In situ energy dispersive EXAFS (EDE) of low loaded $Pt(acac)_2/H_I\ SiO_2$ catalyst precursors on a timescale of seconds and below

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We demonstrate second and sub-second time resolved energy dispersive EXAFS (EDE) for *in situ* interrogation of phase changes in a supported metal catalyst precursor [($\leqslant$5 wt%) $Pt(acac)_2/H_I\ SiO_2$] during thermal decomposition and reduction; the formation of Pt particles is radically altered by the presence H_2, in both kinetic and structural senses.

Extended X-ray absorbtion fine structure (EXAFS) has long been a frontline technique in the determination of local structure and has found widespread application. However, the predominant *modus operandi* is rooted in the interrogation of the steady state, due to the stepwise progression of the monochromator through the energy window of interest. Quick EXAFS (QuEXAFS)[1] allows relatively rapid data acquisition *via* the optimisation of this monochromator movement: EXAFS spectra from supported metal catalysts can be collected on a timescale of $>$20–30 s though timescales of $>$1 min are more common,[2–5] in one case Cu K-edge XANES has been collected in *ca.* 3 s.[6]

EDE (or DEXAFS) utilises an (ideally) elliptically bent monochromator to produce a focused beam containing the required spread of X-ray energies. The EXAFS experiment may therefore be achieved with *no* subsequent monochromator movement.[7] In the present case a four point bending mechanism[8] is used to minimise aberations and produce an extremely small spot size. The speed of data acquisition is therefore limited only by the time required to achieve acceptable statistics. However, simultaneous illumination of the sample with a range of X-ray energies requires extreme spatial homogeneity of the sample. In the case of heterogeneous catalysts, these uniformity requirements have resulted in the predominate use of QuEXAFS[1–6] or pressed disk samples.[7,8b,9] Using this latter approach, EDE has been used on heterogeneous systems on a time scale of (at best) 30 s.[8b,9] Pressed disks present problems in terms of non-uniform gas distribution within the disk,[10a] and possible degradation of the support material structure.[10b,11] We present a methodology that allows fast, high quality, EDE measurements to be made with a sample presentation much more in keeping with catalytic testing.

The mesoporous silicas ($H_I\ SiO_2$), prepared following the procedure previously described,[12] were impregnated with $Pt(acac)_2$ from dry toluene. The $Pt(acac)_2/(H_I\ SiO_2)$ catalyst precursors were then sieved to a particle size of *ca.* 100 μm and packed into a flow microreactor based upon thin walled quartz tubes (*ca.* 2 mm o.d; 0.1 mm wall thickness). A second tube, the reference for the EDE experiment, was packed in the same manner with unloaded mesoporous silica ($H_I\ SiO_2$). This approach is similar to that demonstrated by Clausen *et al.*[2] although the increased diameter of the quartz tube used, allows the insertion of a 0.25 mm, mineral insulated, type K thermocouple directly into the sample. The samples were reacted under flowing N_2 or 10% H_2–90% N_2 gas using a linear sample heating ramp of 4 K min^{-1}. Gases are passed over the catalyst beds under mass flow control.

Fig. 1 shows Pt L_{III} edge EXAFS spectra obtained from $Pt(acac)_2/(H_I\ SiO_2)$ catalyst precursors. Spectrum (a) was obtained from a standard EXAFS experiment (*ca.* 1 h). Spectra (b)–(f) are EDE† obtained for a range of collection times (as indicated). Spectrum (f) is that derived from a 1 wt% $Pt/H_I\ SiO_2$ sample in 21 s. The Pt L_{III}-edge EXAFS-derived‡ structural parameters are summarised in Table 1.

Clearly, good quality EXAFS analysis (one or two coordination shells) can be obtained using this approach down to sub-second acquisition times (at 5 wt%). Analysis of the data obtained in 0.05 s leads to inconsistent structural parameters making it unsuitable for detailed EXAFS analysis. This data is suitable for determination of spectral change in the XANES region. The 1 wt% Pt case represents the current dilution limit of this approach and a reasonable quality of data can be achieved in *ca.* 21 s.

Fig. 2 shows phase corrected Fourier transforms derived from temperature dependent EDE spectra recorded at 8 s acquisition time (scan time 80 ms; 100 scans) for the reduction of a 5 wt% Pt sample under 8 ml min^{-1} 10% H_2–90% N_2 gas. The $Pt(acac)_2$ collapses to form Pt particles over an extremely narrow temperature region (*ca.* 15 K) indicative of some form of autocatalytic kinetics. In the temperature region shown these particles show little evidence of any subsequent increase in size.

Fig. 3 shows the variation in Pt–O and Pt–Pt coordination obtained from such EDE experiments for the following cases: 5 wt% Pt sample thermally decomposed as above in H_2–N_2 (a) and N_2 (c) mixtures; and a 1 wt% Pt sample reduced in H_2–N_2 (b). The particles resulting from the thermal decomposition of this catalyst precursor in pure N_2, and the kinetics of their production, are radically different to those produced *via* reduction in the H_2–N_2 mixture. The degree of particle agglomeration attained after the low *Z* coordination has been removed is significantly different between the case where H_2 is present and where only N_2 is used: with the latter case resulting in significantly smaller Pt particles. The persistence of low *Z* (C/O) coordination in the decomposition of this catalyst precursor therefore has considerable ramifications for the size of the particulate Pt formed.

In summary we have demonstrated that good quality, *in situ*, Pt L_{III} edge EDE can be obtained from low loaded heterogeneous samples on a time scale of seconds and below. The

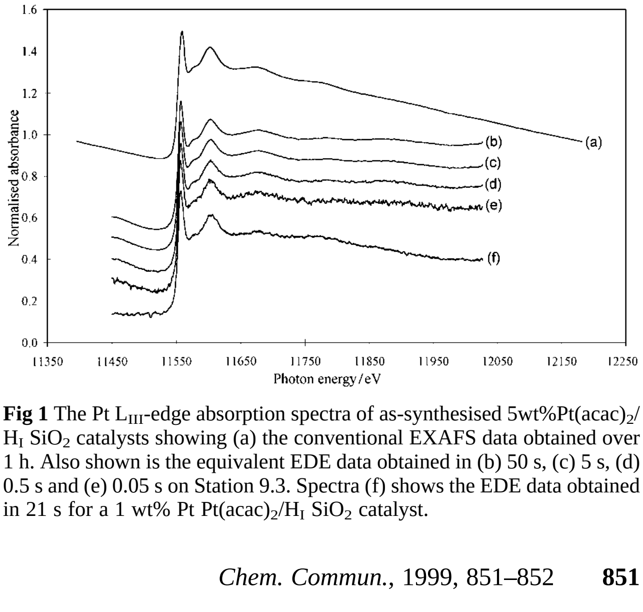

Fig 1 The Pt L_{III}-edge absorption spectra of as-synthesised $5wt\%Pt(acac)_2/H_I\ SiO_2$ catalysts showing (a) the conventional EXAFS data obtained over 1 h. Also shown is the equivalent EDE data obtained in (b) 50 s, (c) 5 s, (d) 0.5 s and (e) 0.05 s on Station 9.3. Spectra (f) shows the EDE data obtained in 21 s for a 1 wt% Pt $Pt(acac)_2/H_I\ SiO_2$ catalyst.

Table 1 Structural and statistical parameters derived from the analysis of the EDE and EXAFS spectra shown in Fig. 1. (a) Δk = 2–12 Å^{-1}, (b)–(f) Δk = 2–10 Å^{-1}. The R factors = ($\int [\chi^T - \chi^E]k^3 dk/[\chi^E]k^3 dk$) × 100% where χ^T and χ^E are the theoretical and experimental EXAFS and k is the photoelectron wave vector; the Debye–Waller factor = $2\sigma^2$, where σ is the root mean square internuclear separation. Values in parentheses are statistical errors generated in EXCURVE (see footnote [b])

Sample	Shell	CN[a]	r/Å[b]	1.5% error in r[b]	$2\sigma^2$/Å^2 [b]	R-factor (%)
(a) 5%Pt(acac)$_2$/H$_I$ SiO$_2$	O	4.0(0.2)	1.991(2)	0.030	0.005(2)	24.4
(Station 7.1, AQ = 1 h)	C	4.0(0.3)	2.934(5)	0.044	0.004(3)	
	O	2.0(0.4)	3.104(9)	0.046	0.004(6)	
	C	2.0(0.4)	3.270(12)	0.049	0.005(6)	
(b) 5%Pt(acac)$_2$/H$_I$ SiO$_2$	O	4.0(0.5)	1.982(6)	0.030	0.010(3)	42.8
(Station 9.3 AQ = 50 s)	C	4.0(1.0)	2.838(10)	0.043	0.002(4)	
(c) 5%Pt(acac)$_2$/H$_I$ SiO$_2$	O	4.0(0.6)	1.981(7)	0.030	0.011(4)	49.6
(Station 9.3 AQ = 5 s)	C	4.0(1.1)	2.824(12)	0.042	0.003(8)	
(d) 5%Pt(acac)$_2$/H$_I$ SiO$_2$	O	4.0(0.9)	1.964(15)	0.030	0.012(5)	61.5
(Station 9.3 AQ = 0.5 s)						
(f) 1%Pt(acac)$_2$/ H$_I$ SiO$_2$	O	4.0(0.8)	1.988(8)	0.030	0.004(2)	70.2
(Station 9.3 AQ = 21 s)						

[a] CN = Coordination number. [b] In accordance with previous studies[16] we note that the true errors in bond lengths are likely to be of the order of 1.5% (as indicated); those for the coordination numbers *ca.* 20%. The variation of Debye–Waller factors the EDE may be due to some inhomogeneity in the sample or in the quartz tubes.

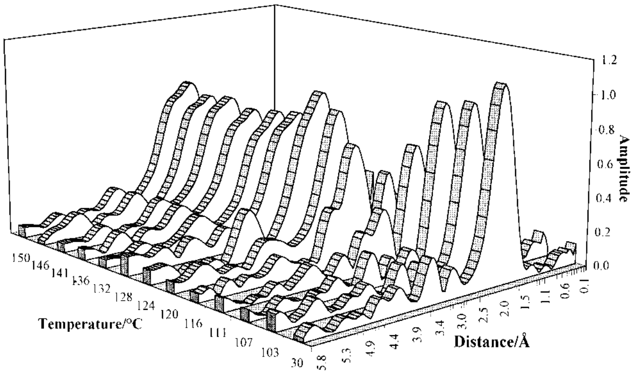

Fig 2 Fourier transforms, phase-shift corrected for oxygen, from EDE spectra derived from the reduction of 5 wt%Pt(acac)$_2$/H$_I$ SiO$_2$ catalysts in 10% H$_2$ in N$_2$ as a function of reduction temperature [heating rate 4 K min^{-1} acquisition time 8 s (scan time 80 ms; 100 scans)].

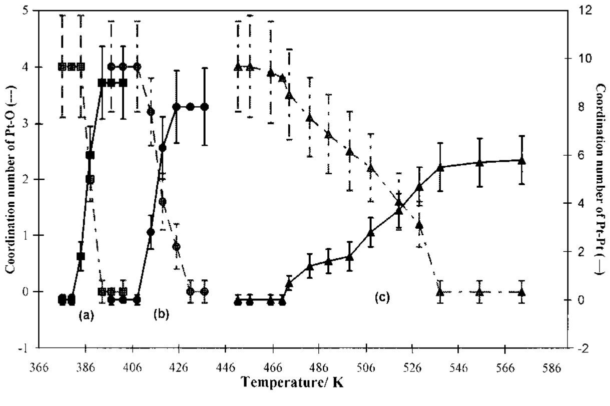

Fig. 3 The variation of Pt–O and Pt–Pt coordination number during the temperature programmed decomposition/reduction of (a) 5 wt%Pt(acac)$_2$/H$_I$ SiO$_2$ catalysts under 10% H$_2$ in N$_2$, (b) 1 wt%Pt(acac)$_2$/H$_I$ SiO$_2$ catalysts under 10% H$_2$ in N$_2$ and (c) 5 wt%Pt(acac)$_2$/H$_I$ SiO$_2$ catalysts under N$_2$.

approach described can be applied on timescales that allow detailed interrogation of the fluxion in supported catalyst phases under non-steady state conditions.

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Notes and references

† EDE experiments were recorded in transmission using a low noise, highly linear, photodiode array (Hamamatsu S4874).[8c]

‡ Normal X-ray absorption spectra were recorded (in transmission mode) on Station 7.1 at the Daresbury Laboratory operating at 2 GeV. All data reduction was carried out using PAXAS,[14] with the spherical wave analysis performed using EXCURV98.[15,16]

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