ESRF	**Experiment title:** **Energy-dispersive EXAFS studies of homogeneous metal catalysts**	**Experiment number:** **CH-280**
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Report:

An ambient temperature stopped-flow cell was used to investigate the activation of nickel ß-diketonate complexes by aluminium alkyls. The stopped-flow system was synchronised with the CCD camera to allow relatively fast reactions to be monitored by Ni K-edge EDE. The data quality achieved by with the new CCD detector and station protocol now allowed EXAFS data to be discerned, rather than merely XANES.[1]

Initially a known system was used for comparison purposes,[1,2] this being the formation of a hex-1-ene dimerisation catalyst by the reaction of $[Ni(acac)_2]_3$ with $AlEt_2(OEt)$ in toluene solution. The results of one reaction over a 24 minute reaction period are shown in Figure 1. Each spectrum was acquired in 200 ms with a 14 s interval between acquisition. The spectra show the formation of the active species, considered to be [Ni(acac)(R)(hexene)] over a 6 minute period. The decay of $[Ni(acac)_2]_3$ appears to be a single exponential; this supports the conclusion that the apparent two step reaction2 was an artefact of slow mixing in an earlier reaction vessel. The reaction of the ß-diketonate with the more reactive $AlEt_3$ forms an organometallic centre within 1.5 minutes, which then slowly (1 hour) forms metal clusters of *fcc* local structure, as shown by previous QuEXAFS experiments at the SRS; these can be modelled best as a 19 atom fragment of the bulk structure.3

Activation of the square planar complex [Ni(dpm)2] {dpm = $OCBu^tCHCBu^tO$} by AlEt2(OEt) and PPh3 was found to give a very fast reaction. In Figure 2, smoothed XANES spectra are given which follow the reaction over 28 s, with spectral intervals of 0.28 s. Observing the development of edge feature, the reaction can be seen to reach completion within 2 s.

Figure 1.

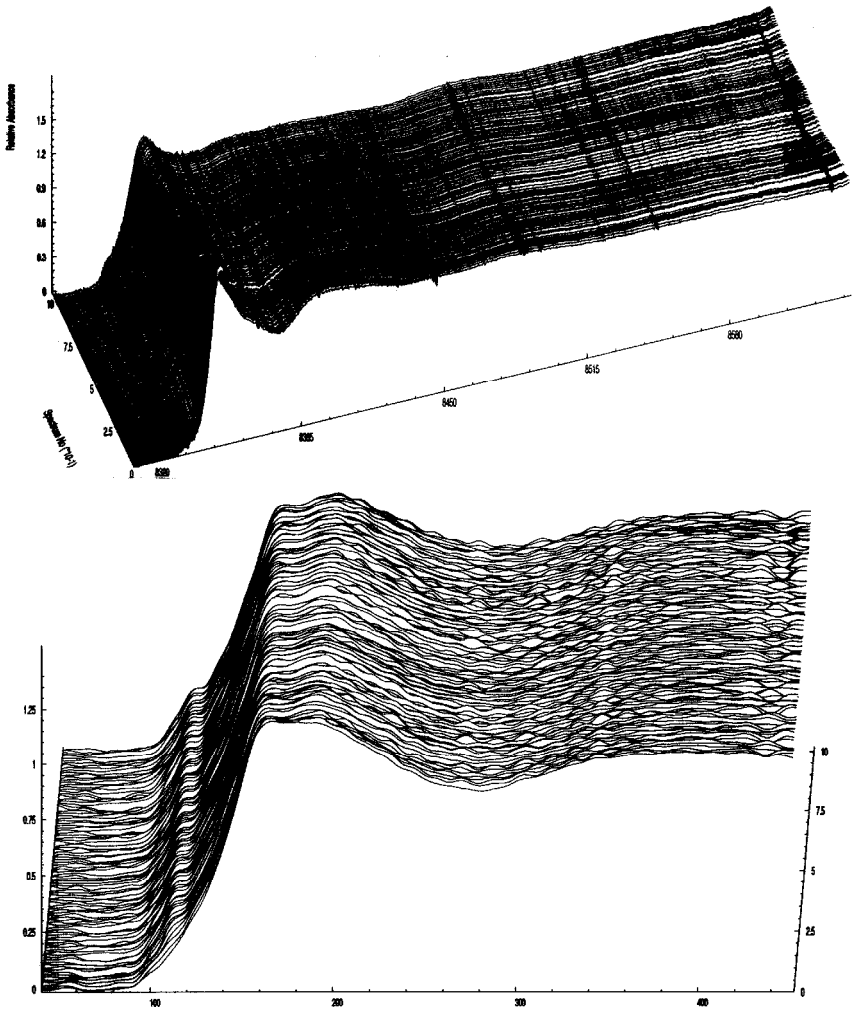

Figure 2

References

1 .J. M. Corker, A. J. Dent, J Evans, M. Hagelstein, and V. L. Kambhampati, *J. Phys. IV France,* 1997,7, C2-879.

2. D. Bogg, M. Conyngham, J. M. Corker, A. J. Dent, J. Evans, R. C. Farrow, V. L. Kambhampati, A. F. Masters, D. Niles McLeod, C. A Ramsdale, and G. Salvini, J. *Chem. Soc., Chem. Commun.,* 1996,647.

3. N. Binsted, A. J. Dent, J. Evans and V. L. Kambhampati, *J. Chem. Soc., Chem. Commun.,*