

	<b>Experiment title:</b> <b>ENERGY-DISPERSIVE EXAFS STUDIES OF HOMOGENEOUS METAL CATALYSTS</b>	<b>Experiment number:</b> <b>CH144</b>
<b>Beamline:</b> <b>ID24</b>	<b>Date of experiment:</b> <b>from: 12/6/96 to: 14/6/96</b>	<b>Date of report:</b> <b>23/8/96</b>
<b>Shifts:</b> <b>6</b>	<b>Local contact(s):</b> <b>M. Hagelstein</b>	<i>Received at ESRF:</i> <b>29 AUG 1996</b>

**Names and affiliations of applicants** (\* indicates experimentalists):

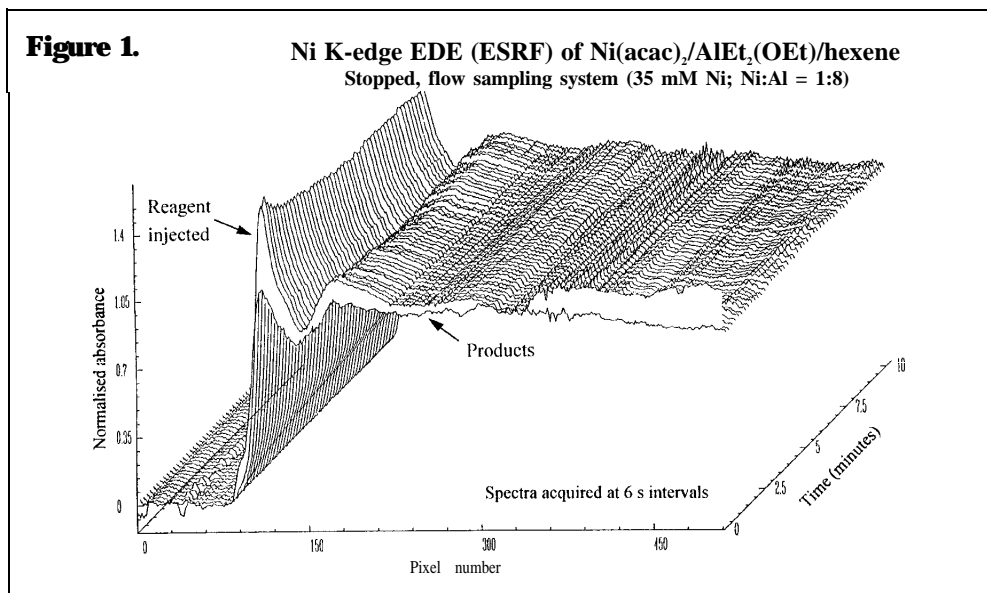
A J Dent*,	Daresbury Laboratory, Warrington, UK
J. Evans*,	University of Southampton, UK
M. Hagelstein*,	ESRF
V L Kambhampati*,	University of Southampton, UK

## Report:

For some years now we have carried out a series of studies using XAS to probe the activation of organometallic catalyst precursors by co-catalysts, dealing particularly with carbonylation reactions and alkene catenations, both of which have wide industrial application. 1 Our initial experiments used scanning XAS and relied on temperature variations to trap reactive species<sup>2</sup>, hence requiring the species to be stable at the solution temperature for a period of hours. More recently though we have refined the experiments, reducing the timescales of the experiments to minutes (by QuEXAFS3) or seconds (by energy dispersive EXAFS, EDE<sup>4</sup>). In this way, structural profiles of solution reaction transients can be identified for the first time

In this study, energy dispersive Ni K-edge EXAFS (EDE) experiments were performed using a modified HiTech Scientific stopped-flow system with Kapton windows and giving a theoretical mixing time of 5 ms. A bent asymmetric-cut Si(111) monochromator in a Bragg geometry cooled by an In-Ga eutectic bath was used; the detector was a **512x512 element Thomson** CCD camera operating in a PDA emulation mode. The ESRF was operating in **16** bunch mode with beam currents of 70-100 mA. EXAFS data were typically acquired 60x40 ms scans (*ca* 3 s acquisition time) on the reaction between [Ni(acac)<sub>2</sub>]<sub>3</sub> and AlEt(OEt)<sub>2</sub> and hex-1-ene in dry toluene (a homogeneous catalyst for the dimerisation of hex-1-ene<sup>5</sup>).

The stopped flow mixing system and cell were used for the first time, and operated successfully. It is intended that for future experiments the solution mixing control will be synchronised with the data acquisition system electronically. An example of one of the stacked plots for the alkylation of the nickel complex is shown in Figure 1.6 This shows the



reduction in white line intensity as the reaction proceeds; kinetic plots from these reaction showed an increase in reaction rate with increased aluminium concentration.

In the brief time allocated for these experiments the potential for stopped flow EXAFS was demonstrated. However, the data quality obtained only provided near-edge features with any reliability.

## References:

- 1 J. Evans, *Chem. Ind.*, 1995, 135.
- 2 J M Corker and J Evans, *J. Chem. Soc., Chem. Commun.*, 1991, 1104
- 3 N A Cruise and J. Evans, *J. Chem. Soc., Dalton Trans.*, 1995, 3089
- 4 D. Bogg, M. Conyngham, J. M. Corker, A. J. Dent, J. Evans, R. C. Farrow, V. L. Kambhampati, A. F. Masters, D. N. McLeod, C. A Ramsdale, and G. Salvini, *J. Chem. Soc., Chem. Commun.*, 1996,647.
5. J. R. Jones and T. J. Symes, *J. Chem. Soc. C*, 1971, 1124.
6. J M Corker, A J Dent, J Evans, M Hagelstein and V L Kambhampati, *J. Physique (C)*, submitted for publication.