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Extended X-ray absorption fine structure (EXAFS) characterisation of the hydroformylation of oct-1-ene by dilute Rh–PEt$_3$ catalysts in supercritical carbon dioxide†

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Dilute EXAFS characterisation has been used to elucidate species involved during the course of the 3 mM Rh-catalysed hydroformylation of oct-1-ene in scCO$_2$; significant metal clustering occurs with a Rh:P ratio of 1:1 but at a 1:3 ratio, metal clustering is not detected, with the presence of monomer species only.

Supercritical carbon dioxide (scCO$_2$) has emerged as a favoured option for the replacement for organic solvents in chemical processing.[1] CO$_2$ has many potential advantages over the commonly used organic solvents, as it reduces the need for petroleum based materials and associated disposal problems, and facilitates separation of catalysts from products. Also the high solubility of gases in scCO$_2$ means that gas transport problems in reaction media are eradicated. However one drawback of scCO$_2$ is that only volatile or relatively non-polar compounds are soluble. Hence, there has been considerable interest in assessing this as a solvent for homogeneous catalysis, in reactions such as alkene hydroformylation.[2,3]

The hydroformylation of alkenes is a very important homogeneous catalysed reaction, industrially producing more than six million tons of aldehydes and alcohols annually.[4] The triarylphosphine rhodium complexes typically used in homogeneous reactions have very low solubility in scCO$_2$. Recently, reports have been published which examine the use of readily available trialkylphosphines, which are readily soluble in scCO$_2$ and show excellent activities in the hydroformylation reaction.[2,3a] Some high pressure IR spectroscopy studies have been conducted on these catalysts with results indicating the solubility of the rhodium–phosphine complex in scCO$_2$[2] and indicating the predominance of three species in toluene under similar conditions.[5]

Within this work, we report the EXAFS characterisation of species present during the course of the hydroformylation of oct-1-ene in scCO$_2$. Due to the dilute nature of the catalytic species ([Rh] = 3 mM) matching those typically used in industrial situations and the requirement for a small sampling window to accommodate the elevated pressures, Beamline ID26 at the European Synchrotron Radiation Facility (ESRF), providing very high X-ray brilliance, allowed these type of measurements to be made and dilution limits to be overcome.[6]

Fig. 1 shows Rh K-edge EXAFS and Fourier transform spectra obtained from various samples and stages in the Rh-catalysed hydroformylation system. Spectrum (a) shows a 10 mM [Rh] [Rh(CO)$_2$(acac)] (acac = acetylacetonate) dissolved in octane, and spectrum (b) shows 2–3 mM [Rh] [Rh(CO)$_2$(acac)] mixed in 1:1 ratio with triethylphosphine (PEt$_3$) in octane. Spectra (c) and (e) show 2–3 mM [Rh] [Rh(CO)$_2$(acac)]:PEt$_3$ in a mixture of oct-1-ene, hydrogen, carbon monoxide and liquid carbon dioxide (l-CO$_2$)‡ with a Rh:P ratio of (c) 1:1 and (e) 1:3. Spectra (d) and (f) show 2–3 mM [Rh] [Rh(CO)$_2$(acac)]:PEt$_3$ in an identical mixture but in super critical carbon dioxide (scCO$_2$)‡ with Rh:P ratio of (d) 1:1 and (f) 1:3. The Rh K-edge EXAFS-derived structural parameters are summarised in Table S1.†

Initially, investigations of the EXAFS and Fourier transform of some known Rh precursors, associated with the starting species present in the hydroformylation reaction ([Rh(CO)$_2$(acac)] and a solution of [Rh(CO)$_2$(acac)]:PEt$_3$; Rh:P = 1) were conducted to investigate the applicability of dilute EXAFS towards the elucidation of the structure of catalytic intermediates in solution and to validate our approach. The EXAFS data for [Rh(CO)$_2$(acac)] is consistent with a 5 shell co-ordination sphere model consisting of 2 carbons at 1.91 Å, 2 oxygens at 2.08 Å, 2 carbons at 2.88 Å, 2 oxygens at 2.97 Å and 1 carbon at 3.28 Å. The Rh–C–O group was treated as a multiple scattering unit (Rh–C 1.91 Å, Rh..O 2.97 Å). This is in good agreement with the crystallographic model of [Rh(CO)$_2$(acac)] previously reported in the literature.[7] The EXAFS and FT of the solution of [Rh(CO)$_2$(acac)] and PEt$_3$ shows significant differences compared with the solution of [Rh(CO)$_2$(acac)] alone, with the Fourier transform showing an increase at the feature around 2.2 Å and a large reduction in the features at 1.8 and 3.0 Å. More detailed analysis show a 5 shell coordination sphere with 1 carbon at 1.81 Å, 2 oxygen at 2.06 Å, 1 phosphorus at 2.25 Å, 1 oxygen at 2.92 Å and 2 carbons at 2.93 Å, again utilising a linear Rh–C–O unit. This model compares very well with the crystallographic model for the analogous species [Rh(CO)(PPh$_3$)(acac)].[8] These results clearly indicate that good quality EXAFS data up to $k \approx 12\text{Å}^{-1}$ can be obtained using this approach,

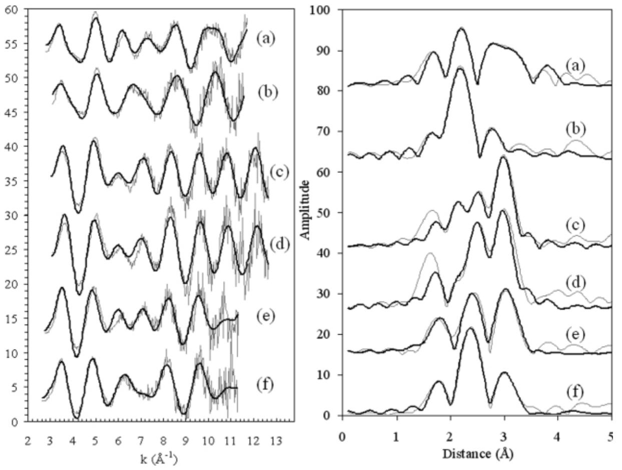

Fig. 1 The Rh K-edge k^3-weighted EXAFS and Fourier transform of (a) 10 mM [Rh] [Rh(CO)$_2$(acac)] dissolved in octane, (b) 2–3 mM [Rh] [Rh(CO)$_2$(acac)] mixed in 1:1 ratio with PEt$_3$ in octane. Spectra (c)–(f) show 2–3 mM [Rh] [Rh(CO)$_2$(acac):PEt$_3$] in a mixture of oct-1-ene, hydrogen, carbon monoxide in (c) l-CO$_2$ at Rh:P = 1, (d) scCO$_2$ at Rh:P = 1, (e) l-CO$_2$ at Rh:P = 3 and (f) scCO$_2$ at Rh:P = 3. Grey and black lines indicate experiment and theoretical fits derived from spherical wave, multiple scattering analysis in EXCURV98.[12]

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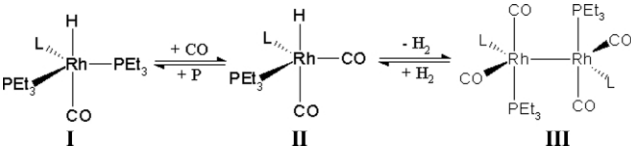
† Electronic supplementary data (ESI) available: data includes the Rh K-edge EXAFS-derived structural/statistical parameters for spectra shown in Fig. 1. See http://www.rsc.org/suppdata/cc/b3/b311331k/

at concentration levels typically used in industry, within a reasonable time scale.§

Therefore, the same technique was applied to the *in situ* elucidation of structures under catalytic conditions ($CO:H_2 = 1:1$) in l-CO_2 and scCO_2.‡ The experiments were conducted to obtain information about the resting state of the rhodium during catalysis under both l-CO_2 and scCO_2 solvent medium and with different Rh:P ratios (1:1 and 1:3) to try and elucidate any differences in the predominant species.

Initially, the 1:3 ratio was investigated as this has been previously been characterised by both *in situ* IR spectroscopy[9] and NMR[10] techniques. In l-CO_2, the resting state could be best modelled to a three-shell model consisting of 2 carbons at 1.94 Å, 2 phosphorus at 2.38 Å and 2 oxygens at 3.10 Å. This model is tentatively assigned to the hydridorhodiumdicarbonylbis(triethylphosphine) intermediate $[RhH(CO)_2(PEt_3)_2]$ (Scheme 1, Species II, L = PEt_3). Two interesting points arise from this fit: a) *no* rhodium shells could be detected indicating that no rhodium clusters or oligomers species are formed and b) attempts to fit a shell of carbon at 2.10 Å to model any acetyl species resulted in a deterioration of the fit and a high Debye–Waller factor, which dampens out this putative contribution. At higher temperatures *i.e.* in the scCO_2 phase, the EXAFS changed significantly suggesting a change in the structure of the catalytic species between the two phases of CO_2. The EXAFS could be best fitted to a three shell model containing 1 carbon at 1.89 Å, 3 phosphorus at 2.38 Å and 1 oxygen at 3.08 Å, which was assigned to the hydridorhodiumcarbonyltris(triethylphosphine) species, $[RhH(CO)(PEt_3)_3]$ (Species I, L = PEt_3), suggesting that all the phosphine is coordinated to the rhodium in the scCO_2 phase. Again, only monomer species were observed with no obvious features that could be associated with Rh–Rh distances. These results are extremely consistent with high-pressure infrared spectroscopy of the Rh–PEt_3 system recently reported in the literature, which presumes that as the temperature of the CO_2 is increased, the dominating species in solution is converted from $[RhH(CO)_2(PEt_3)_2]$ to $[RhH(CO)(PEt_3)_3]$ and related dimers.[2] However, unlike previous work conducted in toluene,[5] no dimer species could be observed thereby suggesting that in both phases of CO_2 the formation of dimer species at this Rh/P ratio is very limited.

Further studies were then conducted on the less well characterised Rh:P ratio of 1:1 to discover how the dominant species in solution compared with that observed for the 1:3 ratio. Interestingly, when the 1:1 ratio was investigated under both phases of CO_2, the EXAFS (which shows additional intensity in the higher k regions) indicated that Rh–Rh bonds *are* present in the resting state species indicating that either oligomer or cluster species are formed; inclusion of this shell reduced the R factor by 17%. For the l-CO_2, the data could be best fitted to a single cluster model containing 3 carbons at 1.99 Å, 1 phosphorus at 2.30 Å, 1 rhodium at 2.72 Å and 3 oxygens at 2.99 Å, which can be tentatively assigned to hexacarbonylbis(triethylphosphine)dirhodium $[Rh_2(CO)_6(PEt_3)_2]$ (Species III, L = CO). However, several important points arise from this fitting: a) EXAFS is an average technique and consequently, the present fit is likely to be due to more than one species in solution (however, attempts to fit a two cluster model to the data, a monomer species such as species I and small rhodium cluster ($N = 3$), did not produce a successful fit to the data), b) the addition of a shell of carbon at 2.07 Å to model an acetyl group leads to only a minimal improvement of the fit and c) a deterioration in the fit was always observed if the shell of phosphorus was not included suggesting that phosphorus is directly attached to the rhodium in the resting state species. For the scCO_2 phase, the EXAFS suggested a very similar model. However, the addition of a second rhodium made a significant improvement to the fit. Therefore, it is hypothesised that on changing phase (liquid to super critical CO_2), there may be an increase in the degree of oligomerisation occurs possibly leading to the partial formation of oligomeric species, such as PEt_3 substituted derivatives of $Rh_4(CO)_{12}$. Again for this system, the fitting of a shell of carbon leads to minimal improvement in the fit and so cannot be thought to be conclusively present.



Scheme 1 Hypothesised resting states for rhodium during hydroformylation (L = CO or PEt_3).

In conclusion, we have demonstrated that good quality EXAFS can be collected in an *in situ* manner at the Rh K-edge on species at dilute concentration levels matching those typically used in industry under l- and scCO_2 conditions. Furthermore, the results have presented several features worthy of note: a) at Rh:P = 1:3, the dominant species at higher temperatures *i.e.* scCO_2 phase is hypothesised to be the monomer $[RhH(CO)(PEt_3)_3]$, consistent with and complimentary to previous published IR studies of this system,[2] b) at a Rh:P = 1:3, both phases of CO_2 prevent oligomerisation/clustering of the rhodium (*c.f.* toluene[5]) with only monomer species present and no clear indication of acetyl ligand and c) a Rh:P ratio of 1:1 leads to oligomerisation of the rhodium to form dimer species in all phases of CO_2.

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Notes and references

‡ The experiments were conducted using equipment designed and tested previously for sc-H_2O studies at the ESRF[11] with the cell consisting of a PEEK tube allowing efficient fluorescence detection and hot air heating to interchange between liquid (ambient temperature) and scCO_2 (43 °C). The cell was initially pressurised with H_2 (10 bar), CO (10 bar) and CO_2 (120 bar) at room temperature for the hydroformylation experiments.

§ Dilute EXAFS was collected using a Canberra 13-element Ge detector, tuned to the Rh K_α fluorescence peak. An average of 8 scans was required with a scan time of 25 min.

1 (*a*) *Chemical Synthesis using supercritical fluids*, Eds. P. G. Jessop and W. Leitner, Wiley-VCH, Weinheim, 1999; (*b*) J. A. Darr and M. Poliakoff, *Chem. Rev.*, 1999, **99**, 495; (*c*) *Green Chemistry: Frontiers in Benign Chemical Synthesis*, P. T. Anastas and T. C. Williamson, Eds., Oxford University Press, Oxford, 1998.
2 M. F. Sellin, I. Bach, J. M. Webster, F. Montilla, V. Rosa, T. Avilés, M. Poliakoff and D. J. Cole-Hamilton, *J. Chem. Soc, Dalton Trans.*, 2002, 4569.
3 (*a*) I. Bach and D. J. Cole-Hamilton, *J. Chem. Soc, Chem. Comm.*, 1998, 1463; (*b*) A. M. Banet Osuna, W. Chen, E. G. Hope, R. D. W. Kemmit, D. R. Paige, A. M. Stuart, Xiao and L. Xu, *J. Chem. Soc, Dalton Trans.*, 2000, 4052; (*c*) J. Ke, B. Han, M. W. George, H. Ya and M. Poliakoff, *J. Am. Chem. Soc.*, 2001, **123**, 3661.
4 P. N. W. M. Van Leeuwen and C. Claver, *Rhodium Catalysed Hydroformylation*, Kluwer, Dordrecht, 2000.
5 J. K. MacDougall, M. C. Simpson, M. J. Green and D. J. Cole-Hamilton, *J. Chem. Soc, Dalton Trans.*, 1996, 1161.
6 C. Gauthier, V. A. Sole, R. Signorato, J. Goulon and E. Moguiline, *J. Sync. Rad.*, 1999, **6**, 164.
7 F. Huq and A. C. Skapski, *J. Cryst. Mol. Str.*, 1974, **4**, 411.
8 J. G. Leipoldt, S. S. Basson, L. D. C. Bok and T. I. A. Gerber, *Inorg. Chim. Acta*, 1978, **26**, L35.
9 M. Dieguez, C. Claver, A. M. Masdeu-Bulto, A. Ruiz, P. W. N. M. Van Leeuwen and G. C. Schoemaker, *Organometallics*, 1999, **18**, 2107.
10 J. M. Brown and A. G. Kent, *J. Chem. Soc, Perkin Trans. 2*, 1987, 1597.
11 D. T. Bowron, R. Weigel, A. Filipponi, M. A. Roberts and J. L. Finney, *Molec. Phys.*, 2001, **99**, 761.
12 N. Binsted, *EXCURV98*, CCLRC Daresbury Laboratory computer programme, 1998.