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Scanning and Energy Dispersive EXAFS Studies of Nickel Alkene Oligomerisation Catalysts

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Abstract. *In situ* EDE and scanning EXAFS studies of homogeneous alkene oligomerisation catalysts are reported. EDE spectra were acquired either on Station 9.3 at the SRS Daresbury Laboratory using a bent Si(220) crystal monochromator (Ni and Br K-edges) or on ID24 at the ESRF using a Si(111) monochromator in a Bragg geometry (Ni K-edge). The catalysts studied were derived from mixtures of $\text{Ni}(\text{acac})_2$ (acac = 2,4-pentanedionato) and $\text{AlEt}_2(\text{OEt})$ or $\text{NiX}_2(\text{PEt}_3)_2$ (X = Cl, Br) and AlEt_3 . For $\text{Ni}(\text{acac})_2/\text{AlEt}_2(\text{OEt})$, Ni K-edge EDE is consistent with a mean structure similar in nature to trimeric $\text{Ni}(\text{acac})_2$ but with partial substitution of acac ligands by alkene and alkyl groups. At 25°C, further breakdown of the trimer occurs to give alkylated monomeric nickel species. For $\text{NiCl}_2(\text{PEt}_3)_2/\text{AlEt}_3$, low temperature Ni K-edge EDE has been used to monitor alkylation of the Ni centre, and for ambient temperature mixtures of $\text{NiBr}_2(\text{PEt}_3)_2/\text{AlEt}_3$, Br K-edge EDE data shows complete loss of Br from the metal centre occurring within minutes of adding AlEt_3 . Instrumental difficulties (detector and beamline set-up) at the current time prevent acquisition of analysable EXAFS in a timescale faster than 0.1-10 s for these types of systems.

1. INTRODUCTION

The oligomerisation of $\text{C}_3\text{-C}_5$ α -olefins for the production of $\text{C}_6\text{-C}_{18}$ plasticiser and detergent range olefins is an important industrial operation. The activation of nickel (usually phosphine) complexes in solution by alkyl aluminium reagents is the preferred route to the formation of alkene oligomerisation catalysts but such systems are often extremely active even at low temperatures making them difficult to study by standard techniques. We have shown previously that the activation of nickel complexes can be monitored by X-ray absorption spectroscopy (XAS): for example, in the case of $\text{NiX}_2(\text{PR}_3)_2$ (X = Cl, Br; R = alkyl) systems, we have shown that Ni...Al interactions (via alkyl bridges) occur in solution [1]. However, conventional scanning EXAFS experiments on dilute catalyst solutions require lengthy acquisition times and averaging of several spectra. Continuing improvements in energy dispersive EXAFS (EDE) techniques have indicated that this technique could be appropriate to these nickel systems. We have therefore begun a programme of work to test the applicability of EDE and learn more about the transmetallation process. We report here the first results of Ni and Br K-edge EDE studies on oligomerisation catalysts derived from $\text{Ni}(\text{acac})_2/\text{AlEt}_2(\text{OEt})$ (acac = 2,4-pentanedionato) and $\text{NiX}_2(\text{PEt}_3)_2/\text{AlEt}_3$.

2. EXPERIMENTAL

EDE measurements were carried out using modified versions of a low temperature cell [2] fitted with a pair of syringe drivers to provide either a continuous or interrupted flow mixing, or alternatively with a modified HiTech Scientific SFA20 stopped flow apparatus. Both systems can be operated remotely from outside the X-ray hut. Spectra (Ni and Br K-edges) were acquired either on Station 9.3 at the SRS Daresbury Laboratory using a bent Si(220) crystal monochromator or on ID24 at the ESRF (Ni K-edge) using a Si(111) monochromator in a Bragg geometry. The detector systems comprised either a 512 element (Reticon) linear photodiode array (PDA) or 1024 element (Hamamatsu) PDA running with a minimum readout time of 2 ms and controlled by a VM-based system (Daresbury) or a Tomson 512 x 512 element CCD camera operating in a PDA emulation mode with 10 ms readout time (ESRF). Background subtracted EXAFS data were obtained using the programme PAXAS [3]; spherical wave curve fitting analyses by least squares refinement of non-Fourier filtered k^3 -weighted data were carried out in EXCURVE, using Von-Barth ground state potentials and Hedin-Lundqvist exchange potentials [4].

3. RESULTS AND DISCUSSION

3.1 Ni K-edge EDE of $\text{Ni}(\text{acac})_2/\text{AlEt}_2(\text{OEt})/\text{hex-1-ene}$ in toluene

Scanning EXAFS measurements [5] have shown that, in the presence of hexene, the predominant species existing in an inactivate solution of $\text{Ni}(\text{acac})_2$ and $\text{AlEt}_2(\text{OEt})$ in toluene at -70°C is trimeric $\text{Ni}(\text{acac})_2$ (5.6 Ni-O bonds at 1.97 Å and 0.8

Ni..Ni bonds at 2.82 Å). Subsequent heating to *ca.* 5°C results in the formation of an active solution containing monomeric nickel species with acac and alkyl/alkene ligands (2.0 Ni-O bonds at 1.92 Å and 3.1 Ni-C bonds at 2.03 Å). We have now begun to investigate this system using EDE. Analysis of Ni K-edge EDE data recorded at Daresbury in 14.5 s at 0°C (4.75 min after the addition of Ni(acac)₂ and hexene to AlEt₂(OEt) using a simple syringe driver cell set-up) showed a reduction in the Ni-O coordination number (4.4 O at 1.97 Å), but maintenance of a Ni..Ni shell (1.3 Ni at 3.09 Å), and in addition, a new shell of *ca.* 2.5 carbons was identified at 2.16 Å. Thus EDE has enabled us to identify an intermediate of a similar nature to the trimeric catalyst precursor, but with partial substitution of the acac groups by alkene and alkyl ligands [5].

Further investigations of this reaction were carried out at the ESRF using a stopped flow cell set-up, affording faster (*ca.* 5 ms) and more homogeneous reagent mixing. The cell was initially flushed through with Ni(acac)₂/AlEt₂(OEt)/hexene solution at ambient temperature and the energy dispersive X-ray absorption spectra recorded were found to be very similar to that observed from scanning measurements, indicating the presence of the monomeric alkylated acac (or product) species. Figure 1 shows the series of XAS spectra obtained at 6 s intervals (each spectrum 50 ms int. time; 100 scans averaged) after the injection of AlEt₂(OEt). Changes in the XANES are apparent immediately on injection of the aluminium reagent: the pre-edge feature, which is present in the initial product spectrum (spectrum a) has disappeared and the white line feature has increased in sharpness and intensity (spectrum b). As the reaction proceeds, the intensity of the white line feature reduces considerably and growth of the pre-edge feature (characteristic of the product) is also observed. Analysis of various sequences of EDE (Figure 1) show that the extent of reaction is greater at higher Al:Ni ratios (and temperatures) and suggests that the approach to the initial equilibrium is rapid (within 40 s). The quality of data, however, is not sufficient to enable full EXAFS analysis to be carried out: instrumental difficulties (both detector and beamline set-up) appear to be the limiting factors.

Figure 1: (i) Ni K-edge EDE of Ni(acac)₂/AlEt₂(OEt)/hex-1-ene (35 mM Ni; Ni:Al 1:8) in toluene at 25°C recorded using a stopped flow sampling system, and (ii) normalised absorbance (white line feature) versus time for various Ni:Al ratios.

3.2 Ni and Br K-edge EDE of NiX₂(PEt₃)₂/AlEt₃ in *p*-fluorotoluene

Scanning EXAFS experiments on low temperature solutions of NiCl₂(PEt₃)₂ and AlEt₃ (or Al₂Me₃Cl₃) have revealed the presence of Ni-C-Al interactions (2.2 Ni-C at 1.93 Å, 2.1 Ni-P at 2.20 Å and 1.5 Ni..Al at 2.98 Å) and we proposed that the Ni..Al interaction may be one stabilising factor for the Ni^{II} organometallic species, possibly retarding β-hydride or reductive elimination to afford metal [1]. Our ³¹P NMR studies [1,2] however have indicated the existence of several species and isomers in solution thus it seemed appropriate to try to study this equilibrium system by the more rapid technique of EDE. Our preliminary Ni K-edge EDE results (Figure 2) on a solution of NiCl₂(PEt₃)₂/AlEt₃ at -2°C (800 ms int. time; 1000 scans averaged) are consistent with but subtly different to those derived from scanning EXAFS measurements (spectra typically acquired over 2-3 hours): 1.2 Ni-C at 1.99 Å, 2.4 Ni-P at 2.24 Å and 1.3 Ni..Al at 3.28 Å (Table 1). Notably, the Ni..Al distance is longer in the EDE case, suggesting the existence of a species with a much weaker Ni-C-Al interaction.

We have also performed EDE experiments at the Br K-edge on ambient temperature mixtures of NiBr₂(PEt₃)₂ and AlEt₃ (Table 2). Analysis of various EDE sequences indicate that complete loss of bromine from the nickel centre occurs within a few minutes after the addition of AlEt₃, the Br K-edge EXAFS (60 ms int. time; 4000 scans averaged) being best fitted by two shells of aluminium atoms at 2.22 and 2.43 Å, suggesting the formation of an aluminium bromide type species.

4. CONCLUSIONS

From our EDE experiments we have been able to identify solution species which are not observed in conventional EXAFS experiments and we can conclude that discussions of the mechanisms of alkene oligomerisation should include reversible transmetalation processes. More importantly these results show that EDE can provide good quality EXAFS data in

timescales of the order 0.1-10 s at present time. With continuing improvements in detector technology, however, it should be possible to obtain analysable EXAFS on complex systems in the sub ms timescale.

Table 1: Ni K-edge EDE results for $\text{NiCl}_2(\text{PET}_3)_2/\text{AlEt}_3/p\text{-fluorotoluene}$ at -2°C (70 mM Ni; Ni:Al = 1:2.5). Numbers in parentheses are statistical errors generated in EXCURVE.

Shell	Coordination number	R/Å	$2\sigma^2/\text{Å}^2$	R-factor/%	E_F/eV
C	1.2(2)	1.99(1)	0.009(2)	29.7	-2.8
P	2.4(1)	2.237(4)	0.0164(8)		
Al	1.3(2)	3.28(2)	0.038(6)		

Table 2: Br K-edge EDE results for $\text{NiBr}_2(\text{PET}_3)_2$ and $\text{NiBr}_2(\text{PET}_3)_2/\text{AlEt}_3$ in $p\text{-fluorotoluene}$ at 25°C (140 mM Ni; Br:Al = 1:3). Numbers in parentheses are statistical errors generated in EXCURVE.

Shell	Coordination number	R/Å	$2\sigma^2/\text{Å}^2$	R-factor/%	E_F/eV
<i>NiBr₂(PET₃)₂</i>					
Ni	1.02(3)	2.291(3)	0.0049(3)	26.6	-6.5
P	1.8(3)	3.19(2)	0.025(3)		
Br	1.0(2)	4.44(1)	0.038(6)		
<i>NiBr₂(PET₃)₂/AlEt₃</i>					
Al	1.5(1)	2.221(7)	0.0125(9)	39.5	6.2
Al	1.4(1)	2.435(7)	0.0061(7)

Figure 2: Ni K-edge EDE and Fourier transform (phase-shift corrected for carbon) of $\text{NiCl}_2(\text{PET}_3)_2$ and AlEt_3 in $p\text{-fluorotoluene}$ at -2°C (70 mM Ni; Al:Ni = 1:2.5). (—) Exp. and (---) spherical wave theory.

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