Supplementary information for Chemical Communications

Fig. 1 shows the photos of the *in situ* cell. The volume of the cell The 25 μm kapton window allowed us to measure XAS spectra in fluorescence mode at Pd K- and Sn L edges. The electrical conductance was measured at a fixed voltage (U =1 V) between two contacts deposited on the sample surface by vacuum evaporation. It was possible to heat the sample up to 400 °C. A system of 6 Bronkhorst mass flow controllers and Valco two-position switching valve was used to prepare different gas mixtures containing H_2, O_2 and He. The studies were carried out under an atmospheric pressure at 100 ml/min gas flow rate. The mass-spectrometer (Pfeiffer) was connected to the outlet of the cell.

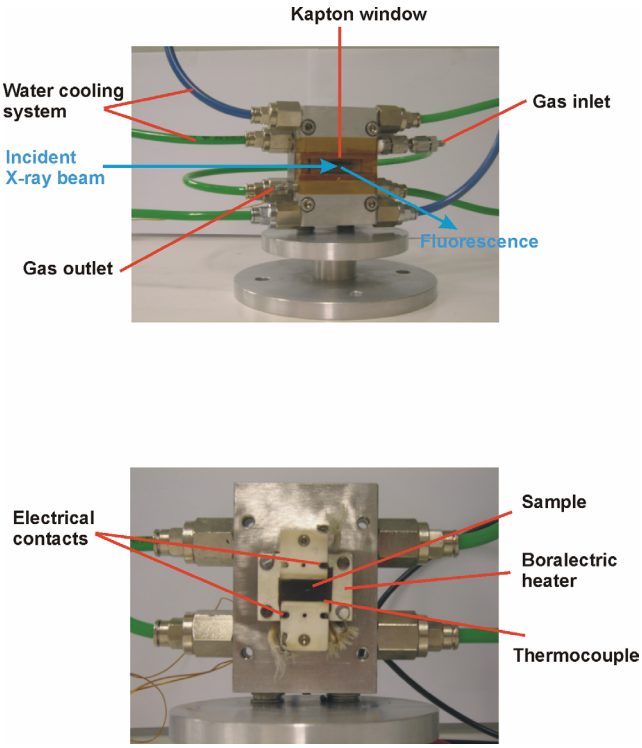

Fig.1 The picture of the *in situ* cell from outside and inside.

Fig. 2 shows the examples of the fitted EXAFS spectra measured at Pd K- and Sn L1- edges for Pd-promoted SnO_2 film in the steady-state conditions (A-H states). Structural and statistical parameters are given in the Table 1.

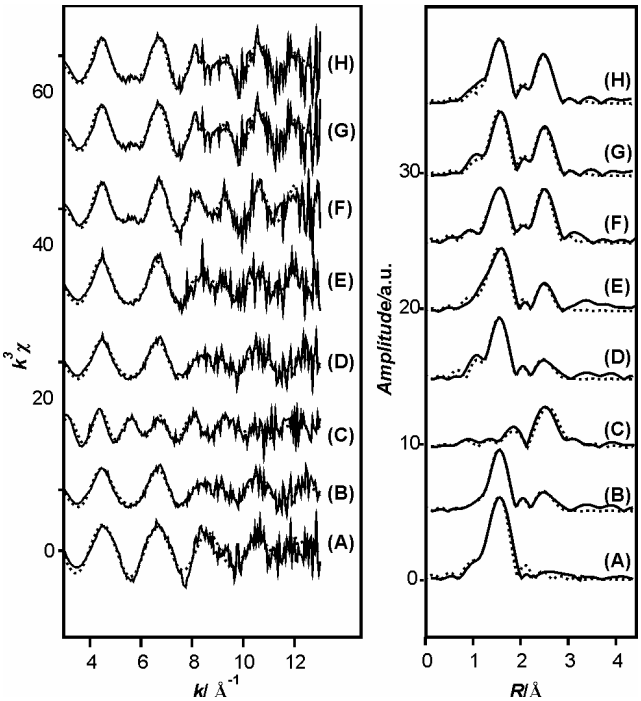

Fig.2 The Pd K EXAFS spectra of Pd- SnO_2 in steady state conditions. Solid lines and dotted line indicate experimental data the best fit.

Table 1 Structural and statistical parameters derived from analysis of XANES and EXAFS spectra.

State	T, K	Gas phase	Scatter	*R* / Å	CN	σ^2/ Å^2	Sn^{2+} /%	Pd^{2+} /%
A	573	20%O_2	O	2.015(9)	3.9(6)	0.004(1)	<1.5	100
			Pd	-	-	-		
B	573	20%O_2	O	2.02 (1)	2.8(6)	0.004(2)	<1.5	75
			Pd	2.73(2)	1(1)	0.011(7)		
C	573	1000ppm	O	-	-	-	9	0
		H_2	Pd	2.74(1)	8(2)	0.019(2)		
D	573	20%O_2	O	2.02 (1)	2.7(6)	0.005(2)	<1.5	74
			Pd	2.74(2)	1(1)	0.012(7)		
E	373	20%O_2	O	2.04(1)	3.1(8)	0.005(3)	<1.5	74
			Pd	2.73(2)	1(1)	0.010(7)		
F	373	20%O_2	O	2.03(1)	2.3(7)	0.004(3)	<1.5	64
			Pd	2.73(1)	3(1)	0.0010(3)		
G	373	1000ppm	O	2.03(1)	2.5(7)	0.004(2)	<1.5	62
		H_2	Pd	2.73(1)	2(1)	0.009(3)		
H	373	20%O_2	O	2.03(1)	2.6(7)	0.005(2)	<1.5	61
			Pd	2.74(1)	2(1)	0.009(3)		

EXAFS analysis is performed for Pd (*R* = bond length, *CN* = coordination number and σ^2 = Debye Waller factor). Sn^{2+} and Pd^{2+} concentrations are calculated from XANES data.