The nature of the active site in bis(imino)pyridine iron ethylene polymerisation catalysts

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Abstract

Mössbauer and electron paramagnetic resonance (EPR) spectroscopic studies reveal that the iron centres in bis(imino)pyridine iron(II) olefin polymerisation pre-catalysts of the type $LFeCl_2$ are oxidised upon treatment with methylaluminoxane (MAO) to give an active species that contains iron solely in the +3 oxidation state. © 2002 Published by Elsevier Science B.V.

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1. Introduction

In recent years there has been a phenomenal growth of interest in the discovery and development of late transition metal olefin polymerisation catalysts [1–3]. One of the most significant developments has been the discovery of highly active ethylene polymerisation catalysts based on iron, a metal that previously had no track record for catalysing polyethylene chain growth. The catalysts are stabilised by bis(imino)pyridine ligands [4,5] and afford highly linear polyethylene, whose density, molecular weight and molecular weight distribution fall within the range of commercially relevant high-density polyethylenes (HDPEs) [6].

There has been much interest in understanding the mechanism by which these catalysts operate [7–10]. It has generally been assumed that treatment of the dihalide Fe(II) pre-catalysts [LFeCl$_2$] with excess methylaluminoxane (MAO) affords a cationic iron(II) alkyl species. However, considerable difficulties have been encountered in preparing well-defined cationic iron alkyl complexes bearing the bis(imino)pyridine ligand due, it has been presumed, to the instability of the dialkyl precursors. With a view to circumventing such dialkyl species, we have also investigated cationic precursors, but these too have failed to yield [LFe–R]$^+$ products [11]. Furthermore, iron(III) pre-catalysts [LFeCl$_3$] have been shown to afford catalysts with similar activities and polymer

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(1)   (2)
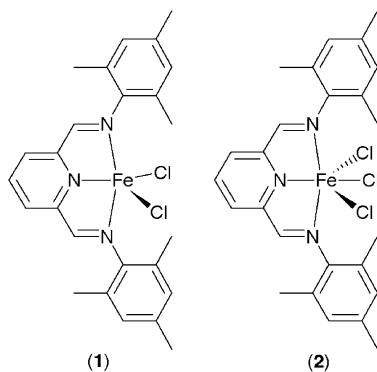
Scheme 1.

product characteristics to those generated from iron(II) precursors [5,6] (Scheme 1).

In order to obtain more insight into the nature of the active species, we have carried out a series of

Mössbauer and electron paramagnetic resonance (EPR) studies on the divalent [LFeCl$_2$] and trivalent [LFeCl$_3$] precursors **1** and **2** {L = 2, 6-bis[(2,4,6-trimethylphenylimino)methyl]pyridine} and the species arising from their treatment with excess MAO. These results indicate that a cationic iron(II) alkyl is *not* the active species.

2. Experimental

Complexes **1** and **2** were prepared as previously described [6]. Solvents were dried by prolonged reflux over a suitable drying agent under a dinitrogen atmosphere, and freshly distilled and de-gassed prior to use. MAO was obtained from Aldrich Chemical Company. All other reagents were purchased from commercial suppliers and used as received.
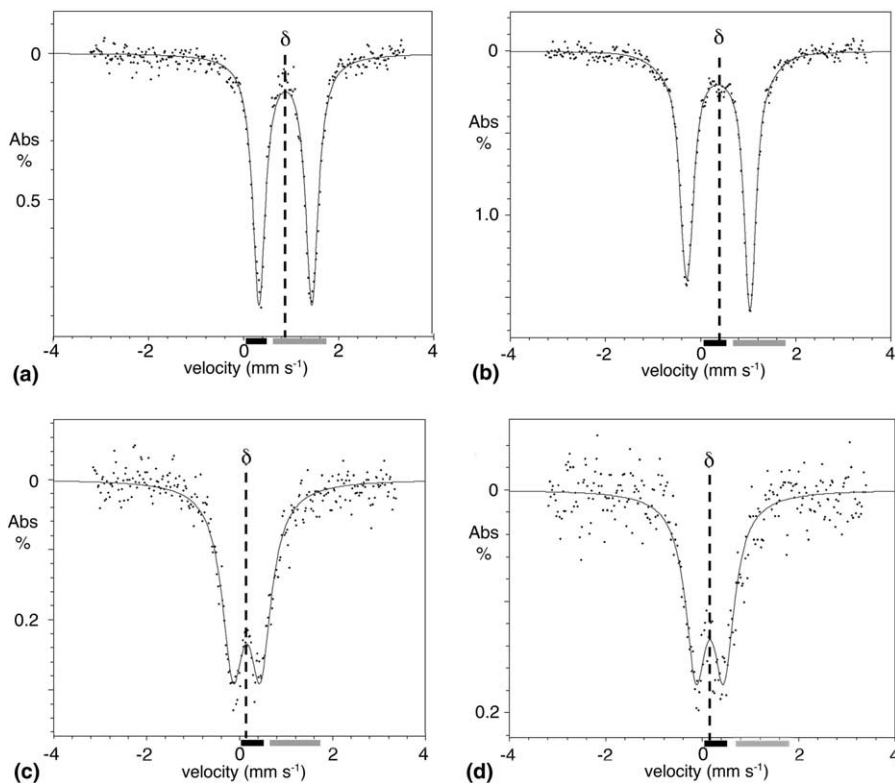

Fig. 1. Mössbauer spectra of (a) LFeCl$_2$ (**1**); (b) LFeCl$_3$ (**2**); (c) **1** after treatment with 100 equivalents MAO; (d) **2** after treatment with 100 equivalents MAO {L = 2,6-bis[(2,4,6-trimethylphenylimino)methyl]pyridine}. The black bar on the velocity scale indicates the typical range of isomer shifts (δ) found for HS Fe(III) species; the grey bar indicates the typical range of isomer shifts for HS Fe(II) species.

^{57}Fe Mössbauer spectra were recorded on finely ground powders under an argon atmosphere at ambient temperature using a Wissel MR-260 constant acceleration spectrometer with a triangular drive waveform. Spectra were folded to remove baseline curvature and were calibrated relative to α-Fe.

X-band EPR spectra were recorded at ambient temperature and under dinitrogen on a Varian V4500-15 spectrometer operating at ca. 9.5 GHz.

3. Results and discussion

3.1. Mössbauer studies

Mössbauer spectroscopy allows a probe of the ^{57}Fe nucleus by γ-radiation and yields information on the oxidation state, spin state and coordination environment of the absorbing isotope in the bulk sample. For ^{57}Fe, the first nuclear excited state is split into two sublevels by the presence of an electric field gradient across the nucleus, resulting in the observation of a quadrupole doublet. The Mössbauer spectra are characterised by two parameters, the isomer shift δ and quadrupole splitting ΔE_Q. The Mössbauer spectrum of the iron(II) pre-catalyst **1** is shown in Fig. 1(a).

An isomer shift of $\delta = +0.90$ mm s^{-1} ($\Delta E_Q = 1.12$ mm s^{-1}) is consistent with d^6-high-spin (d^6-HS) Fe(II) centres which generally appear between +0.6 and +1.7 mm s^{-1} [12]. This electronic configuration is also in accord with the experimentally determined magnetic moment of 5.29 BM [6]. The spectrum of the iron(III) pre-catalyst **2** is shown in Fig. 1(b); the isomer shift of $\delta = +0.37$ mm s^{-1} ($\Delta E_Q = 1.34$ mm s^{-1}) lies in the range typical for d^5-HS Fe(III) systems (+0.1 to +0.5 mm s^{-1}) [12]. An asymmetry in the line intensities in this spectrum is attributed to a correlated distribution in possible isomer shift and quadrupole splitting values, due in turn to a distribution in the environments of the Fe(III) ions.

The Mössbauer spectra, after activation of **1** and **2** separately with 100 equivalents of MAO, are shown in Figs. 1(c) and (d), respectively. The spectra are virtually identical, both showing a doublet resonance with an isomer shift of +0.16

mm s^{-1} ($\Delta E_Q = 0.58$ and 0.59 mm s^{-1}, respectively). This shift lies well outside the range of HS Fe(II) species but is consistent with HS Fe(III). In addition, the absence of a signal in the HS Fe(II) range +0.6 to +1.7 mm s^{-1} indicates that no Fe(II) species remains upon treatment of **1** with 100 equivalents MAO, nor is any Fe(II) species formed upon activation of the Fe(III) precursor **2** by MAO. In both cases, a single new iron complex is formed, most likely a HS Fe(III) species.

3.2. Electron paramagnetic resonance studies

EPR spectroscopy provides a useful technique for distinguishing between Fe(II) and Fe(III) valence states, since Fe(II) is EPR silent whereas Fe(III) is EPR-active. The room temperature X-
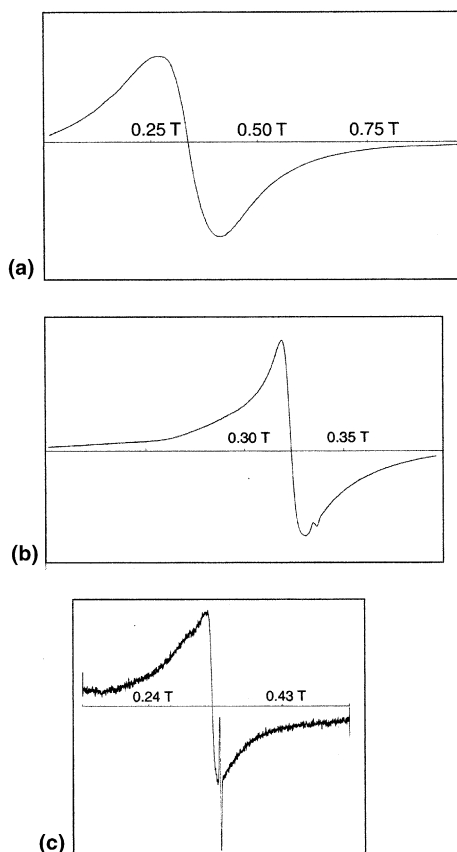

Fig. 2. EPR spectra of (a) LFeCl$_3$ (**2**); (b) **1** after treatment with 100 equivalents MAO; (c) **2** after treatment with 100 equivalents MAO.

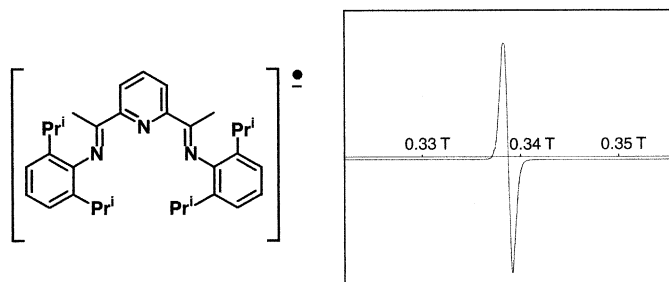Fig. 3. EPR spectrum of [L′K(OEt$_2$)] {L′ = 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]pyridine}.

band EPR spectrum of **2** in toluene solution is shown in Fig. 2(a), revealing a very broad featureless resonance ($g_{eff} \approx 2.00$, peak–peak separation ≈ 300 G), consistent with HS Fe(III) with a d^5 configuration [12]; the Fe(II) pre-catalyst **1** expectedly does not give an EPR signal. However, upon activation of **1** by 100 equivalents of MAO, the EPR spectrum shown in Fig. 2(b) is obtained, confirming the presence of HS Fe(III). The EPR spectrum resulting from activation of **2** by 100 equivalents of MAO is shown in Fig. 2(c) and, although slightly less broad, is very similar to the spectrum shown in Fig. 2(b). Interestingly, both spectra reveal a sharp resonance at $g_{eff} \approx 2.00$ superimposed on the main broadened signal. This is believed to be attributable to a small amount of a species containing a radical derived from bis (imino)pyridine freed from the metal centre. A viable candidate for this species is a bis(imino)pyridyl radical species of the type shown in Fig. 3. In a separate study, it has proved possible to isolate such a species by treatment of bis(imino)pyridine L′ with KC$_8$ in Et$_2$O to give [L′K(OEt$_2$)], which was crystallographically characterised (L′ = 2,6-bis[1-(2,6-diisopropylphenylimino)ethyl]-pyridine) [13]. The room temperature EPR spectrum of [L′K(OEt$_2$)] in toluene solution consists of a sharp and extremely intense resonance at $g_{eff} = 2.00$ (peak–peak separation ≈ 10 G).

4. Conclusion

The near 100% conversion of the Fe(II) pre-catalyst into an Fe(III) species upon treatment with excess MAO, and the similarities of the Mössbauer and EPR spectra of catalysts derived from Fe(II) or Fe(III) precursors, suggest that similar Fe(III) species account for the active sites in these bis(imino)pyridine iron catalysts. The precise nature of the sites remains to be determined; possibilities include a dicationic iron(III) alkyl species [LFe–R]$^{2+}$, or a chloro, alkyl species [LFe(Cl)(R)]$^+$. It is also possible that the bis(imino)pyridine ligand is formally reduced by electron transfer from the iron centre to give a radical anion ligand of the type identified in [FeL$_2$] species, where L is a sterically less encumbered bis(imino)pyridine ligand [14,15].

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