Electronic supplementary information:

Towards the ALD Thin Film Stabilized Single-Atom Pd_1 Catalysts

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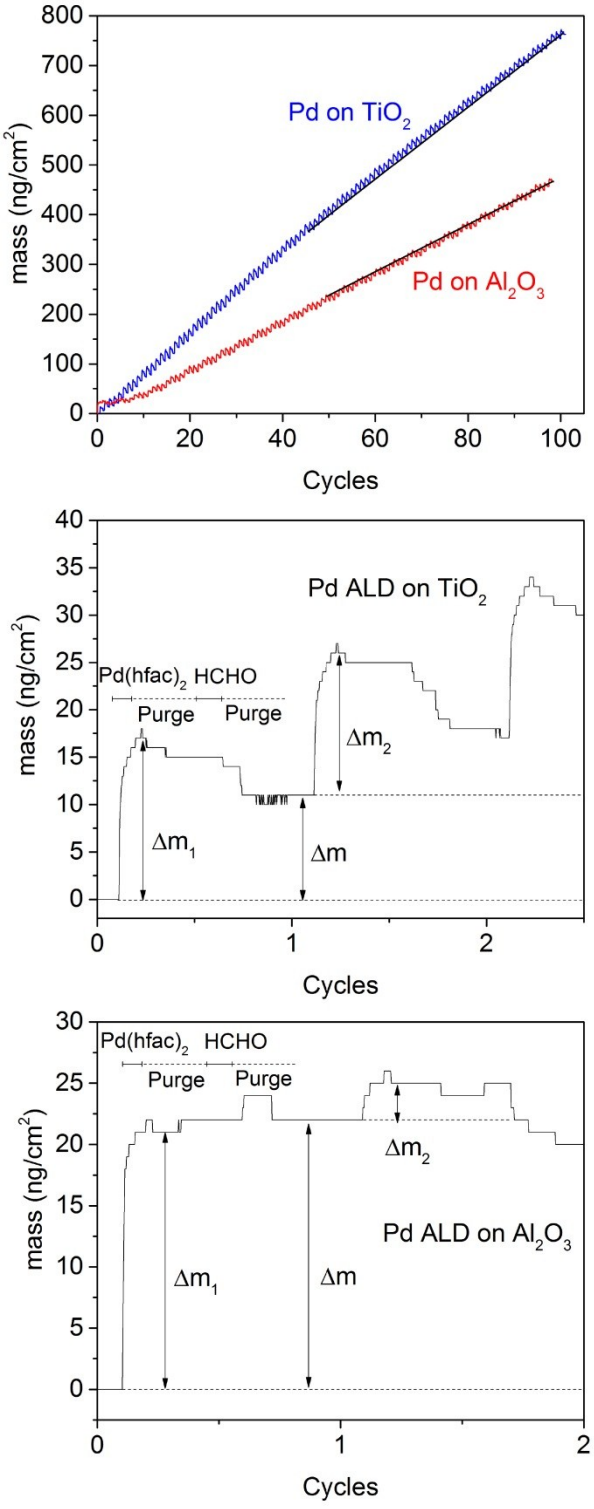

Figure S1. *In situ* QCM studies of Pd ALD using $Pd(hfac)_2$ and formalin as precursors at 200 °C. (a) 0-100 cycles, (b) first two cycles of Pd ALD on TiO_2, (c) first two cycles of Pd ALD on Al_2O_3.

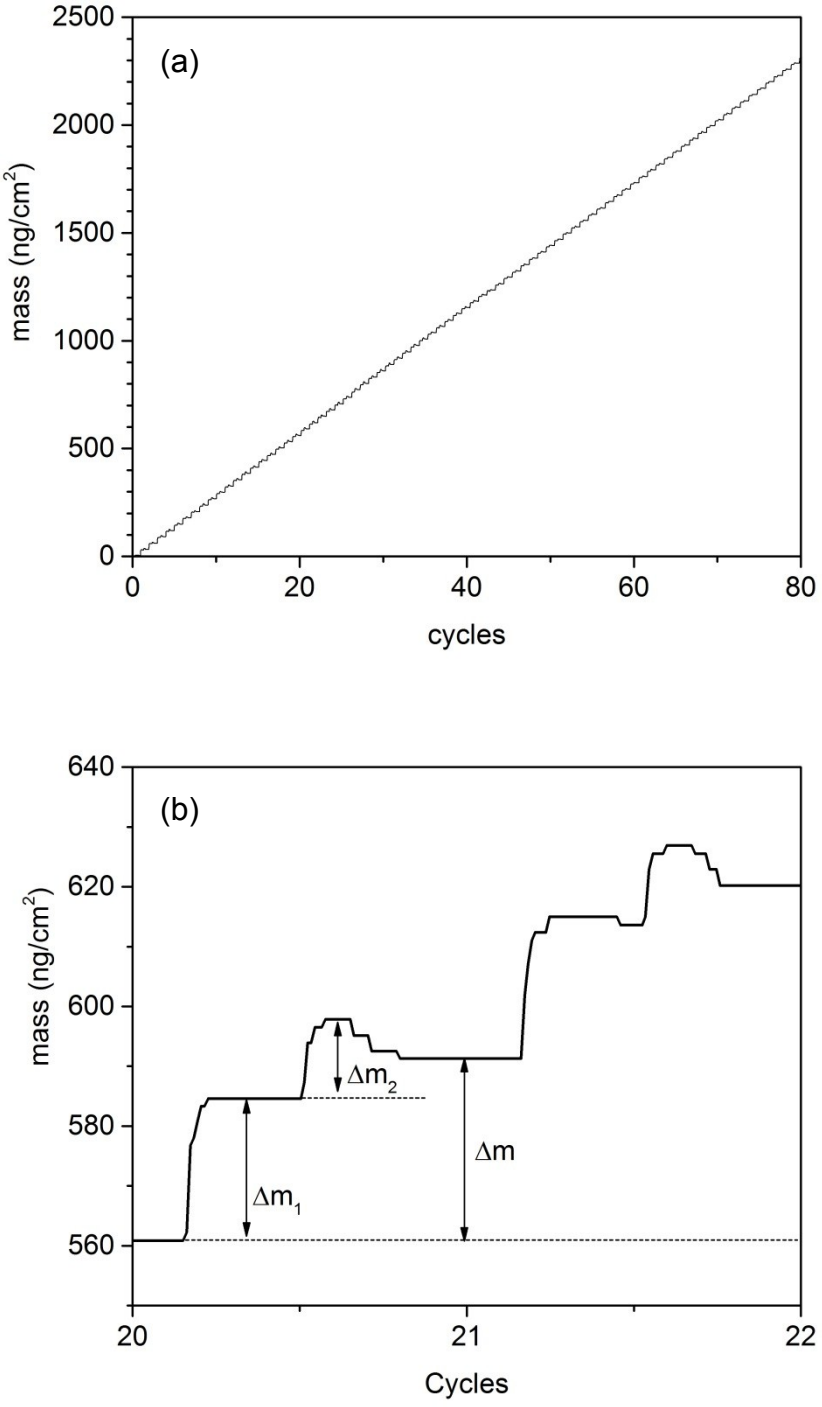

Figure S2. *In situ* QCM studies of TiO_2 ALD using $TiCl_4$ and H_2O as precursors at 100 °C. Δm_1 and Δm_2 represent the mass gain during $TiCl_4$ and H_2O exposure, respectively. The total mass gain Δm of a complete TiO_2 ALD cycle is ca. 0.3 μg/cm^2. As the TiO_2 density of 4.5 g/cm^3, the growth rate of TiO_2 is ca. 0.67 Å per ALD cycle.

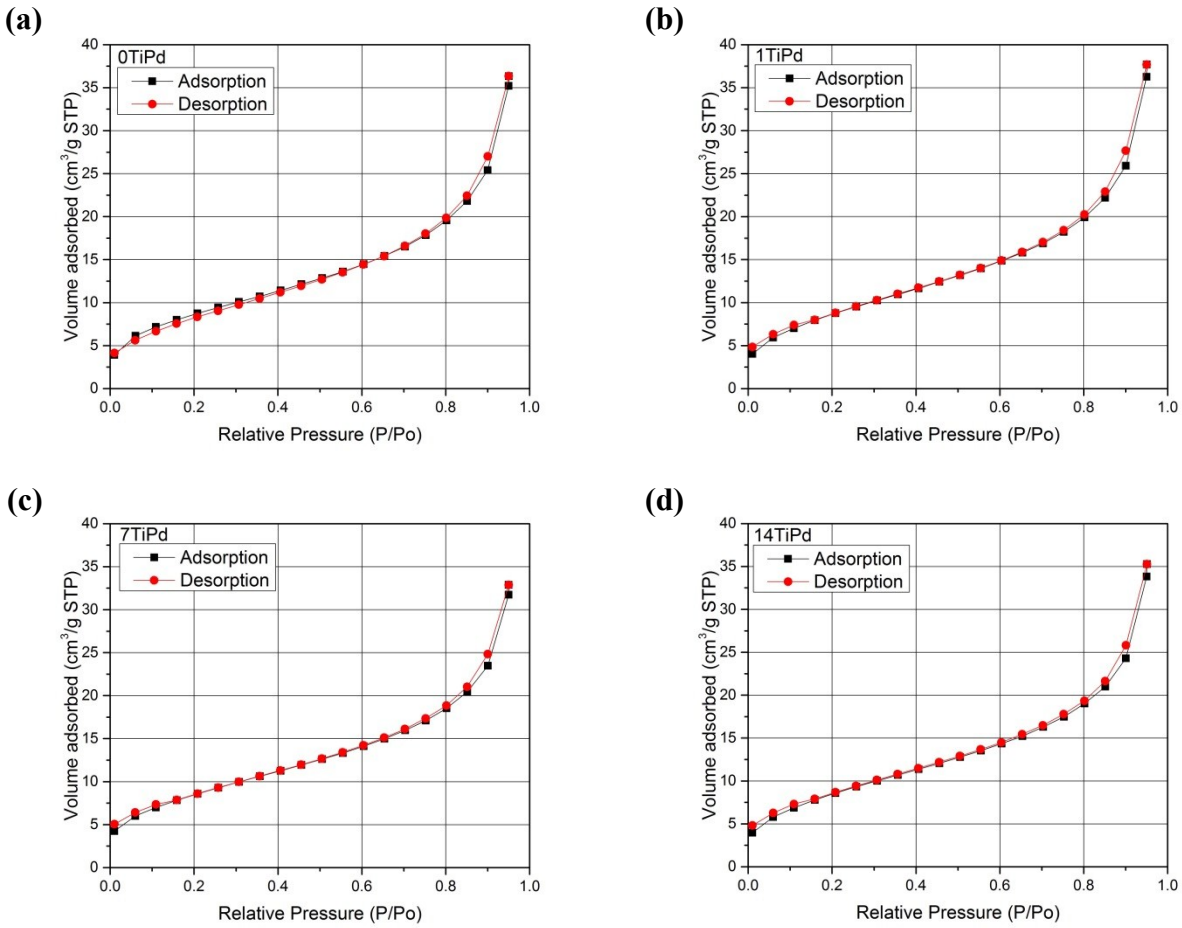

Figure S3. BET surface area of (a) 0TiPd, (b) 1TiPd, (c) 7TiPd, and (d) 14TiPd.

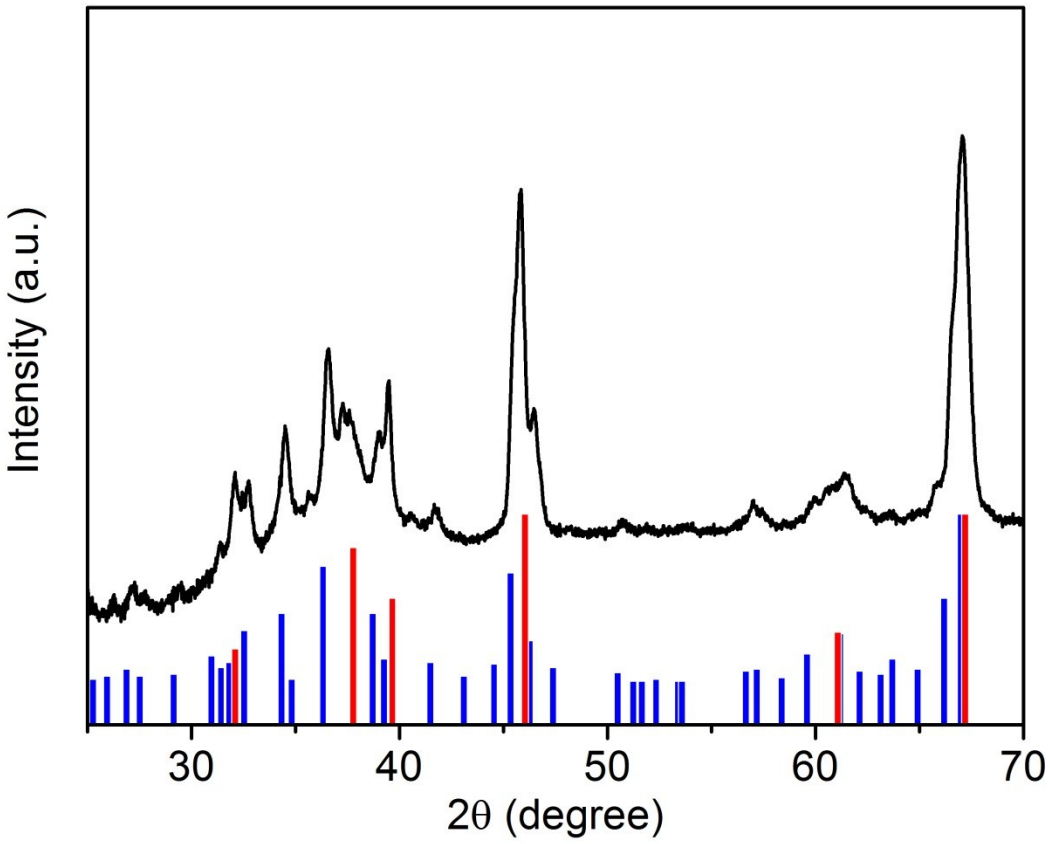

Figure S4. XRD of Spherical Al_2O_3 (black) compared with gamma-Al_2O_3 (red) and delta-Al_2O_3 (blue).

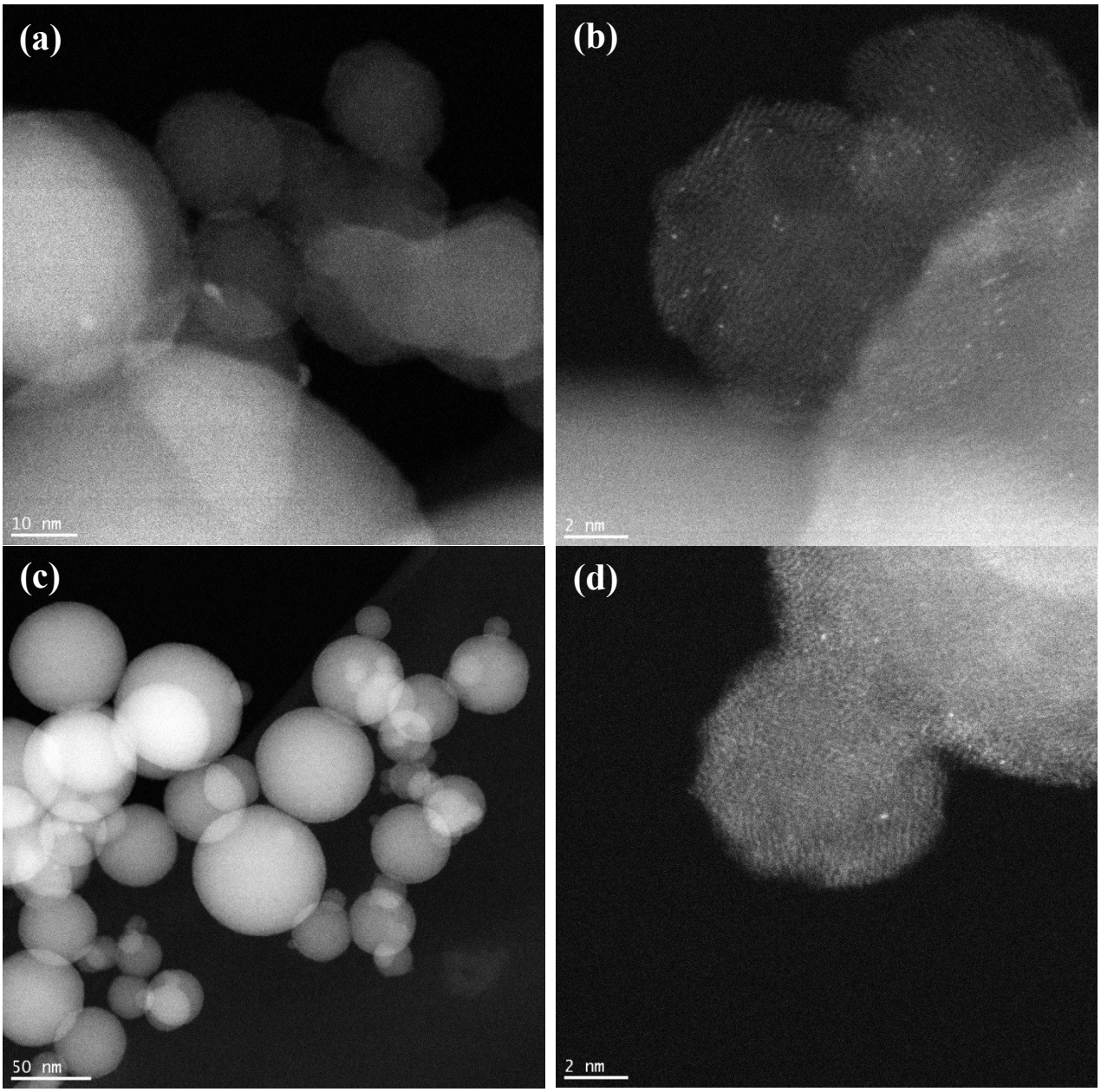

Figure S5. HAADF-STEM images of single atom catalysts: (a) and (b) 7TiPd$_1$, (c) and (d) 14TiPd$_1$.

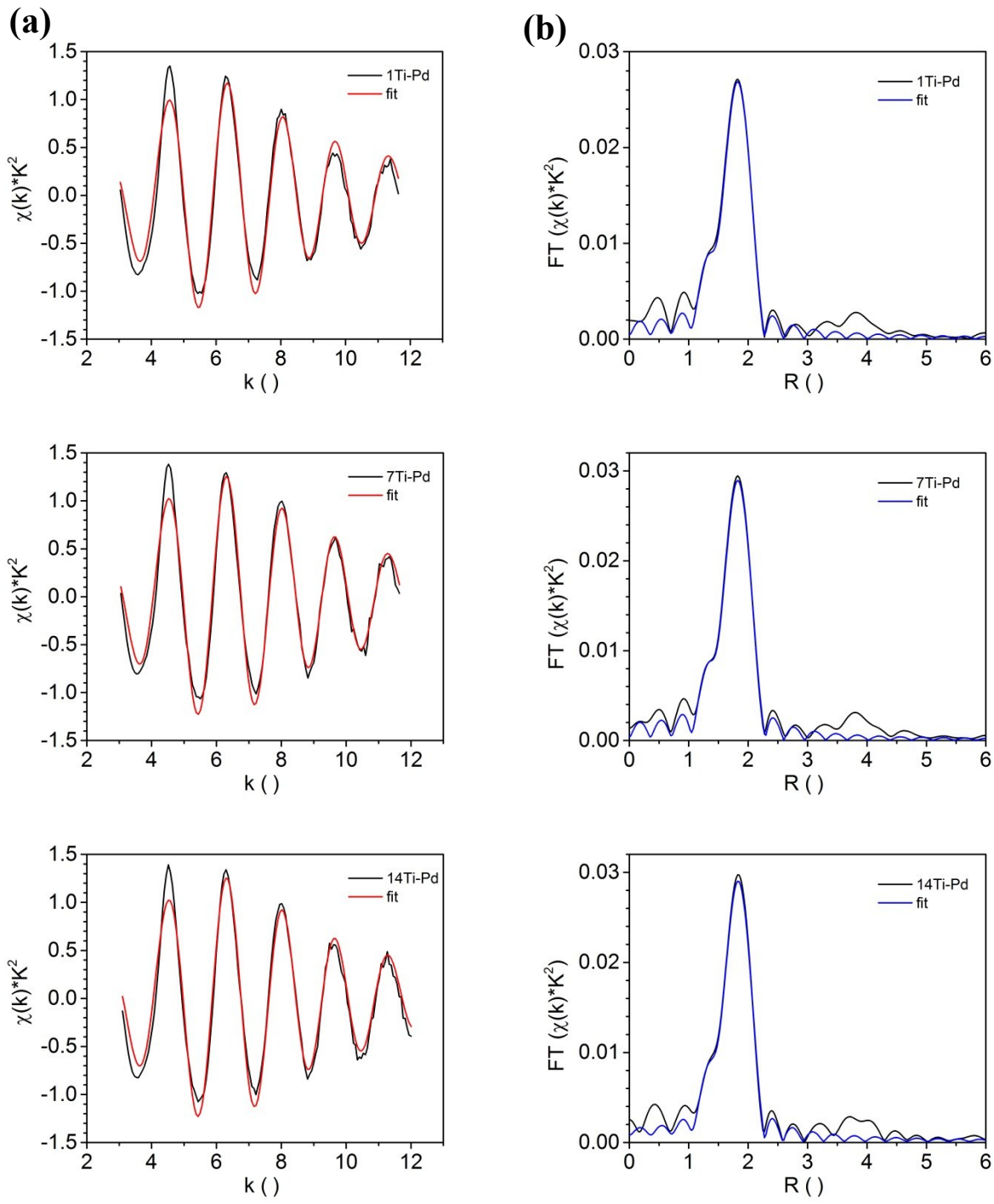

Figure S6. Pd K edge XAFS fittings of the as-prepared catalysts in (a) k-space, and (b) Fourier transform**.**

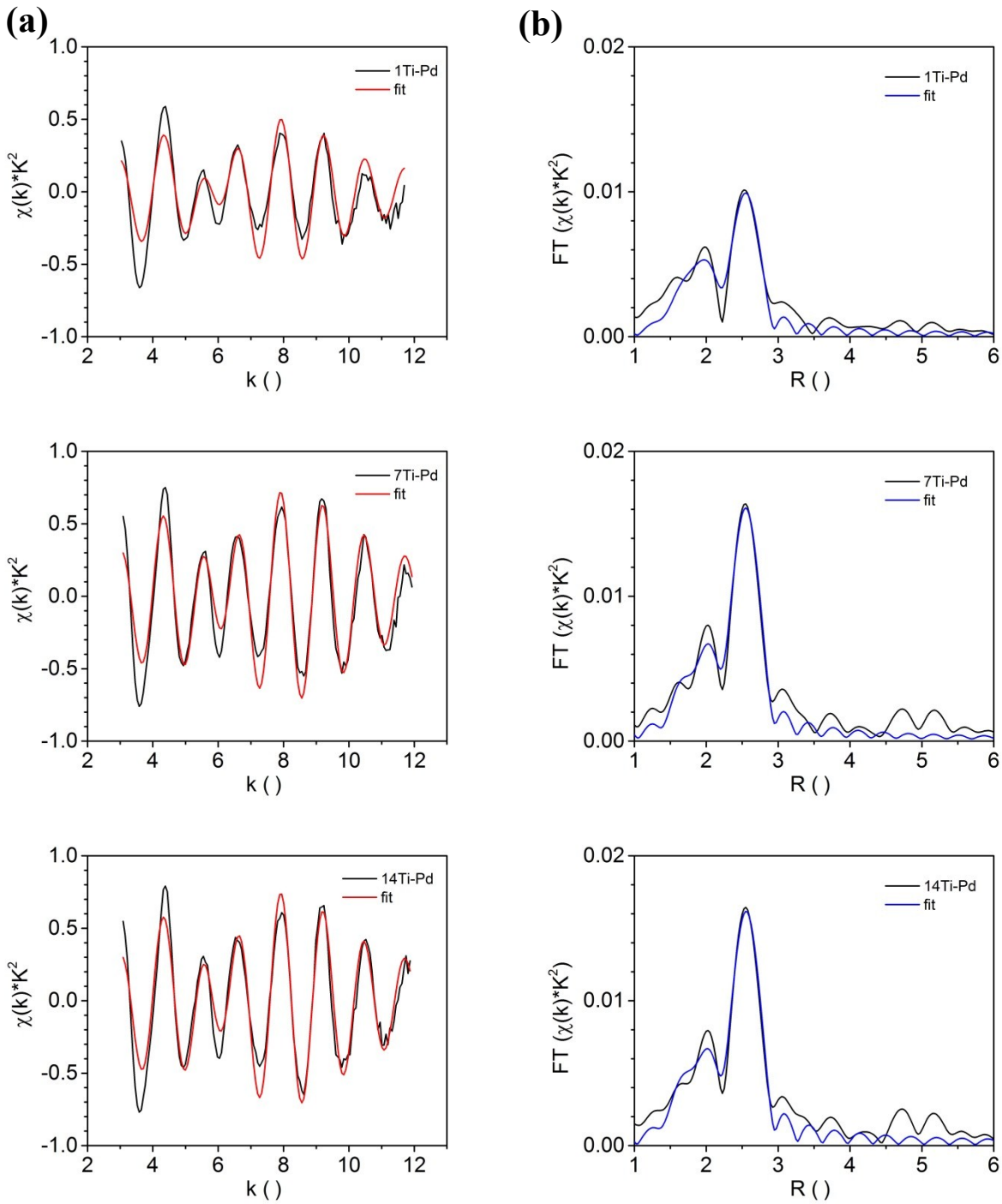

Figure S7. Pd K edge XAFS fittings of Pd catalysts after hydrogen reduction at 250 °C in (a) k-space, and (b) Fourier transform**.**

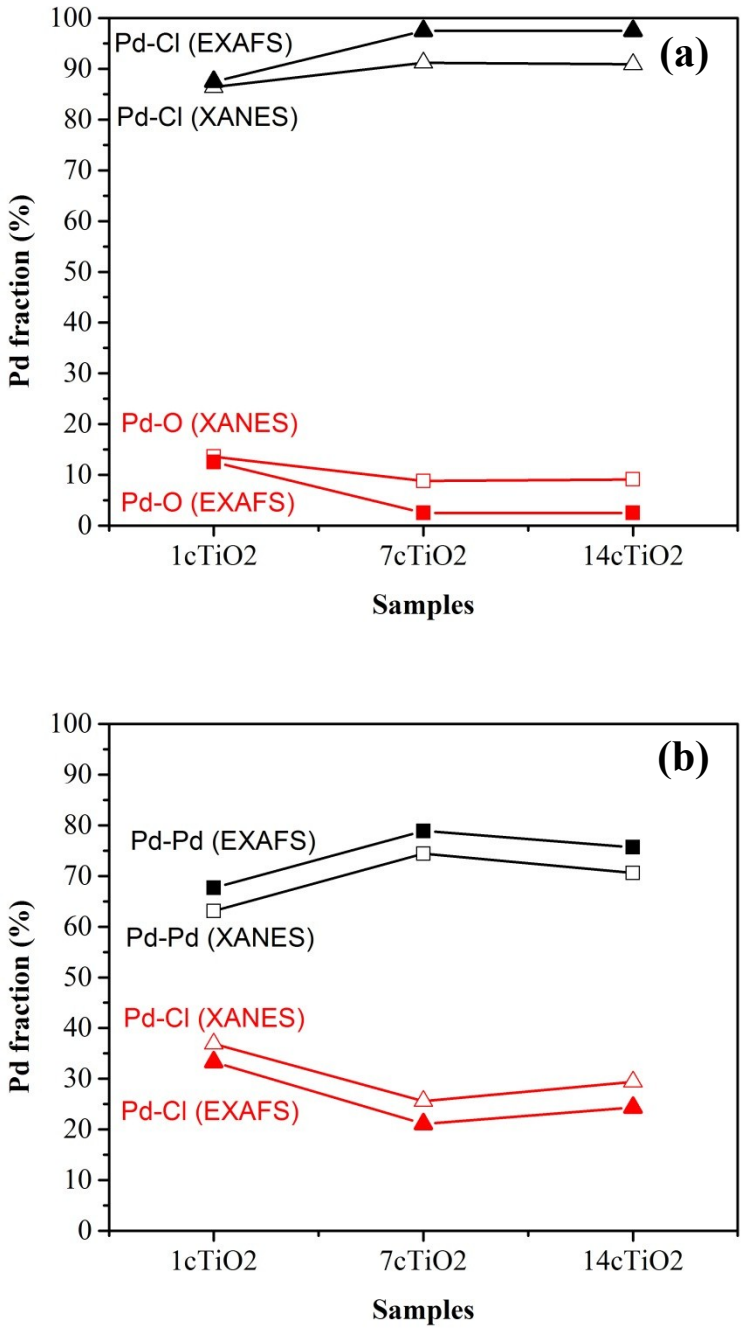

Figure S8. Composition of Pd obtained from Pd K edge XANES and EXAFS spectra for the (a) as-prepared Pd_1 catalysts, and (b) Pd_1 catalysts after hydrogen reduction

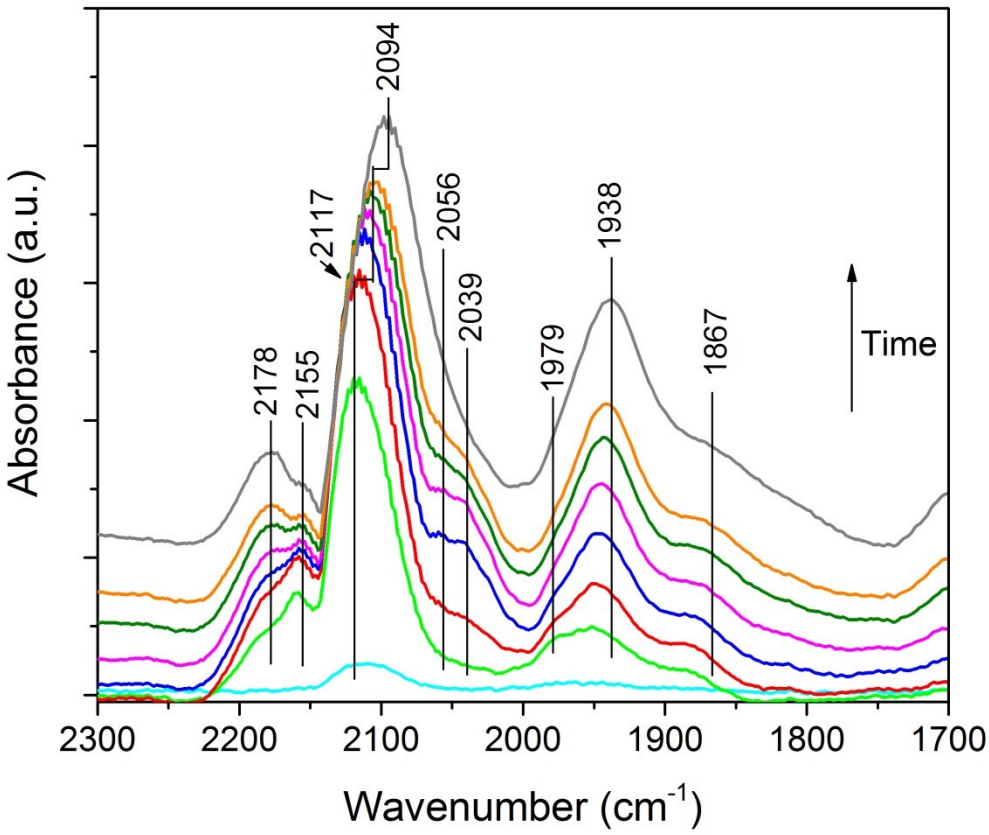

Figure S9. DRIFTS spectra of CO adsorption on 14TiPd. The spectra were obtained after room temperature flow of CO over time. After 0.5 minutes (cyan), 1 minute (green), 2 minutes (red), 4 minutes (blue), 6 minutes (magenta), 8 minutes (olive), 10 minutes (orange) and 30 minutes (gray).

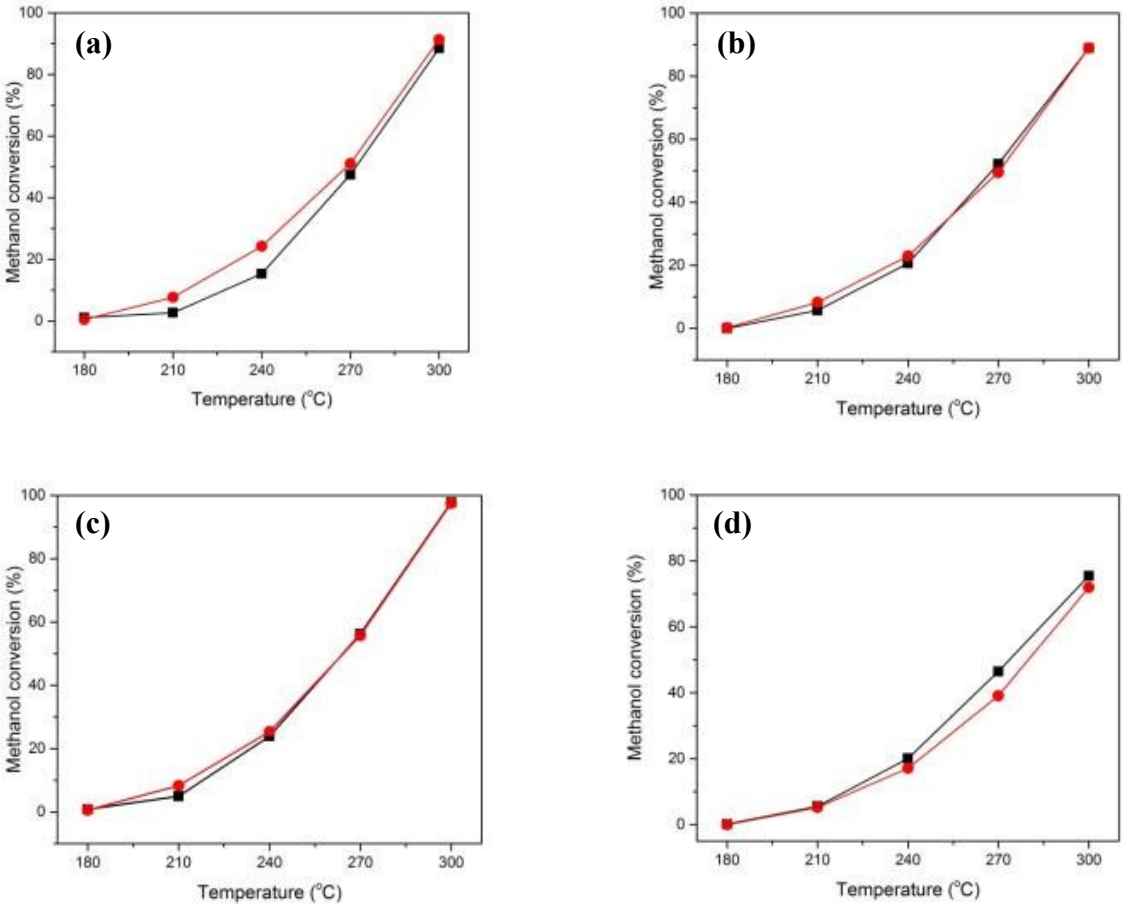

Figure S10. Methanol decomposition light-off curves using the catalyst (a) 0TiPd, (b) 1TiPd, (c) 7TiPd, and (d) 14TiPd. *Black*, Heating; *Red*, cooling.

Table S1. BET surface areas of Pd catalysts for methanol decomposition.

Catalysts	[a]Surface area (m^2/g)	CO Chemisorption (μmol/ g catalyst)
Bare Al_2O_3	33.8 ± 0.5	-
0TiPd	31.7 ± 0.2	32.0
1TiPd	32.9 ± 0.2	60.7
7TiPd	31.4 ± 0.2	64.9
14TiPd	31.9 ± 0.2	67.2
Commercial Pd/Al_2O_3	89.7 ± 0.3	790.1

[a] BET measurement has ~ 1% systematic error

Table S2. Pd K edge XANES Linear Combination Fit.

	Pd-O	Pd-Cl	Pd-Pd
1TiPd1 in air	13.6%	86.4%	-
1TiPd1 reduced	-	36.9%	63.1%
7TiPd1 in air	8.8%	91.2%	-
7TiPd1 reduced		25.6%	74.4%
14TiPd1 in air	9.1%	90.9%	
14TiPd1 reduced	-	29.4%	70.6%

The XANES LCF generally has 10% systematic error.

Reference

1 Y. Lei, J. L. Lu, H. Y. Zhao, B. Liu, K. B. Low, T. P. Wu, J. A. Libera, J. P. Greeley, P. J. Chupas, J. T. Miller and J. W. Elam, *Journal of Physical Chemistry C*, 2013, **117**, 11141-11148.