Asian Journal of Chemistry Vol. 15, No. 2 (2003), 1097–1102

Time-Resolved Energy Dispersive EXAFS Measurement of Oligomerisation Reaction Catalysed by Nickel Homogeneous Catalyst on Addition of Triphenylphosphine and $AlEt_2(OEt)$ as Co-Catalyst

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Energy dispersive EXAFS (EDE) data have been analysed for the nickel (3-diketonate catalysts, $Ni(dpm)_2$, using curved wave theory with *ab initio* phase shifts. The derived parameters for metal compounds were in good agreement, within experimental error of 0.02–0.05 Å for the bond distances. Time-resolved EDE studies on $Ni(dpm)_2 : PPh_3 : AlEt_2(OEt)$: 1-hexene of 1 : 2 : 4 : 20 were acquired within 0.24 s for each spectrum. The growth of a pre-edge feature and change at the top of the edge can be clearly seen to show that the reaction reached completion in less than 6 s. A stopped flow system was used for *in situ* time-resolved EDE studies on the nickel systems at room temperature. EDE measurements using a new rectangular Si(III) monochromator and Hamamatsu S4874 photodiode array at Station 9.3, Daresbury Laboratory have yielded consecutive spectral data taken at 1-1000 accumulations with 2-30 ms integration time to follow the changes during initiation of the catalytic reaction.

Key Words: EXAFS, Time-resolved, Oligomerisation, Nickel homogeneous catalysist.

INTRODUCTION

The oligomerisation of alkenes such as ethane, propene and butadiene using homogeneous catalysts has received much attention recently[1]. We are interested in using the adducts of $Ni(dpm)_2(PPh_3)_2$, which is pseudo-octahedral, in order to study the selectivity of phosphines as co-catalysts. The catalytic activity of (3-diketonato nickel complexes towards alkene oligomerisation on addition of co-catalysts was strongly affected by the nature of β-diketonato substituents. Previously, numerous workers have investigated the mechanism of nickel oligomerisation, *e.g.*, $Ni(acac)_2$, $Ni(sacsac)_2$ and $Ni(cod)_2$ with alkyl-aluminium, $AlEt_2(OEt)$ and $AlEt_3$ using XAS, EXAFS and QuEXAFS spectroscopies[2, 3].

These systems are often extremely active towards alkene oligomerisation, even at low temperature, making them difficult to study by standard technique. We have now reported the NiK-edge energy dispersive EXAFS results which probe the local structure of the major species present during the activation and operation of the active 1-hexene oligomerisation catalysts.

EXPERIMENTAL

In this study, energy dispersive EXAFS experiments were performed using a

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modified HiTech 19 Scientific stopped-flow system with Kapton windows and giving a theoretical mixing time of 5 ms. A bent asymmetric-cut Si(220) monochromator in a Bragg geometry cooled by an In-Ga eutectic bath was used[4–6]. Calibration of spectra with respect to a Ni foil monitor and background subtraction was achieved using the program PAXAS[7]. Curve fitting analysis by least squares refinement of the non-Fourier filtered k^3-weighted data was carried out within EXCURVE, using spherical wave method with *ab initio* phaseshifts and backscattering factors[8]. The statistical validity of shells was assessed by published means[9, 10].

RESULTS AND DISCUSSION

The mixing of the solutions $Ni(dpm)_2(PPh_3)_2$, [Ni] (60 mM) and $AlEt_2(OEt)$, [Al] (240 mM) in the cell was investigated using the four point bender monochromator at Station 9.3. For convenience the data were all recorded at room temperature. Time-resolved EDE recorded 30 consecutive spectra with 50 accumulations of 24 ms integration time as shown in Fig. 1. The first spectrum taken after 1.2 s shows similarity with the precursor **1**. Indeed, it has been possible to fit with two β-diketonate ligands consisting 3.9 (3) oxygen atoms at 1.923 (11) Å in the first coordination sphere and 1.8 (4) phosphorus atoms at 2.346 (48) Å in the second coordination sphere[11].

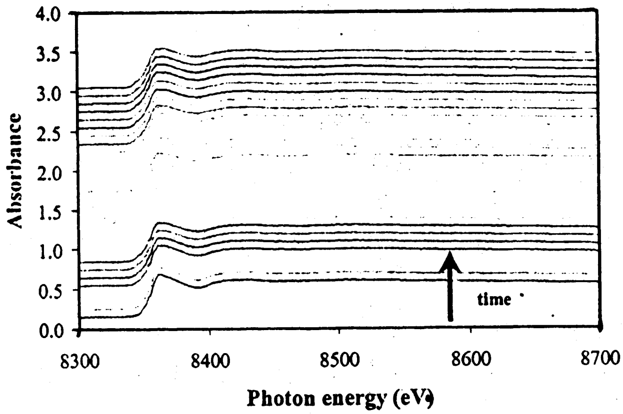


Fig. 1. Time-resolved dispersive EXAFS spectra for the reaction of $Ni(dpm)_2 : PPh_3 : AlEt_2(OEt)$: 1-hexene of 1 : 2 : 4 : 20. This data was collected at a rate of 1.2 s per frame. Each frame comprised 50 accumulations with 24 ms integration time.

Initially, we refined the parameters for all shells apparent in the first coordination sphere within the range of Fourier filtering (1 to 3.2 Å). Although the Fourier transform of the k^3-weighted spectrum seems to contain structure approximately up to 3.0 Å, the outer shells are clearly contaminated with noise, and were not seriously examined.

The resulting structural parameters (summarised in Table-1) were plotted *vs.* time, and as displayed in Fig. 2, showed the reduction in oxygen coordination number from 3.9 to 2.0 carbon atoms after 3.6 s from the addition of the co-catalyst. This follows from the appearance of averaged atoms in the first oxygen/carbon shell. The 2nd spectrum recorded after 2.4 s may correspond to 2, with two ligands dpm [3.8 (4) oxygen atoms at 1.918 (3) Å], and only one ligand PPh_3 [1.1 (5) phosphorus atom at 2.448 (11) Å] bonded to the nickel centre indicating a square-pyramidal geometry in the intermediate changes. A plausible sequence is proposed in Fig. 3.

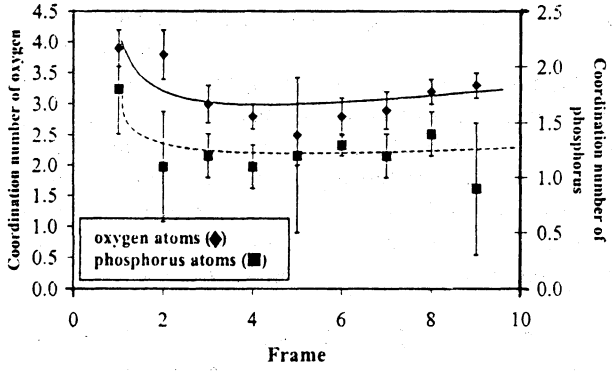


Fig. 2. Variation of coordination number with time for the reaction $Ni(dpm)_2 : PPh_3 : AlEt_2(OEt)$: 1-hexene of 1 : 2 : 4 : 20. This data was collected at a rate of 1.2 s per frame.

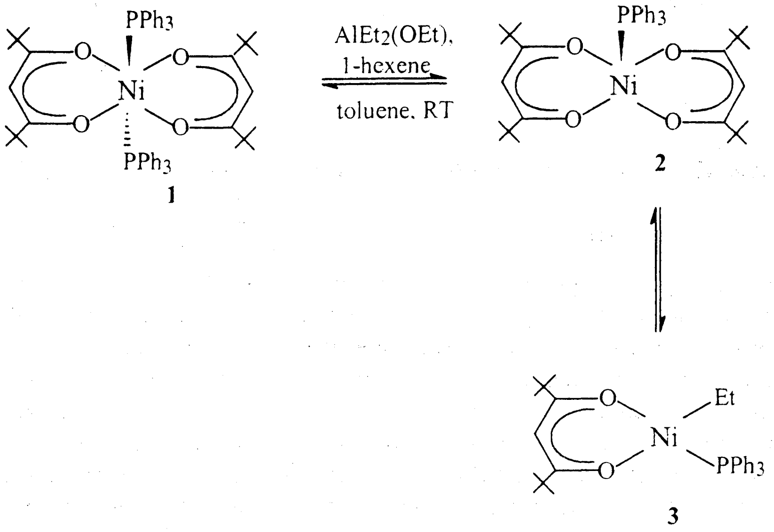
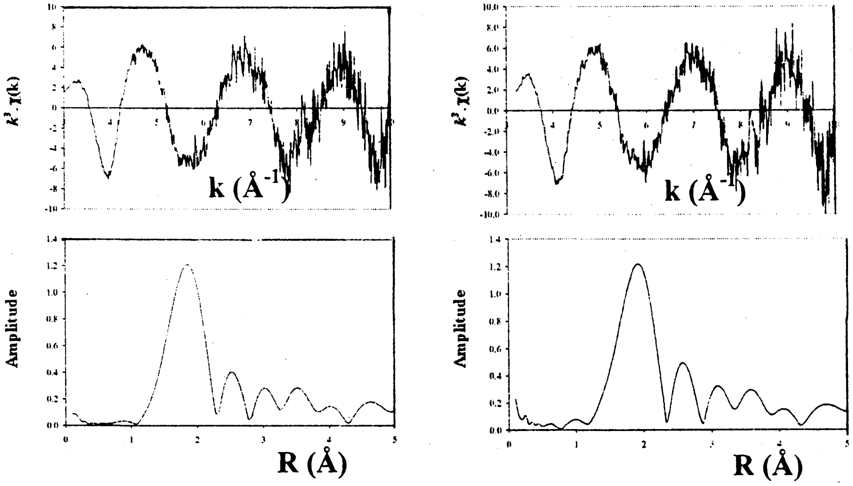
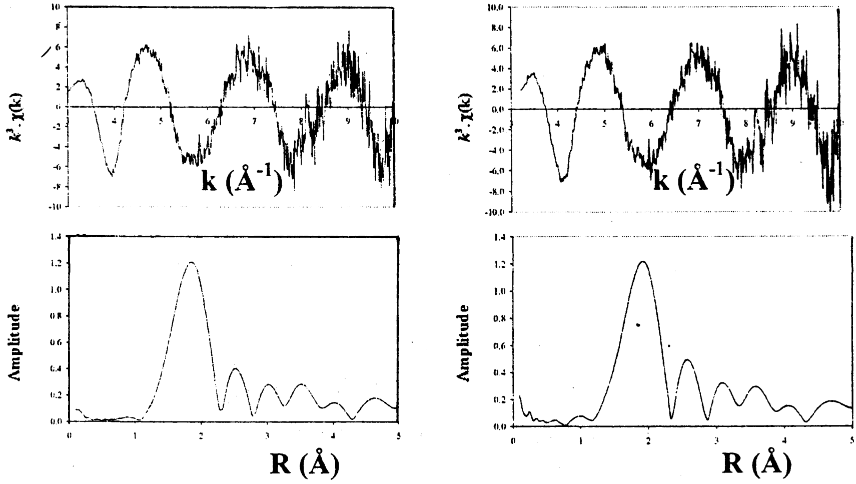


Fig. 3. Proposed sequence for the reaction of $Ni(dpm)_2 : PPh_3 : AlEt_2(OEt)$: 1-hexene of 1 : 2 : 4 : 20 from the resulting structural parameters derived from time-resolved dispersive EXAFS.

Attempts to fit the spectra with another loss of ligand PPh_3 as $Ni(dpm)_2$ were unsucecssful. The changes in the structure also identified by EXAFS oscillations zero crossing at 3.7, 4.2 and 5.5 k Å^{-1} (Fig. 4a) compared to 3.5, 4.2 and 5.3 k Å^{-1} (Fig. 4b). Spectra recorded after the 3rd spectrum (0.72 s) indicate a loss of one dpm with a reduction in the coordination number of the first row atoms by 2.0 oxygen in the first coordination sphere. The first combined oxygen/carbon shell is fitted with 3.0 (3) atoms at 1.917 (41) Å.



(a) frame 1/30 (b) frame 2/30



(c) frame 5/30 (d) frame 9/30

Fig. 4. The EDE Ni K-edge k^3-weighted EXAFS and Fourier transform, phaseshift corrected for oxygen, of the reaction of Ni(dpm)$_2$ + pph$_3$ + AlEt$_2$(OEt) + 1-hexene; 1 : 2 : 4 : 20; Ni[60 mM] : Al[240 mM], 50 accumulations with 24 ms.

The 1.2 (2) phosphorus atom refined at 2.116 (3) Å from the nickel, as organometallic **3** as derived from the curve fit for the 5th spectrum. These Ni-P bonds were derived as approximately 2.1–2.2 Å are shorter than in the starting material after loss of one dpm group and one PPh$_3$ group. This observation is similar to $Ni(acac)PEt_3(R)$ observed by Corker[1] on addition of PEt_3 to $Ni(acac)_2$ with $AlEt_2(OEt)$, and those derived in the crystal, *viz.* (Ni-O 1.88 Å and Ni-P 2.13 Å). Using EDE, Kambhampati[11] reported structural parameters of 3 Ni-C/O 1.89 Å and 1 Ni-P 2.11 Å for the transmetallation of $[Ni(acac)_2]_3$ with $AlEt_2(OEt)$ and PEt_3 on 1-hexene oligomerisation.

TABLE-1

STRUCTURAL PARAMETERS DERIVED FROM THE TIME-RESOLVED EDE RECORDED 30 CONSECUTIVE SPECTRA, 50 ACCUMULATIONS AT 24 ms INTEGRATION TIME

Frame	EF	R (%)	FI (10^{-3})	CN	R (Å)	A (Å^{-2})
1	2.85	50.71	8.2	3.9 (3) O 1.8 (4) P	1.923 (11) 2.346 (48)	0.006 (2) 0.018 (20)
2	2.46	48.31	7.8	3.8 (4) O 1.1 (5) P	1.918 (3) 2.448 (11)	0.008 (17) 0.010 (11)
3	8.49	49.59	7.5	3.0 (3) O/C 1.2 (2) P	1.917 (41) 2.116 (3)	0.022 (20) 0.001 (3)
4	5.29	49.76	7.4	2.8 (2) O/C 1.1 (2) P	1.905 (14) 2.103 (3)	0.024 (2) 0.003 (1)
5	6.27	47.18	7.2	2.5 (5) O/C 1.2 (7) P	1.919 (10) 2.092 (8)	0.005 (24) 0.006 (30)
6	7.22	45.24	6.5	2.8 (3) O/C 1.3 (1) P	1.918 (38) 2.101 (26)	0.024 (19) 0.007 (3)
7	11.94	46.43	7.2	2.9 (3) O/C 1.2 (2) P	1.864 (14) 2.099 (6)	0.015 (2) 0.003 (1)
8	9.27	44.86	6.4	3.2 (2) O/C 1.1 (2) P	1.894 (58) 2.100 (27)	0.022 (20) 0.001 (3)
9	7.80	44.03	5.9	3.3 (2) O/C 0.9 (6) P	1.878 (11) 2.112 (5)	0.017 (1) 0.003 (1)

Statistical errors are given in parentheses.

During the refinement, the Debye-Waller factors for the oxygen and carbon shells began to get unrealistically low and high respectively. The separate shells gave interchangeable bond distances in the first and second shells, and led to unrealistic coordination numbers and unexpected structural parameters. Larger coordination numbers gave rise to strong correlation between coordination numbers and bond distances. This means that the values for the oxygen and carbon shells are in a sense invalid. However, the short useable part of the spectrum can be analysed only up to 10 k Å^{-1} and high correlations between similar backscattering properties were apparent in bond distances for the oxygen and carbon shell to the nickel centre. Carbon, a weaker backscattering shell, is a little less well defined, having larger standard deviations. The 7th to 9th spectra gave similar observations within experimental error to this spectra with the mechanism proposed. An average of oxygen and carbon combined shell for the first shell is refined within 1.88 Å to 1.92 Å, usually being weighted toward the shorter shell due to non-Gaussian distribution distances and because of the $1/r^2$ dependence inherent in the theory. The spectrum showed the changes completed after 10.8 s and in agreement with the UV observation, where the rapid initial rate is monitored.

Conclusions

On addition of PPh_3 at room temperature, some evidence was present for the formation of $Ni(dpm)_2(PPh_3)$ but this may need to be further investigated at time scales of less than a second. Consistency in 3 Ni-O/C 1.89 Å and Ni-P 2.11 Å of $Ni(dpm)(Et)(PPh_3)$ were derived from the curve fitted data of the EDE spectra (Fig. 5). Precise structural parameters on first coordination sphere in the catalyst are limited due to the difficulties in resolving the shell for the oxygen and carbon due to their similar backscattering.

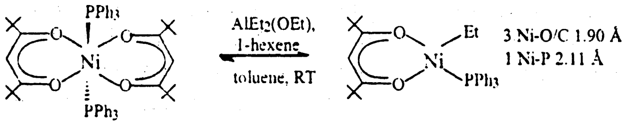


Fig. 5. Structural parameters monitored by EDE during catalysis

The success of these time-resolved EXAFS experiments has shown that this method is reliable to use for further investigations on reactions with a millisecond dead time. Improvement of the EDE method is still under way and development of the system, especially the detector and computing system, will promise a better time resolution.

ACKNOWLEDGEMENTS

We would like to thank the Synchrotron Radiation Source, Daresbury Laboratory, Warrington for the research grants and Universiti Putra, Malaysia for the sponsorship to Dr. Abdul Rahman.

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(*Received*: 25 November 2002; *Accepted*: 22 January 2003) AJC-2985