5 mL/min), with and without the Pd-C shell.

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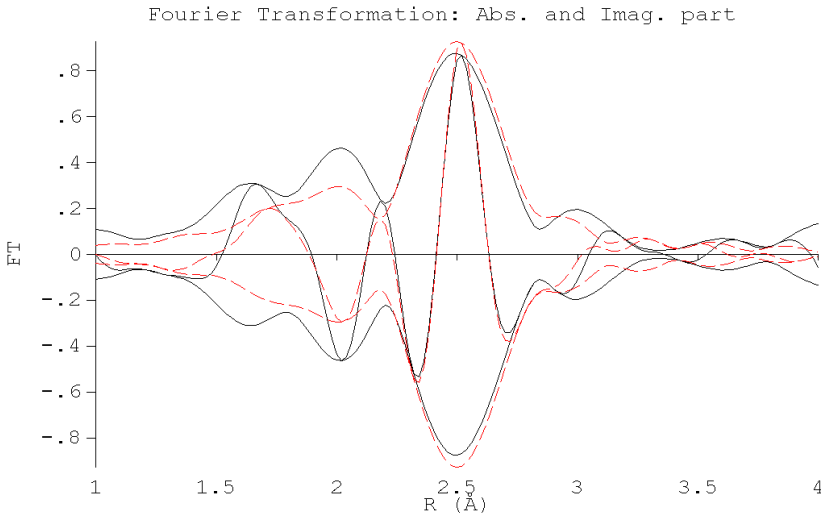
	Scat. pair	CN	R (Å)	DWF ($10^{-3}Å^2$)	ΔE_0 (eV)
Without Pd-C shell	Pd	7.7	2.76	2.6	6.9
	Pd	5.7	3.76	6.4	14.3
With Pd-C shell	Pd	7.7	2.76	2.6	6.9
	C	2.0	2.28	27.9	-8.6
	Pd	5.7	3.76	6.4	14.3

(a)



(b)

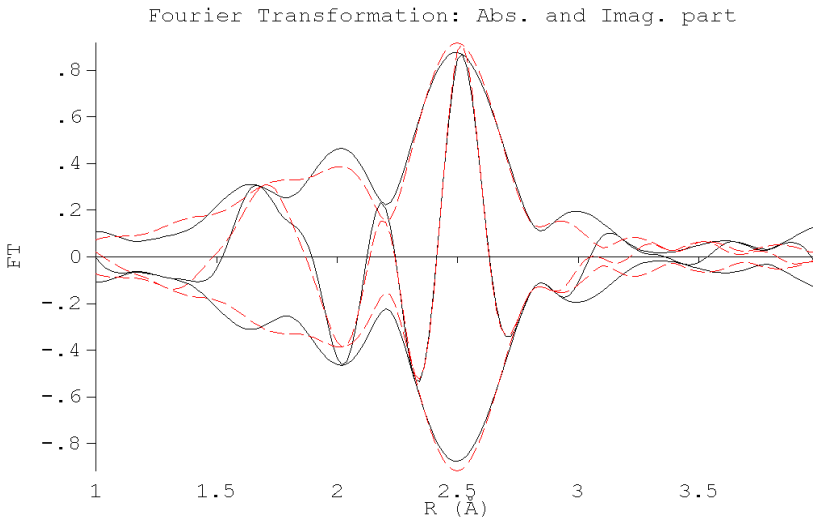


Figure S6. The fitting of Pd K edge spectra of Pd/SiO_2 -2.8 during reactions at 40 ^oC (flow =57.1 mL/min), (a) without the Pd-C shell, and (b) with the Pd-C shell using the shorter fitting range in R-space.

Table S4. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2 -2.8 at during reactions at 40 ^oC (flow = 57.1 mL/min) with and without the Pd-C shell.

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	Scat. pair	CN	R (Å)	DWF ($10^{-3}Å^2$)	ΔE_0 (eV)
Without Pd-C shell	Pd	6.6	2.76	2.4	7.7
With Pd-C shell	Pd	6.6	2.76	2.4	7.7
	C	2.2	2.28	16.4	-4.4

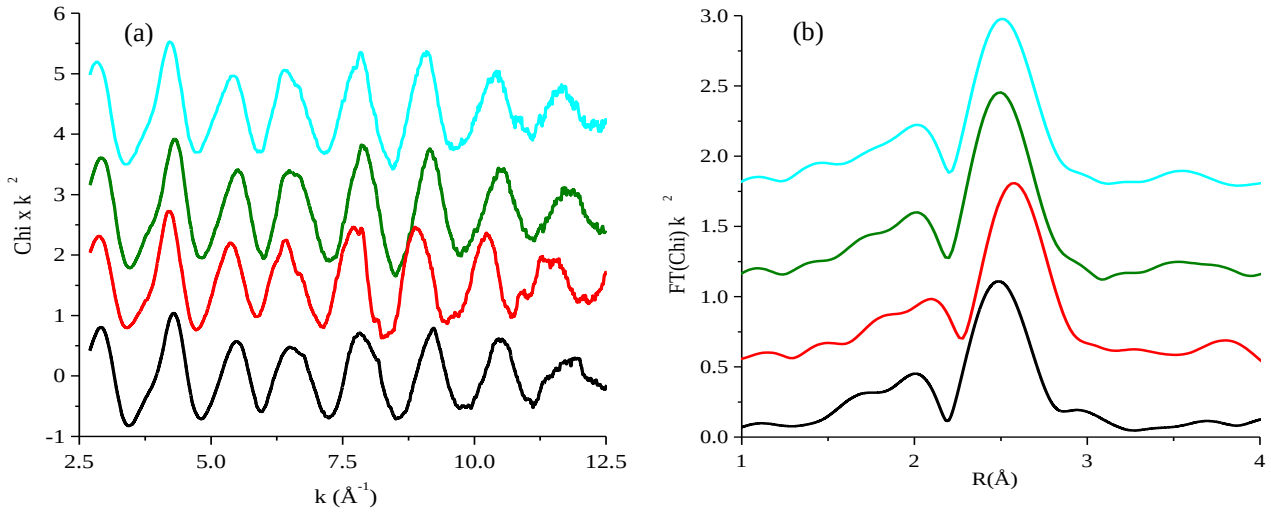

Figure S7. Pd K edge XANES of Pd/SiO_2-10.5 at 150 °C in H_2 (black), 40 °C in H_2 (red), during reaction at 40 °C at a gas flow of 24.5 (green) and 57.1 mL/min (cyan). (b) Chi-functions and (b) Fourier transforms.

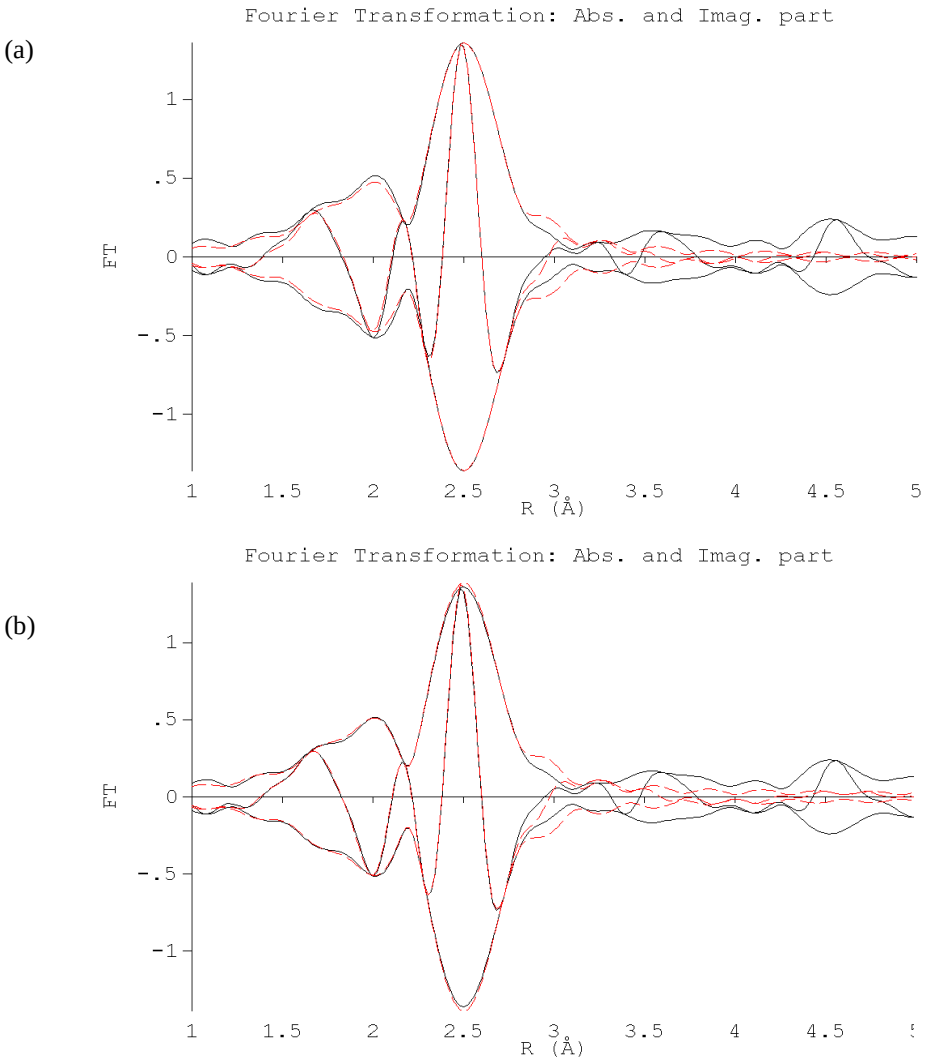

Figure S8. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2-10.5 during reactions at 40 ^oC (flow = 24.5 mL/min), (a) without the Pd-C shell, and (b) with the Pd-C shell using the shorter fitting range in R-space.

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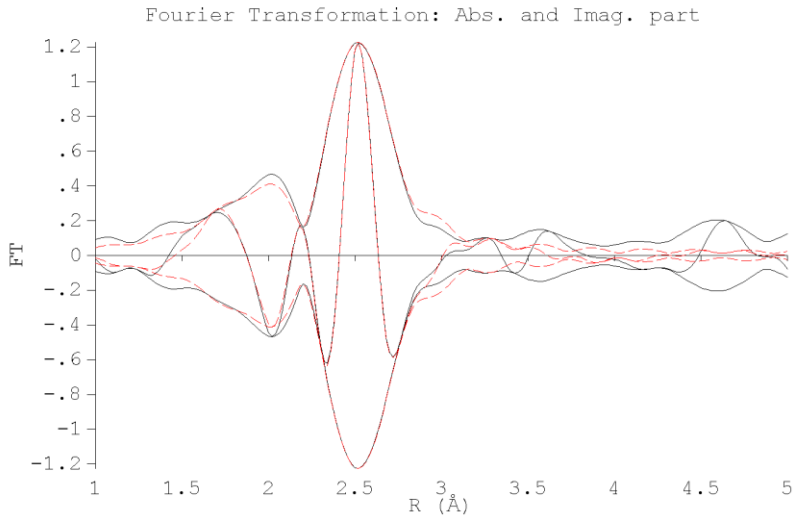
Table S5. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2-10.5 during reactions at 40 ^oC. (flow = 24.5 mL/min) with and without the Pd-C shell.

	Scat. pair	CN	R (Å)	DWF ($10^{-3}Å^2$)	ΔE_0 (eV)
Without Pd-C shell	Pd	12.0	2.75	3.8	5.4
With Pd-C shell	Pd	12.0	2.75	3.8	5.4
	C	1.2	2.33	55.1	-11.2

(a)



(b)

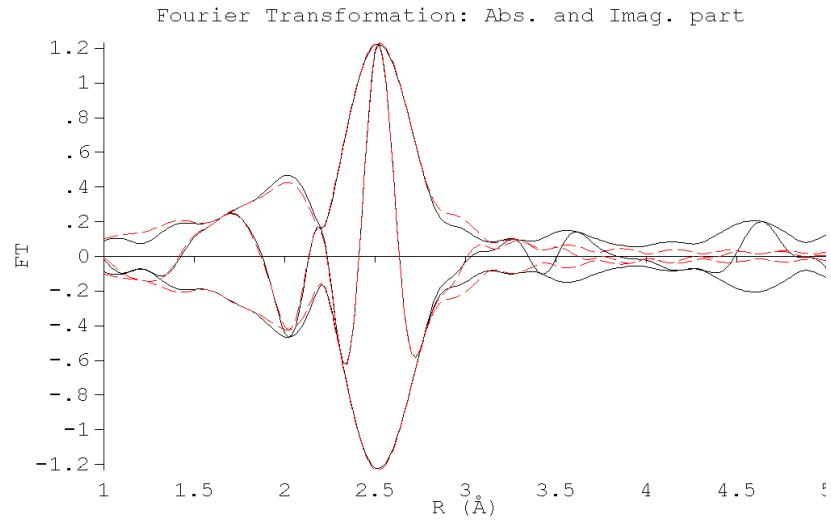


Table S9. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2-10.5 at during reactions at 40 ^oC (flow = 57.1 mL/min), (a) without the Pd-C shell, and (b) with the Pd-C shell using the shorter fitting range in R-space.

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Table S6. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2-10.5 during reactions at 40 ^oC. (flow = 57.1 mL/min) with and without the Pd-C shell.

	Scat. pair	CN	R (Å)	DWF ($10^{-3}Å^2$)	ΔE_0 (eV)
Without Pd-C shell	Pd	11.9	2.77	4.4	6.5
With Pd-C shell	Pd	11.9	2.77	4.4	6.5
	C	1.0	2.00	9.5	10.0

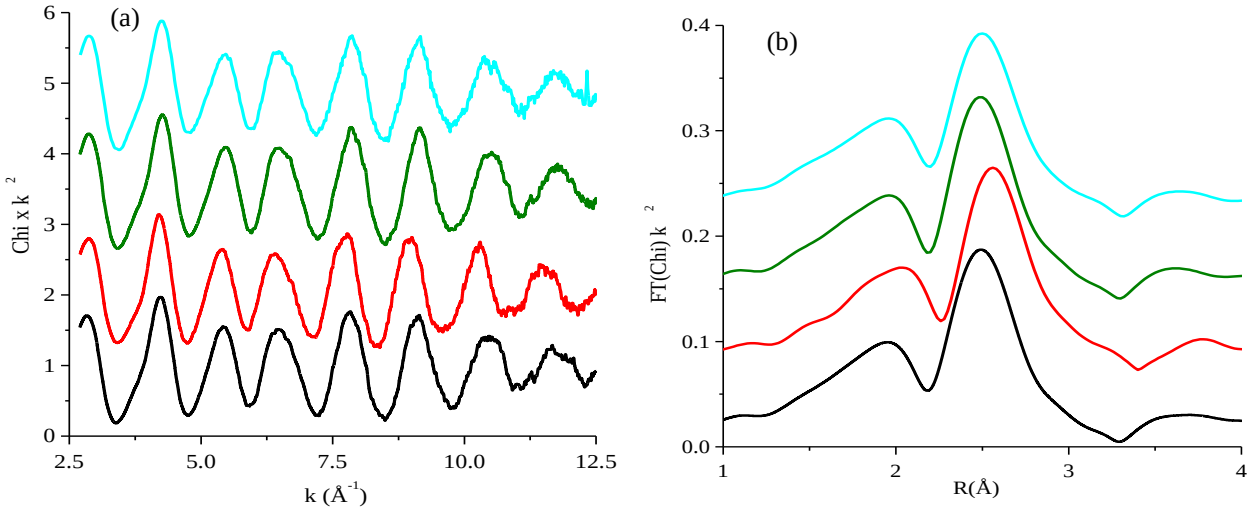
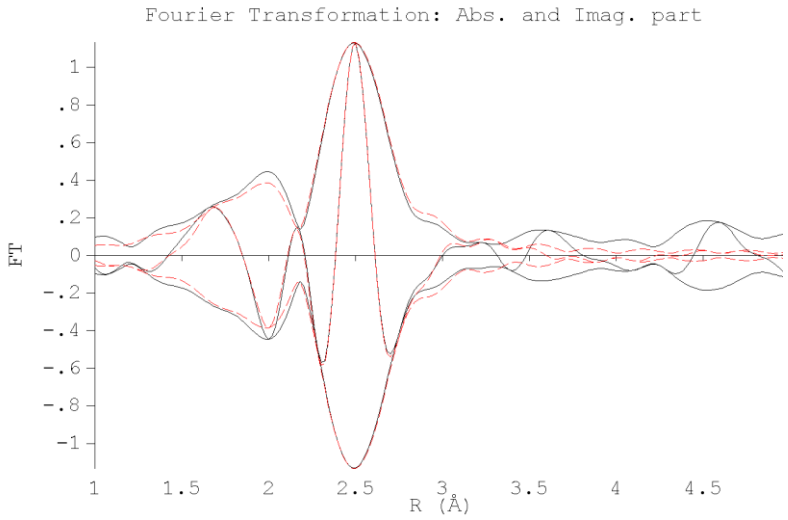


Figure S10. Pd K edge XANES of Pd/SiO_2-10.5 at 150 °C in H_2 (black), 100 °C in H_2 (red), during reaction at 100 °C at a gas flow of 24.5 (green) and 57.1 mL/min (cyan). (a) Chi-functions and (b) Fourier transforms

(a)



(b)

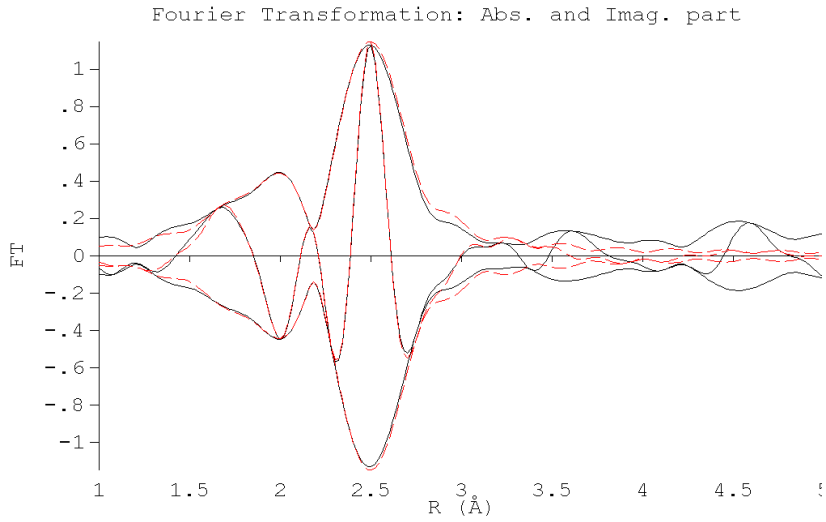
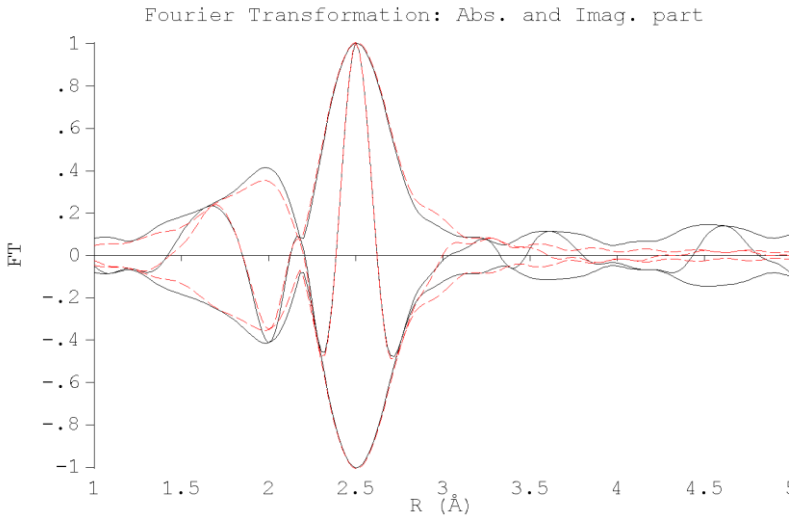


Table S11. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2 -10.5 during reactions at 100 ^oC. (flow = 24.5 mL/min), (a) without the Pd-C shell, and (b) with the Pd-C shell using the shorter fitting range in R-space.

Table S7. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2 -10.5 during reactions at 100 ^oC. (flow = 24.5 mL/min) with and without the Pd-C shell.

	Scat. pair	CN	R (Å)	DWF ($10^{-3}Å^2$)	ΔE_0 (eV)
Without Pd-C shell	Pd	11.0	2.74	4.7	6.6
With Pd-C shell	Pd	11.0	2.74	4.7	6.6
	C	0.3	2.41	1.9	-16.3

(a)



(b)

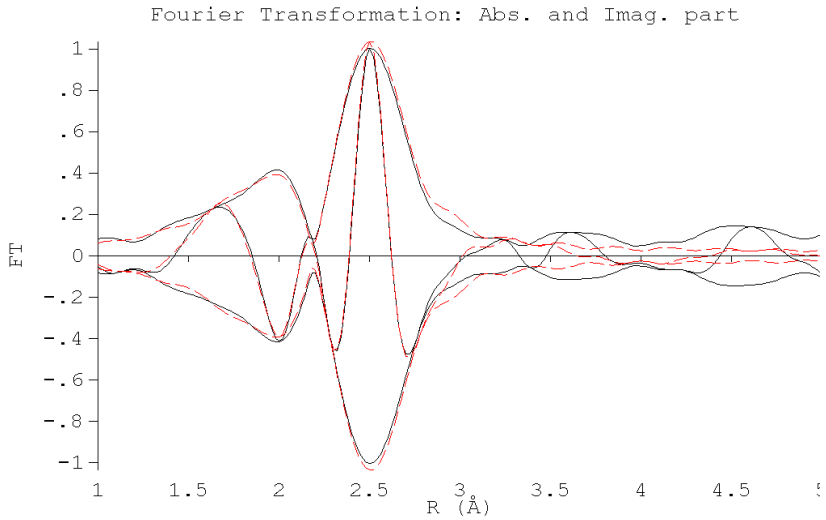


Table S12. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2 -10.5 at during reactions at 100 ^oC. (flow = 57.1 mL/min), (a) without the Pd-C shell, and (b) with the Pd-C shell using the shorter fitting range in R-space.

Table S8. EXAFS parameters of the Pd K edge spectra of Pd/SiO_2 -10.5 during reactions at 100 ^oC. (flow = 57.1 mL/min) with and without the Pd-C shell.

	Scat. pair	CN	R (Å)	DWF ($10^{-3}Å^2$)	ΔE_0 (eV)
Without Pd-C shell	Pd	11.2	2.75	5.8	6.5
With Pd-C shell	Pd	11.2	2.75	5.8	6.5
	C	1.3	2.20	46.1	-6.4

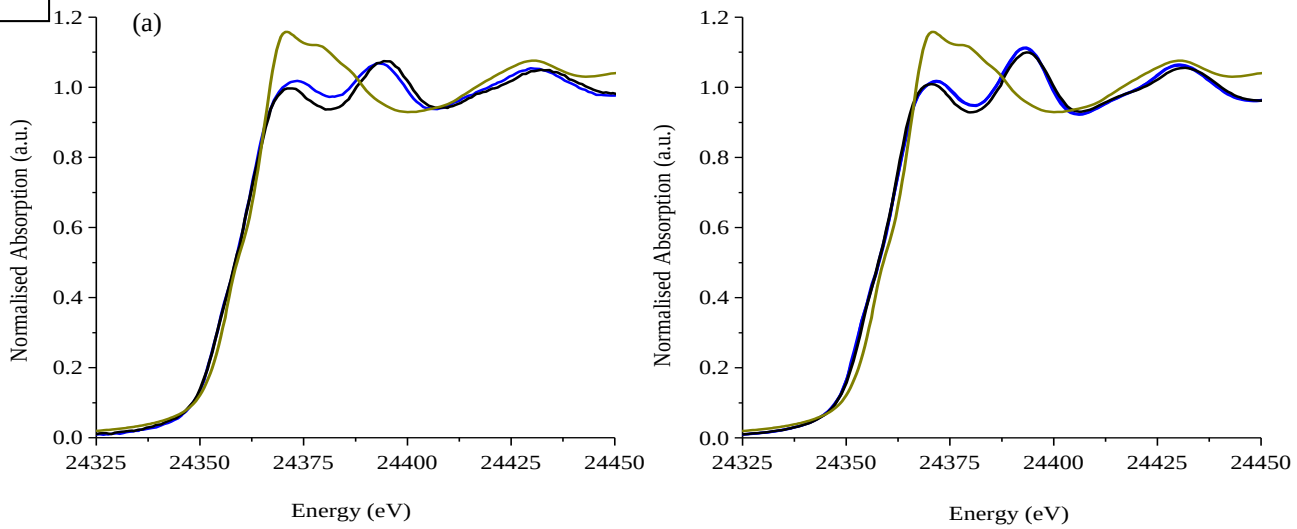


Figure S13. Comparison of the Pd K edge XANES spectra of palladium oxide (Dark yellow), as a reference compound, to that of the catalysts at 150 °C in H_2 (black), and at 40 °C in 1-pentyne (blue). (a) Pd/SiO_2-2.8 and (b) Pd/SiO_2-10.5.