

The partial oxidation of methane over Pd/Al₂O₃ catalyst nanoparticles studied *in-situ* by near ambient-pressure X-ray photoelectron spectroscopy

Rachel Price^a, Tuğçe Eralp-Erden^b, Ethan Crumlin^c, Sana Rani^c,
Sonia Garcia^b, Richard Smith^b, Liam Deacon^d, Chanan Euaruksakul^d,
Georg Held^{a,d}

^a Department of Chemistry, University of Reading, Reading, RG6 6AD, UK

^b Johnson Matthey Technology Centre, Blounts Court Road, Sonning Common,
Reading, RG4 9NH, UK

^c Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California,
94720, USA

^d Diamond Light Source, Harwell Science and Innovation Campus, Didcot, OX11 0QX,
UK

Supporting Information

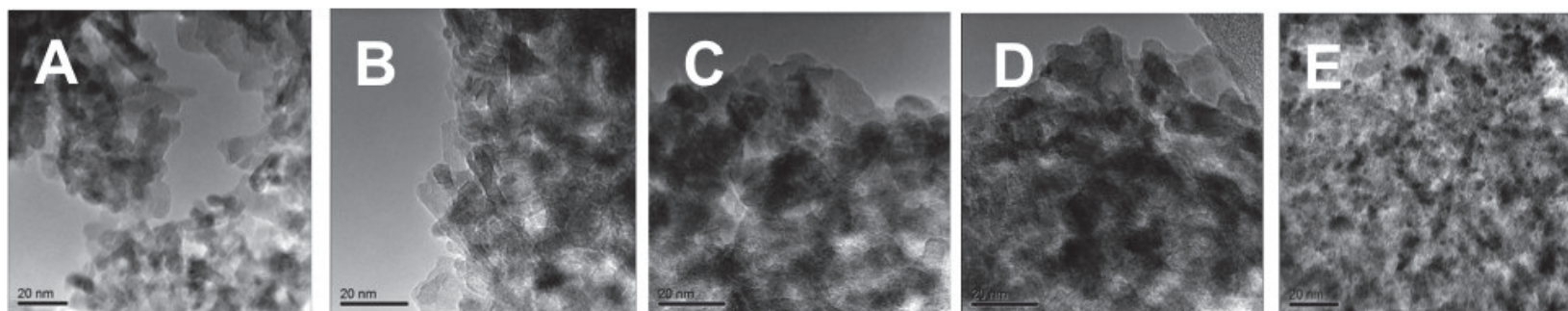


Figure 1: Transmission electron microscope images of Catalysts A-E. Tecnai F20 transmission electron microscope. The samples were analysed using 200 kV and 30 μ m C2 aperture at a variety of magnifications ranging from 5 nm - 100 nm.

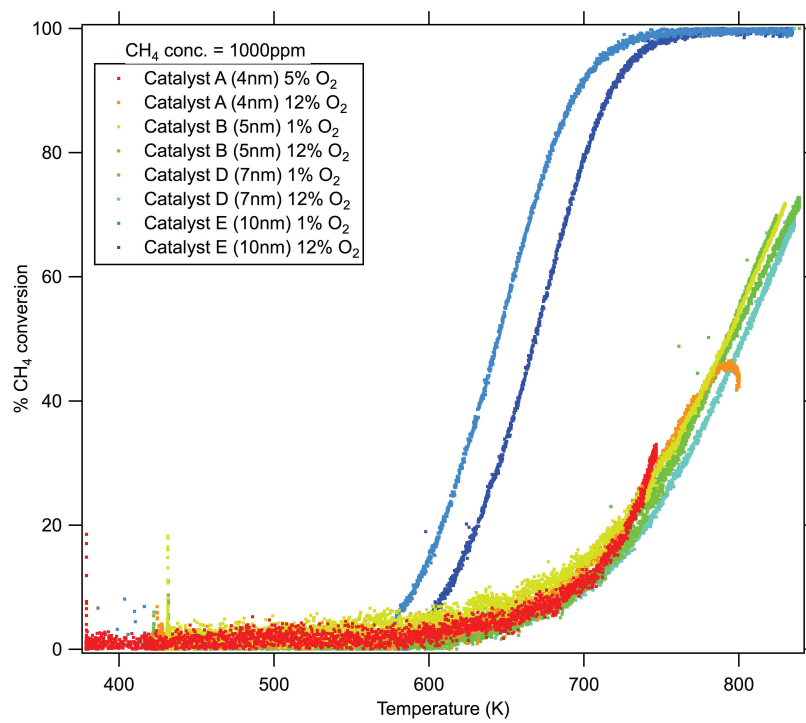


Figure 2: Reactivity of Catalysts A (4 nm), B (5 nm), D (7 nm) and E (10 nm) in terms of methane conversion to products CO and CO₂ under various O₂ concentrations

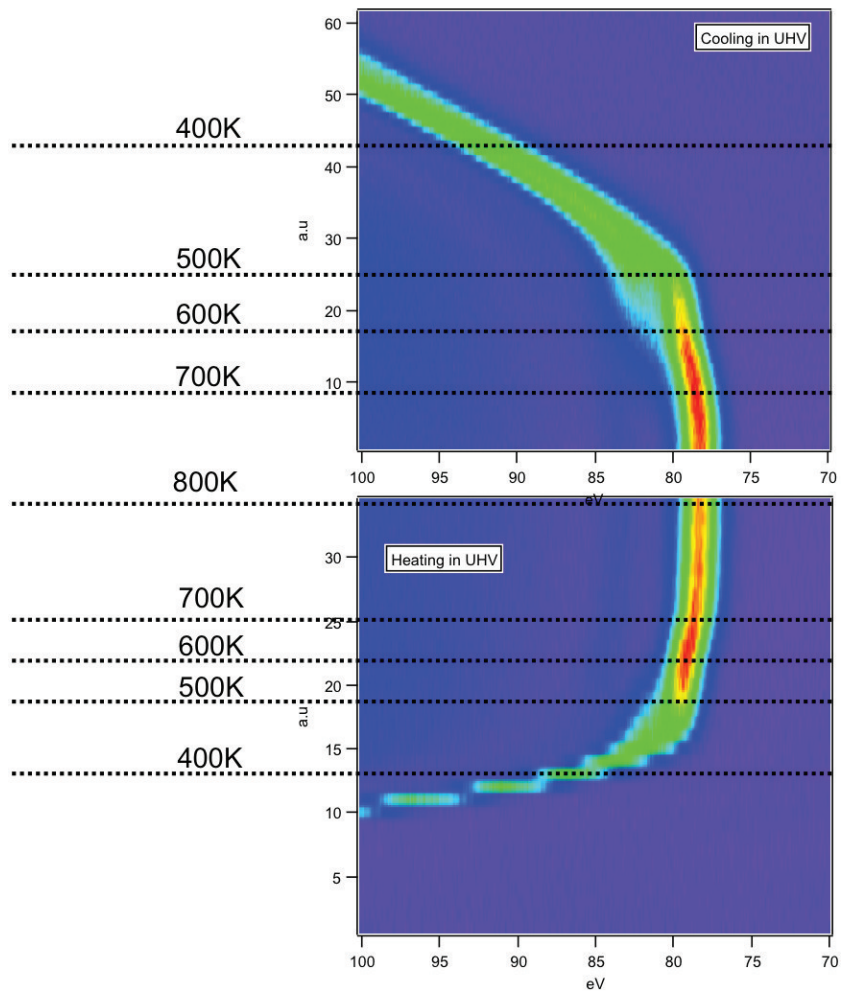


Figure 3: Time-resolved AP-XPS following the Al 2p region heating to 800 K and cooling back down to 300 K. A temperature effect is observed as the Al 2p peak shifts to higher binding energies, indicating the insulating nature of alumina is reduced with higher temperatures.

Fitting Procedure

The Pd 3d spectra were fitted using an unconventional fitting procedure in which the FWHM and mixing parameters were taken from the corresponding Al 2p spectrum. Charging of the alumina support affects the position, broadening and splitting of, both the Al 2p peak and the Pd 3d peaks in the same way. In order to fit the Pd 3d peaks correctly, the Al 2p peaks were first fitted using a pseudo-Voigt function (see main paper). The full width of half maximum (FWHM, τ) and mixing parameters (m) were fitted to the raw data. The same values were subsequently used to fit the corresponding Pd 3d spectrum. The energy axis of the Pd 3d spectra was also shifted to the same extent for a binding energy correction. Figure 4 shows an example of a fitted typical Al 2p spectrum taken under reaction conditions. The fitting parameters used to fit the singlet peak are 2.9 eV (τ) and 0.1 (m), as indicated in the figure. The literature value for Al 2p alumina peak is 74.5 eV [1], and so in this case $\Delta E = -4.4$ eV.

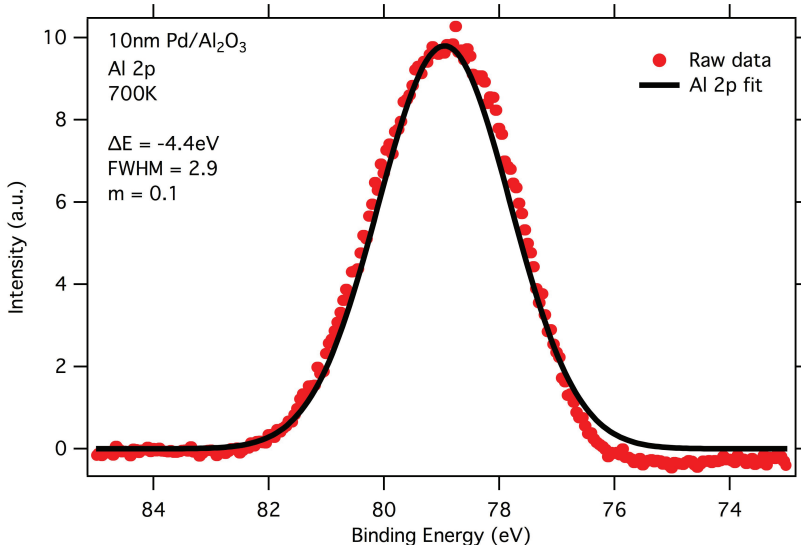


Figure 4: Fitted NAP-XP spectrum of Al 2p region.

The same parameters (τ and m) were used to fit the Pd 3d spectrum that was taken at the same incident photon energy and under the same reaction conditions (Figure 5). The Pd 3d spectrum is shifted along the energy axis by ΔE (-4.4 eV) in order to correct the binding energy. The energy separation and the intensity ratios between the spin-orbit components Pd 3d_{5/2} (low binding energy, 335-337 eV) and Pd 3d_{3/2} (high binding energy, 340-342 eV) are always kept fixed at 5 eV (± 0.3 eV) and 1.5, respectively, [2, 3] and are not dependent on the Al 2p spectrum.

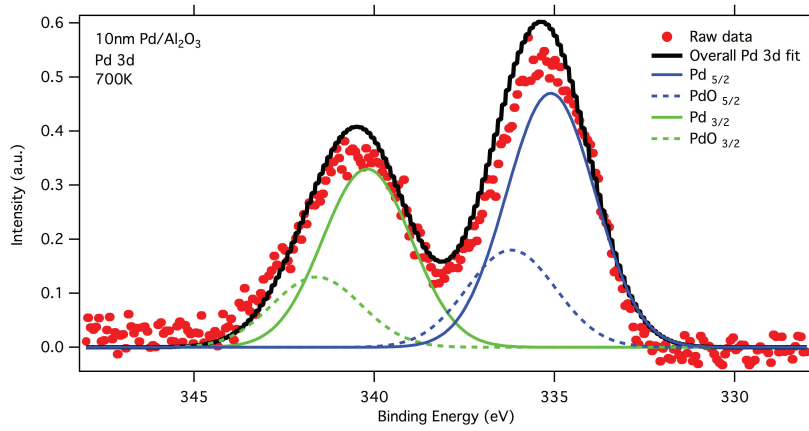


Figure 5: Fitted NAP-XP spectrum of Pd 3d region.

In some cases, the Al 2p peak was split into two peaks due to inhomogeneous charging of the support. In these cases two peaks were fitted for each Pd species (Pd and PdO Pd 3d_{3/2}, Pd and PdO Pd 3d_{5/2}). Figure 6 shows an example fit of a split peak in the Al 2p region at 550 K. The text in the figure indicates the binding energy shift (ΔE) of each fitted peak from the literature value of 74.5 eV. These are the values used to correct the binding energy scale of the corresponding Pd 3d peaks (see Figure 7).

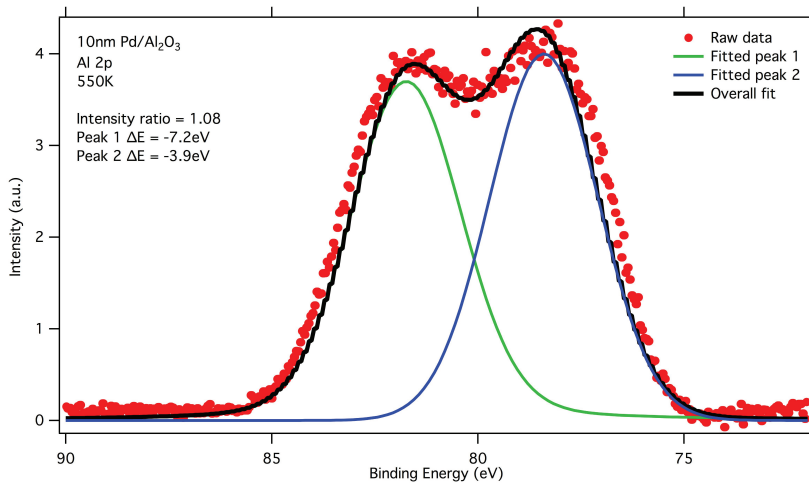


Figure 6: Fitted NAP-XP spectrum of Al 2p region.

In this example, the FWHM (τ) of the fitted Al 2p peaks 1 and 2 is 2.8 eV and the mixing parameter (m)

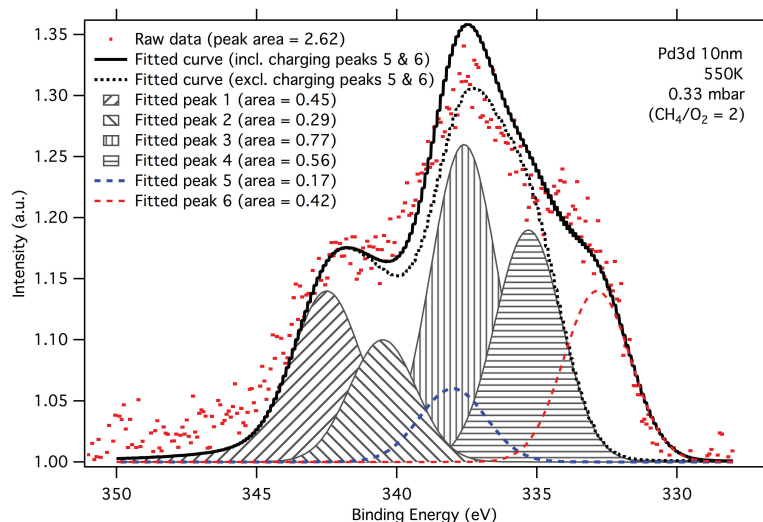


Figure 7: Fitted NAP-XP spectrum of Pd 3d region using parameters obtained from fitting Al 2p spectrum recorded at the same photon energy and under the same reaction conditions (550 K, 0.33 mbar, $\text{CH}_4/\text{O}_2 = 2$). The legend indicates which Al 2p peak was used to shift the binding energy scale (Peak 1 or Peak 2). Intensity ratios between Peak 1 and Peak 2 of the same species are fixed at 1.08. Intensity ratios between Pd $3d_{5/2}$ and Pd $3d_{3/2}$ of the same species are fixed at 1.5.

is 0.1. These values were included in the fit function for the corresponding Pd 3d spectrum in Figure 7, recorded at the same time in the reaction and with the same photon energy. The energy separation and intensity ratios between the spin-orbit components are again kept constant at 5 eV and 1.5 respectively. The intensity ratio of the Al 2p peaks was used when fitting the split Pd 3d peaks and kept fixed, which in this example is 1.08. The splitting of the Al 2p peak and the corresponding binding energy shift accounts for the feature in the raw Pd 3d spectrum at 332 eV, which is not usually indicative of a Pd species.

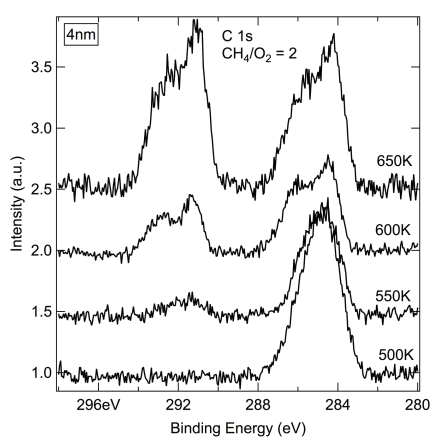
The fitting parameters used for each spectrum shown in Figures 1-5 in the main manuscript are outlined in Table 1. All values (τ (FWHM), m (mixing), ΔE for peaks 1 and 2 (binding energy shift from literature value), peak separation (difference in binding energy between peaks 1 and 2) and the intensity ratio (peak 2/peak 1) are obtained from fitting the Al 2p spectra.

Catalyst	Temp. (K)	τ (eV)	m	ΔE Peak 1 (eV)	ΔE Peak 2 (eV)	Peak Sep. (eV)	Int. Ratio
A (Fig. 1)	500	3.0	0.1	-7.9			
A (Fig. 1)	550	3.2	0.0	-8.3	-4.4	3.9	1.1875
A (Fig. 1)	600	3.0	0.0	-6.5	-3.25	3.25	1.07
A (Fig. 1)	650	2.0	0.1	-4.3			
A (Fig. 1)	700	3.1	0.0	-4.8			
B (Fig. 2)	500	2.3	0.1	-4.35			
B (Fig. 2)	550	2.2	0.1	-4.1			
B (Fig. 2)	600	1.7	0.1	-3.55			
B (Fig. 2)	650	1.8	0.1	-3.55			
B (Fig. 2)	700	1.8	0.1	-3.4			
C (Fig. 3)	500	2.6	0.0	-5.4			
C (Fig. 3)	550	2.25	0.0	-4.5			
C (Fig. 3)	600	2.7	0.1	-4.2			
C (Fig. 3)	650	2.05	0.1	-4.1			
C (Fig. 3)	700	2.2	0.0	-4.0			
D (Fig. 4)	500	2.45	0.0	-8.0			
D (Fig. 4)	550	2.3	0.0	-5.45			
D (Fig. 4)	600	2.05	0.1	-4.45			
D (Fig. 4)	650	1.9	0.1	-4.1			
D (Fig. 4)	700	1.9	0.1	-3.95			
E (Fig. 5)	500	3.1	0.0	-9.1	-5.6	3.5	1.48
E (Fig. 5)	550	2.8	0.1	-7.2	-3.9	3.3	1.08
E (Fig. 5)	600	2.6	0.0	-4.2			
E (Fig. 5)	650	2.7	0.0	-4.6			
E (Fig. 5)	700	2.9	0.1	-4.45			

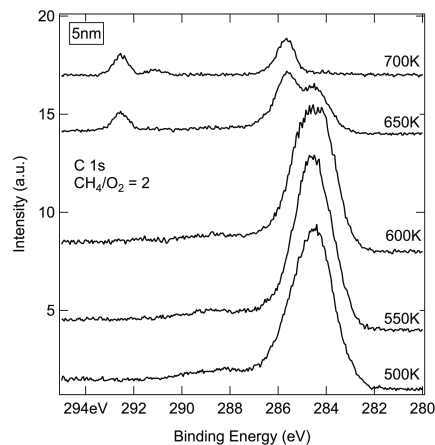
Table 1: Fitting parameters for the spectra shown in Figures 1 to 5 of the main text .

C 1s Spectra

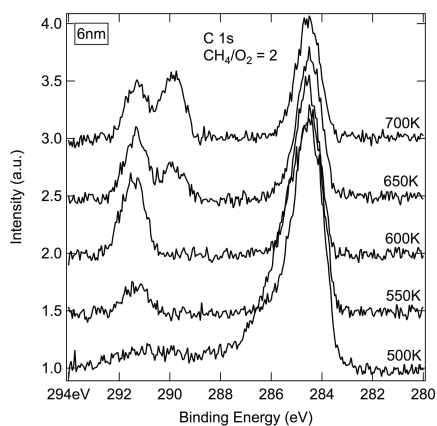
C 1s spectra were recorded alongside Pd 3d and Al 2p under reaction conditions at different temperatures (Figure 8). Each catalyst shows a peak at 285 eV, which could represent sample impurities, a PdC surface species, CH₄ from the gas phase, or a combination of all three. A second peak at ≈ 292 eV appears in the C 1s spectrum for all catalysts at temperatures above 600 K. From the gas phase spectra shown in Figure 9 (taken after the sample had been retracted a few millimetres from the analyser cone) this can be identified as CO₂. At higher temperatures, where partial oxidation is favoured, another peak at 290 eV appears. This represents the formation of CO.



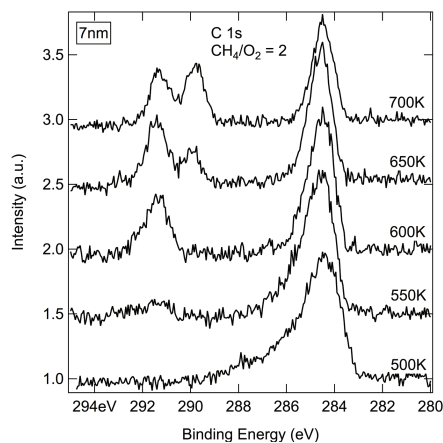
(a) Catalyst A, 4nm



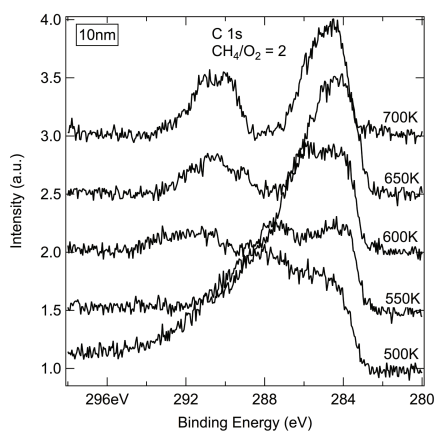
(b) Catalyst B, 5nm



(c) Catalyst C, 6nm



(d) Catalyst D, 7nm



(e) Catalyst E, 10nm

Figure 8: NAP-XPS C 1s spectra taken under reaction conditions at different temperatures

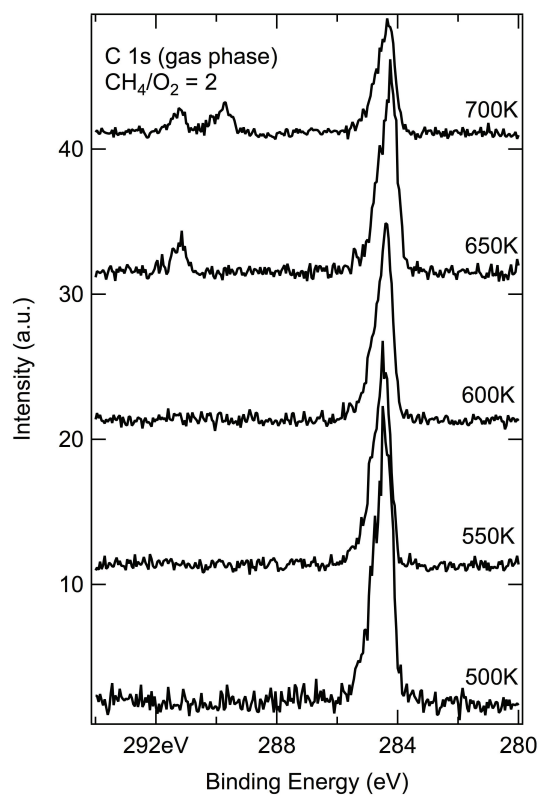


Figure 9: C 1s spectra taken under partial oxidation of methane conditions. The sample is retracted back from the analyser so only photoelectrons from the gas phase molecules are detected. The peaks represent CH₄, CO and CO₂ at 285 eV, 290 eV and 292 eV respectively.

References

- [1] B. Strohmeier, *Surface Science Spectra* **3**, 141 (1994)
- [2] D. Zemlyanov, B. Aszalos-Kiss, E. Kleimenov, D. Teschner, S. Zafeiratos, M. Havecker, A. Knop-Gericke, R. Schlögl, H. Gabasch, W. Unterberger, K. Hayek, B. Klötzer, *Surface Science* **600**, 983 (2006)
- [3] W. Griffith, S. Robinson, *Pd Palladium: Palladium Compounds* (Springer Science, 2013)