

TIME-RESOLVED ENERGY DISPERSIVE EXTENDED X-RAY ABSORPTION OF FINE STRUCTURE (EXAFS) MEASUREMENT OF OLIGOMERISATION REACTION CATALYSED BY NICKEL HOMOGENEOUS CATALYST AND ALKYL-ALUMINIUM CO-CATALYST

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ABSTRACT

Energy Dispersive EXAFS (EDE) data has been analysed for the nickel (3-diketonate catalysts, Ni(dpm)₂, using curved wave theory with *ab initio* phaseshifts. The derived parameters for nickel intermediate compounds were in good agreement, within experimental error of 0.02-0.05 Å for the bond distances. A stopped flow system was used for *in situ* time-resolved EDE studies on the nickel systems at room temperature. The growth of a pre-edge feature and change at the top of the edge can be clearly seen to show the reaction reached completion in less than 6 s indicates averaged distances of 3 Ni-O/C 2.00 Å.

Key words: Energy Dispersive Data (EDE), Nickel B, diketonate & *ab initio* phaseshifts.

INTRODUCTION

The oligomerisation of alkenes such as ethene, propene and butadiene using homogeneous catalysts has received much attention recently. A variety of nickel catalysts have been reported¹ to be active in producing -olefins from alkenes such as butene, hexene and octene. Keim² and coworkers and others have developed a number of nickel-based catalysts for alkene oligomerisation. The ethene oligomerisation reaction using Ni(cod)₂ and the ligand PPh₂CH₂C(CF₃)₂OH in toluene at 50°C, gives a system that catalyses the formation of higher olefins (C₄-C₂₀) from ethene. Linear and α-olefins, which are important compounds in the industrial synthesis of surfactants and plasticisers, are mainly produced by the oligomerisation of ethene. Higher α-olefins can be obtained from ethene through oligomerisation technologies, such as those used by Ethyl

Corporation (alkylaluminium co-catalyst) and Shell³ (SHOP - Shell Higher Olefins Process), which, with approximately a one million ton capacity in 1990, is one of the largest applications of homogeneous catalysis by a transition metal.

In particular, these systems are often extremely active towards alkene oligomerisation, even at low temperature, making them difficult to study by standard technique. This research will extend the scope of previous EXAFS studies on the activation of homogeneous nickel catalysts with alkyl aluminum reagents by concentrating on different catalyst precursors and improved time resolution. Extensive Ni K-edge EXAFS has proved useful for studying nickel catalysed propene dimerisation⁴ and oligomerisation. These studies probed the local structure of the major species present during the activation and operation of the active catalysts after addition of aluminium co-catalysts.

EXPERIMENTAL

In this, study energy dispersive EXAFS 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(220) monochromator in a Bragg geometry cooled by an In-Ga eutectic bath was used⁵⁻⁶. Calibration of spectra with respect to a Ni foil monitor and background subtraction was achieved using the program PAXAS⁷. 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 factors⁸. The statistical validity of shells was assessed by published means⁹⁻¹⁰.

RESULTS AND DISCUSSION

Extensive investigation of the system was carried out on a ratio of $\text{Ni(dpm)}_2\text{:AlEt}_2(\text{OEt})$ of 1:6 in the presence of 1 -hexene, where dramatic changes in the white line can be clearly seen in Figure 1. The 30 consecutive spectra were performed with a 16 ms integration time and 1000 accumulations. Single frame took 16 s, and reached completion within 8 min. Preliminary XANES analysis showed the intermediate reaction occurs in between the 1st to the 8th frame indicating changes of structural parameters takes place. Particular interest has focused on the application of EDE to study the first ten spectra, 20th, 30th (last consecutive spectrum) and after 20 minutes. Each spectrum was analysed in detail concerning the first and second coordination

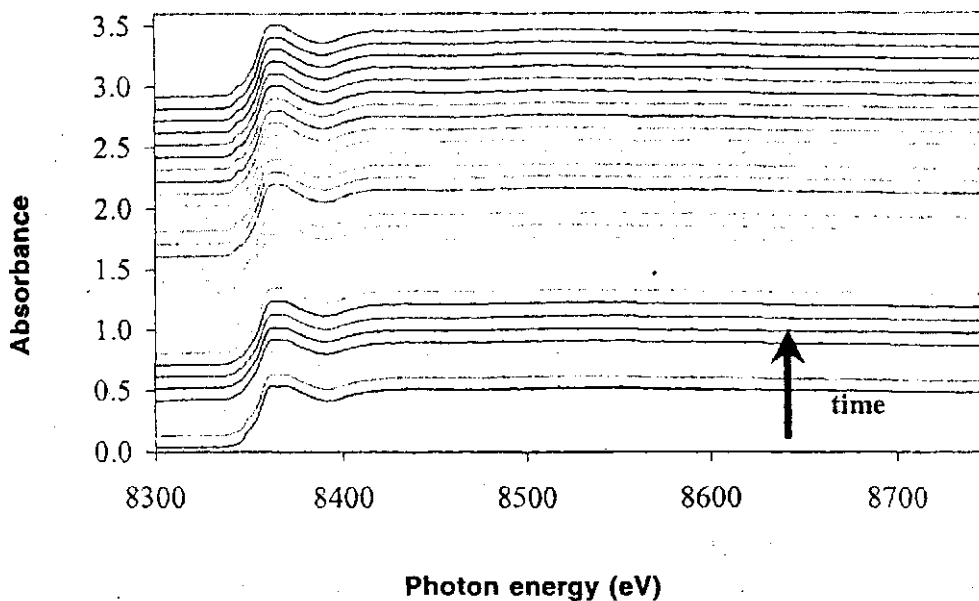


Figure -1 : The 30 consecutive spectra were performed at 16 ms integration time, 1000 accumulations. Singles frame took 16 s, and reach completion within 8 min. for $\text{Ni(dpm)}_2\text{:AlEt}_2(\text{OEt})$:1 -hexene of 1:6:20 [Ni] (60 mM) using stopped-flow techniques.

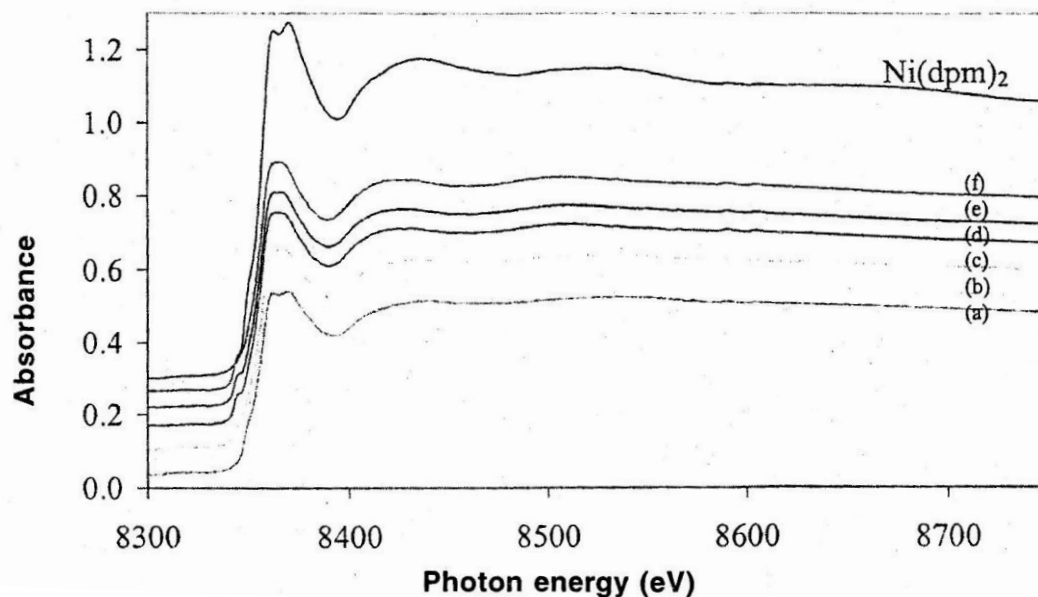


Figure -2 : Normalised Ni K-edge EDE spectra of Ni(dpm)_2 in toluene comparing the (a) 1st, (b) 2nd, (c) 9th, (d) 20th, (e) 30th and (f) after 20 min spectra for the reaction of $\text{Ni(dpm)}_2\text{:AlEt}_2(\text{OEt})\text{:1-hexene}$ of 1:6:20 [Ni] (60 mM).

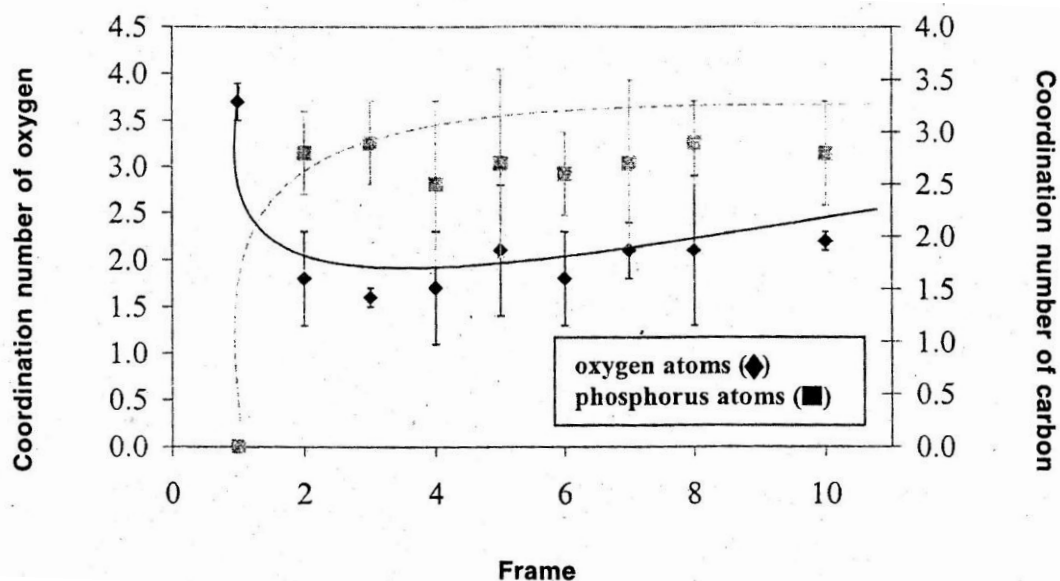


Figure -3 : The relationship between coordination number with time as derived from curve fitting for the dispersive EXAFS measurements of $\text{Ni(dpm)}_2\text{:AlEt}_2(\text{OEt})\text{:1-hexene}$ of 1:6:20 [Ni] (60 mM).

Table-1 :The Ni K-edge EXAFS analysis results for the reaction of Ni(dpm)₂:AlEt₂(OEt):1-hexene of 1:6:20, [Ni] (60mM) at room temperature using time-resolved EDE.

Frame	EF(eV)	R (%)	FI (X10 ⁻³)	CN	R(Å)	A(Å ⁻²)
1	6.69	44.67	6.0	3.7 (2) O	1.843 (3)	0.010
2	3.30	48.57	8.3	1.8 (5) O 2.8 (4) C	1.892 (35) 1.931 (42)	0.008 0.010
3	3.41	44.94	7.4	1.6 (1) O 2.8 (4) C	1.889 (26) 1.941 (28)	0.008 0.008
4	5.04	46.77	7.6	1.7 (6) O 2.5 (8) C	1.888 (55) 1.934 (26)	0.008 0.010
5	3.56	47.54	7.7	2.1 (7) O 2.7 (9) C	1.898 (31) 1.932 (29)	0.008 0.012
6	5.45	44.18	6.7	1.8(5) O 2.6 (4) C	1.898 (15) 1.927 (44)	0.008 0.012
7	3.6	44.26	6.8	2.1 (3) O 2.7 (8) C	1.905 (29) 1.937 (45)	0.008 0.012
8	4.94	41.76	6.3	2.1 (8) O 2.9 (4) C	1.902 (18) 1.927 (45)	0.008 0.012
10	3.32	42.77	7.3	2.2(1) O 2.8 (5) C	1.922 (26) 1.956 (41)	0.008 0.012
30	5.15	40.73	6.0	1.8(6) O 3.0 (5) C	1.919 (28) 1.970 (25)	0.008 0.008
20 min	4.07	36.39	4.4	1.8(5) O 3.1 (8) C	1.930 (40) 1.972 (31)	0.008 0.010

(Statistical errors are given in parentheses)

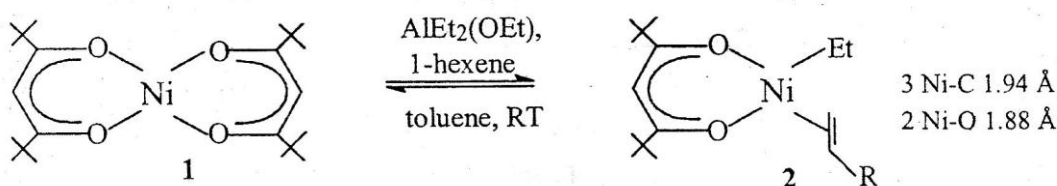


Figure -4 : Reaction consistent with the dispersive EXAFS results for the Ni(dpm)₂ catalyst reaction with AlEt₂(OEt) in timescales of 16 s (1000 scans x 16 ms).

sphere. The edge structure of the Ni K-edge spectrum shows a marked growing peak at the shoulder before the edge¹¹.

Figure 2 showed the normalised spectrum of the reagent solution is compared with 1st, 2nd, 9th, 20th, 30th and after 20 minutes indicates a changing process during the reaction. As observed above, 1.000 scans provide a better signal to noise ratio, although significant time resolution is lost. A good fit to all these spectra and their Fourier transform were obtained with a good approximation to the Ni-O (1.85 to 1.95 Å) and N-C bond distance (1.90 to 2.00 Å)¹². Refining the coordination numbers and bond distances for Ni-O and Ni-C produces the data as tabulated in Table 1. The decreased in oxygen coordination number in the first shell was noted 30 s after the addition of AlEt₂(OEt) indicating a change in the square planar geometry of Ni(dpm)₂. This was followed by the appearance of carbon atom coordination number in the second shell with 2.8 (4) carbon atoms and maintained to 3.1 (8) carbon atoms after 20 minutes as shown in the Figure 3. Time-resolved EDE and curve fitting analysis proposed¹³ a reaction as displayed in Figure 4.

Comparison of each spectrum showed that species 1 is observed in the first spectrum. The resulting background subtracted, k³-weighted, Ni K-edge dispersive EXAFS and Fourier transform are presented in Figure 5 (a-d), together with the best experimental fits. It is assumed that the precatalyst started to react with the co-catalyst within 16s (Figure 5a). After 32 s, a reduced number of oxygen atoms in the first coordination sphere correspond to species 2 (Figure 5b). The coordination number shows one ligand dpm is attached to the nickel centre (average of 1.6 to 2.2 oxygen atoms) within experimental error¹⁴. The second shell is fitted with a carbon atom from the ethyl group and hexene, and shows some inconsistency that either 2 or 3 carbon atoms are bonded. At this point, it is crucial to confirm whether intermediate forms first

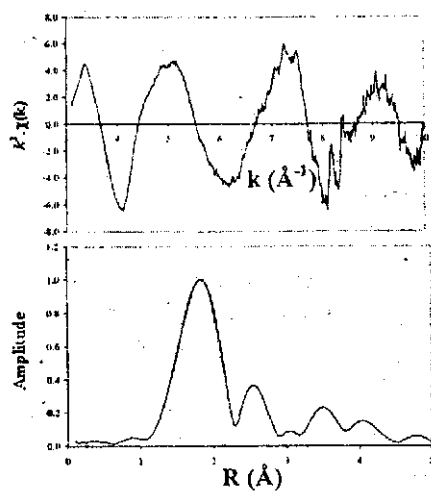
or the product is being produced as initial rapid changes occurred from 1st to the 10th spectrum¹⁵.

Analysis of the 5th spectrum (Figure 5c) revealed the apparent of 2.7 (9) carbon atoms at 1.932 (27) Å, meanwhile, on 6th spectrum, 2.6 (4) carbon atoms is fitted at 1.927 (22) Å on the second shell. Analysis of the final (30th) spectrum shows more consistent parameters and corresponds to species 2. 3.0 (5) carbon atoms are fitted at 1.970 (25) Å in the second shell. The spectrum was also recorded after 20 minutes of reaction. Analysis of the spectrum (Figure 5d) indicated that organometallic 2 is present in the solution, with 3.1 (8) carbon atoms well defined at 1.972 (31) Å. The solution remained homogeneously dark brown. However, detection on the dimplisation of hexene and oligomeric α -olefin was not investigated in this research.

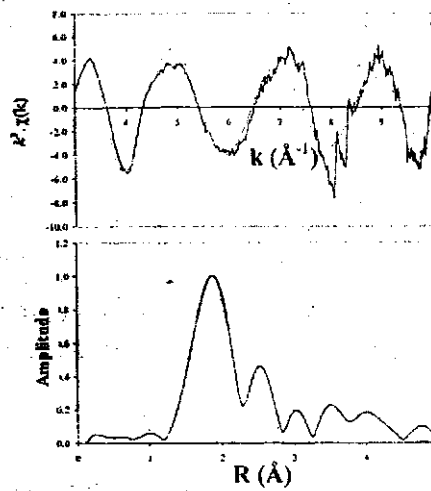
The experiment with the higher ratio was performed on the Ni(dpm)₂ catalyst using AlEt₂(OEt) of 1.6 M solution as 1:13.3 ratio of Ni(dpm)₂:AlEt₂(OEt). This run using 100 accumulations with 20 ms integration time showed changes after the 6th spectra but the data quality is not very good.

CONCLUSIONS

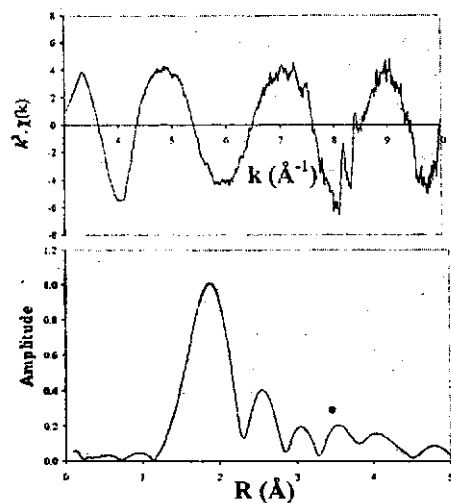
The characterization of the organometallic complex at different ratios of alkyl-aluminum co-catalyst, Ni(dpm)₂:AlEt₂(OEt) of 1:1, 1:2, 1:4, 1:6 and 1:13.3, and also different scan times, 1 to 1000 accumulations showed some consistency in the derived parameters support the reliability of dispersive EXAFS. Time-resolved EDE studies on Ni(dpm)₂/AlEt₂(OEt)/l-hexane of different ratios (1:1:20, 1:2:20, 1:4:20, 1:6:20, 1:8:20 and 1:13:20) at room temperature monitored the formation of Ni(dpm)C₂H₅(R), R=alkyl. The derived structural parameters from EDE gave averaged distances of Ni-O 1.86 Å and



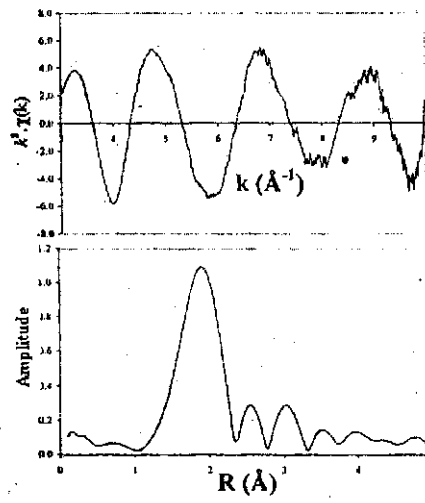
(a) frame 1/30



(b) frame 2/30



(c) frame 6/30



(d) after 20 minutes

Figure -5 :The EDE Ni K-edge K^3 - weighted EXAFS and Fourier transform, phaseshift corrected for oxygen, of the reaction of $\text{Ni(dpm)}_2 + \text{AlEt}_2(\text{OEt}) + 1\text{-hexene}$ of 1:6:20; Ni [60 mM]:Al[360mM], 1000scans, $t = 16\text{ms}$.

Ni-C2.00A. The $\text{Ni(dpm)}_2\text{:AlEt}_2(\text{OEt})\text{:1-hexene}$ of ratio of 1:6:20 were acquired within 16 s for each spectrum, EDE measurements using a new rectangular Si(111) monochromator and Hamamatsu S4874 photodiode array at Station 9.3, Daresbury Laboratory have yielded consecutive spectra data taken at 1-1000 accumulations with 2-30 ms integration time to follow the changes during initiation of the catalytic reaction. Using the stronger reagent of AlEt_3 , EDE was able to follow the reaction within 31 ms (15 ms dead-time).

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.

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REFERENCES

1. Corker J.M. and Evans J., *J. Chem. Soc. Chem. Commun.*, 1104 (1991)
2. Behr A., Keim W. and Kraus G., *J. Organometal. Chem.*, **251**,377 (1983)
3. Jones J. R. and Symes T. J., *J. Chem. Soc(C)*, 1124 (1971)
4. Bogg D., Conyngham M., Corker J.M., Dent A.J., Evans J., Farrow R.C., Kambhampati V.L., Masters A.F., Niles D. McLeod, Ramsdale C.A., and Salvini G., *J. Chem. Soc. Commun.*, 647 (1996)
5. Gurman S.J., *J. Phys. C*, 21, 3699 (1988)
6. Binsted N., Gurman S.J. and Ross I., *J. Phys. C*, **19**, 1845 (1986)
7. Binsted N., PAXAS - *Programme for the Analysis X-ray Absorption Spectroscopy*, University of Southampton, (1988).
8. Binsted N., Campbell J.W., Gurman S.J. and Stephenson PC, *EXCURVE* **92**, Daresbury Laboratory, Warrington, UK, (1992)
9. Joyner R.W., Martin K.J. and Meehan P, *J. Phys. C*, 20, 4005(1987)
10. Filliponi A., *J. Phys.: Condens Matter*, 7,9343(1995)
11. Kambhampati V.L., *PhD Thesis*, University of Southampton, (1998)
12. Cotton F.A. and Wise J.J., *Inorg. Chem.*, **5**,1200(1966)
13. Wilke G., Bogdanovic B., Hardt P., Heimbach P., Walter D. and Zimmermann H., *Ang. Chem. Int. Engl. Ed.*, 5,151(1965)
14. Jones J.R. and Symes T.J., *J. Chem. Soc(C)*, 1124(1971)
15. Takamatsu M., Yamamoto T. and Yamamoto Y., *Bull. Chem. Soc. Jpn.*, **55**, 325(1982)

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