

In situ, time resolved, and simultaneous multi-edge determination of local order change during reduction of supported bimetallic (Pt–Ge) catalyst precursors using energy dispersive EXAFS†

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In situ, time resolved, simultaneous multi-edge energy dispersive EXAFS (EDE) reveals Ge precursor induced perturbations of the reduction of supported Pt(acac)₂ to form Pt particles, and details the subsequent thermally induced formation of PtGe species.

Many heterogeneously catalysed processes may be enhanced through the formation of alloyed, rather than elemental, metal particles (*e.g.* hydrocarbon reforming, PtSn,¹ PtRe¹ and PtGe^{2,3} rather than Pt) or *via* addition of other oxides (*e.g.* ZnO to Cu/Al₂O₃ in methanol synthesis⁴). It is therefore of considerable interest to delineate the details of how these interactions evolve during synthesis, and are affected by the synthetic approach applied.

Time resolved measurements have the potential for gaining an understanding of the processes resulting in a given catalyst; indeed the combination of Quick EXAFS (QuEXAFS)⁵ [or energy dispersive EXAFS (EDE)⁶] and XRD has been reported, but only for the interrogation of a one-elemental edge in EXAFS (Cu K in both cases). EDE has the potential for extremely rapid data acquisition, and therefore considerable potential for quantitative structural and kinetic determinations: we have previously demonstrated this for heterogeneous systems on a timescale of 1–8 s for supported metal systems.^{7,8} EDE also potentially allows truly simultaneous multiple edge sampling and analysis. This situation cannot be achieved by QuEXAFS,^{5,9} as this still requires movement of a monochromator through a given energy window. Here we show the application of EDE to follow the changes that lead to the formation of Pt/Ge alloy particles from mono-metallic precursors supported upon H₂SiO₂ mesoporous silicas *via in situ* sampling of the Pt L_{III} and Ge K edges simultaneously. PtGe catalysts have been shown to exhibit enhanced properties in hydrocarbon reforming reactions^{2,3,10,11} particularly, increased selectivity toward aromatics¹⁰ and tolerance towards sulfur,¹¹ the latter property being associated with the formation of PtGe alloy particles, which requires reduction at 773 K in H₂ for typical H₂PtCl₂/GeCl₄/Al₂O₃ derived catalysts.¹¹

The preparation of the mesoporous silica has been described previously.¹² In the current case Pt was incorporated in these supports through impregnation [Pt(acac)₂] in dry toluene. The toluene was subsequently removed by rotary evaporation and drying. GeBu₄ was incorporated by injection under vacuum to the pre-prepared Pt(acac)₂/H₂SiO₂ sample. The final catalyst precursors contained 5 wt% Pt and 1.9 wt% Ge yielding a Pt:Ge ratio of 1:1. EDE experiments were performed using a flow microreactor described previously,^{7,8} based around thin walled quartz tubes, into which the sieved (*ca.* 100 μm) particles of catalyst precursors were packed into a bed (10 mm long). The experimental conditions used for reduction of these samples under 10% H₂–N₂ (8 ml min⁻¹) were identical to those

described previously for the reduction of the analogous elemental [Pt(acac)₂/H₂SiO₂] system.⁷ The EDE measurements were made on station 9.3 at the SRS using a four-point bending mechanism¹³ to manipulate a Si[111] monochromator. Spectra were recorded in 8 s (8 ms × 1000 scans). Data reduction was carried out using PAXAS¹⁴ with multiple scattering spherical wave analysis performed using EXCURVS98.¹⁵ Errors in coordination number are quoted at a fixed ±10%.

Fig. 1 shows EDE spectra derived simultaneously from both Pt L_{III} and Ge K edges whilst the Pt(acac)₂/GeBu₄/H₂SiO₂ sample was heated to 673 K under a flow of H₂–N₂. At least two regions of change can be observed as the sample is reduced. The first, occurring in the range 450–473 K, is observed only in the Pt edge spectra with the Ge EXAFS remaining essentially constant. It is only at higher temperature (> 543 K) that changes in the Ge EXAFS, together with further changes in the Pt spectra, are evident. Fig. 2 shows representative *k*³ weighted EXAFS from both Pt and Ge edges at 543 K during *in situ* reduction of the sample; Table 1 summarises both the local order and statistical data resulting from spherical wave analysis. The EDEXAFS (8 s of acquisition time) from the Pt edge may be reasonably analysed in the range 2–11 Å⁻¹; for the Ge edge this data length is reduced to *ca.* 9 Å⁻¹. At temperatures as low as 543 K, Pt–Ge interactions and alloy formation are indicated. At this temperature it also reveals the persistence of Ge–C interactions.

Fig. 3 shows the results of a comprehensive analysis of the spectra shown in Fig. 1 and gives a detailed insight into the formation of the PtGe particles. The temperature dependence of the Pt–Pt, Pt–Ge, Ge–Pt coordination numbers are shown in the temperature range 300–673 K; no Ge–Ge interactions were observed. This clearly shows that the reduction of the precursor

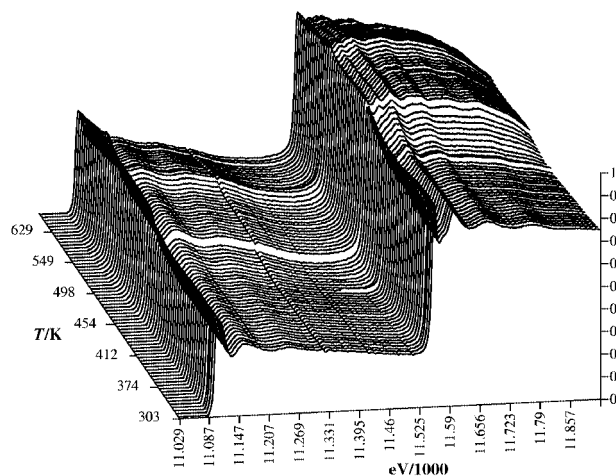


Fig. 1 EDEXAFS spectra for the Pt L_{III} and Ge K edges in the temperature range 298–670 K. Each spectra represents a total acquisition time of 8 s (1000 acquisitions @ 8 ms each).

† Electronic supplementary information (ESI) available: background to EDE measurements. See <http://www.rsc.org/suppdata/cc/b0/b008809i/>

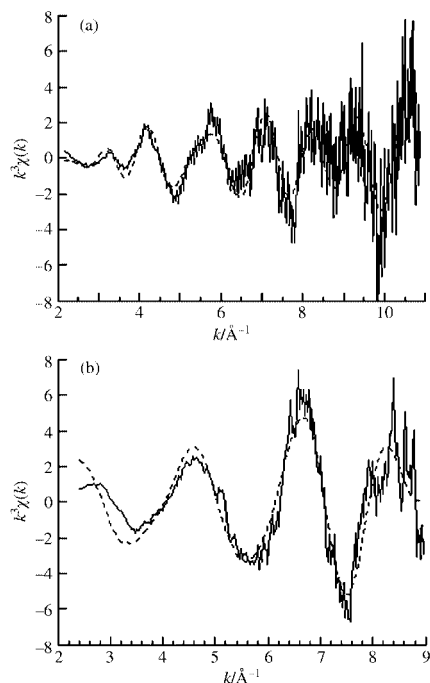


Fig. 2 Representative k^3 EXAFS for (a) Pt L_{III} and (b) Ge K edges derived from data shown in Fig. 1 for $T = 543$ K; experiment (—); fit derived from explicit analysis in EXCURV98 (- - -).

Table 1 Structural and statistical parameters derived from the dual edge analysis shown in Fig. 2^a; method as in ref. 7

Edge	Shell	CN	$r/\text{Å}$	1.5% error in r	$2\sigma^2/\text{Å}^2$	R factor (%)
Ge K	C	1.9(0.2)	1.98(2)	0.0297	0.004(3)	46.3
	Pt	2.0(0.3)	2.52(2)	0.0378	0.011(3)	
Pt L_{III}	Ge	0.5(1)	2.42(1)	0.0363	0.006(3)	62.3
	Pt	7.3(3)	2.74(1)	0.0411	0.020(2)	

^a $\Delta k(\text{Pt } L_{III}) = 2\text{--}12 \text{ Å}^{-1}$.

system to form Pt–Ge alloy particles occurs in at least three stages and allows determination of the effect of Ge on the reductive process.

The initial reduction stage appears to involve only the formation of Pt clusters with no concomitant formation of Pt–Ge bonds. The formation of the Pt particles however is very different to that observed for the analogous Pt only system.⁷ The initial reduction is similar in terms of light-off temperature, however, whereas the elemental system develops a Pt–Pt coordination of $10 (\pm 1)$ over a *ca.* 20 K temperature range, the Pt–Ge sample displays a much slower evolution of Pt–Pt coordination: over a *ca.* 40 K temperature window only a metastable coordination of $4 (\pm 0.4)$ is reached. At temperatures > 440 K the observed Pt–Pt coordination slowly rises to a

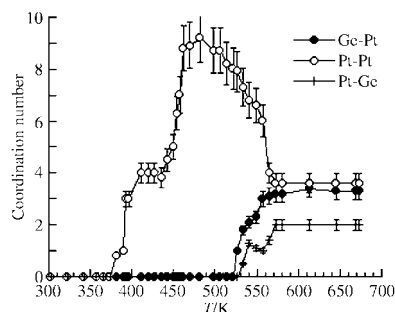


Fig. 3 Temperature dependence of Pt–Pt, Pt–Ge, Ge–Pt coordination during reduction of the $\text{Pt}(\text{acac})_2/\text{GeBu}_4/\text{H}_4\text{SiO}_2$ sample from analysis of individual spectra shown in Fig. 1. Error bars are shown at a fixed $\pm 10\%$.

maximal Pt–Pt coordination of $9 (\pm 1.8)$ attained at *ca.* 475 K. Low Z (C/O) coordination (from the Pt L_{III} edge) is also retained over a considerably extended temperature range relative to that observed in the elemental system.

At temperatures above *ca.* 460 K the Pt–Pt coordination starts to decline indicating either the onset of alloy formation and/or a morphological change in the particulate Pt. Concomitant changes in the Ge environment start to be observable with a gradual loss of low Z (C/O) coordination. Above > 500 K a signal fitting Pt–Ge components is apparent. These interactions continue to evolve until a stable phase emerges above 570 K, characterised from the Ge edge by an average coordination of 3.4 Pt coordination, and from the Pt edge by 3.4 Pt and 2 Ge. It is not however until 650 K that the fitting of low Z components at the Ge K edge is not observed to produce a significant reduction in obtained R factor.

Reduction of the mixed organometallic system results in significant alloy formation at temperatures *ca.* 250 K lower than seen in more conventional systems supported upon Al_2O_3 ,¹¹ though carbon retention from cracking of the ligands initially present persists to *ca.* 650 K. The EDEXAFS results also indicate the production of alloy particles that are smaller than the elemental particles produced from the Pt-only system;⁷ this differential is deemed to be a direct result of the Ge induced modification of the initial stage of the reductive process.

This work shows that considerable structure/phase information may be derived from explicit analysis of the EXAFS from two edges interrogated simultaneously. This methodology could be used for the simultaneous interrogation of a number of systems containing elements showing K or L_{III} edges in the correct energetic proximity (see ESI†), for example Pt–Au, Cu–Ni and the aforementioned, Cu–Zn system.

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