

# EXAFS analysis of a chiral alkene polymerisation catalyst incorporated in the mesoporous silicate MCM-41

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The chiral metallocene *rac*-ethylenebis(1-indenyl)zirconium dichloride, when immobilised on the surface of methylalumoxane-modified mesoporous silica MCM-41, is an effective catalyst for the production of highly isotactic polypropene with a unique spherulite morphology; Zr K-edge EXAFS studies of the organometallic–inorganic composite reveal not only an intact indenyl ligand framework after the immobilisation, but also the presence of a short Zr–C bond and the absence of the chloride ligands.

We have recently reported that the modification of the mesoporous silicate MCM-41 with an excess of methylalumoxane (MAO) effectively removes the protic sites on the surface silanol groups, yielding a high surface area material (although the surface area is reduced from on average 900 to 400 m<sup>2</sup> g<sup>-1</sup>).<sup>1</sup> Subsequent treatment with saturated solutions of (EBI)ZrCl<sub>2</sub> [EBI = *rac*-ethylenebis(1-indenyl)zirconium dichloride] in toluene produces a hybrid organometallic–inorganic composite material in which the organometallic moiety has been grafted onto the surface of the MCM-41. This hybrid organometallic–inorganic material is active in the stereoselective polymerisation of propylene to yield highly isotactic polypropylene. The as produced polymer exhibits a higher melting point and has a distinct spherulite morphology atypical of polymers produced from an analogous homogeneous system. We suggest that the heterogeneous catalyst is effective due to the adsorptive capacity of the mesoporous silica support, and whilst not being homogeneous in nature, it allows a great deal of contact between the catalytic centres and propene. We believe that the spherulite polymer morphology is formed as a result of the channels inherent to MCM-41, as it has been observed that a similar catalyst on ordinary amorphous silica does not produce the same morphology. X-Ray powder diffraction indicates that the hexagonal framework of the mesoporous material is retained after reaction with both MAO and the organometallic catalyst precursor, but provides no information regarding the nature of the local atomic environment of the organometallic metal centre. We have recently used EXAFS to verify the status of organometallic molecules successfully grafted onto the walls of MCM-41,<sup>2</sup> and one of us (T. M.) used both XANES (X-ray absorption near edge structure) and EXAFS to determine the local structure around titanium centres incorporated into MCM-41.<sup>3</sup>

In order to study the local coordination around the zirconium catalyst, X-ray absorption spectroscopy was used to measure the Zr K-edge EXAFS. Data was collected on Station 9.2 at the SRS, Daresbury Laboratory, UK.† Data analysis of the EXAFS was performed using the XFIT(WIN95) suite of programs<sup>5</sup> employing both single and multiple scattering techniques.

The observed EXAFS data and the corresponding Fourier transform, together with the calculated fits are shown in Fig. 1. The EXAFS structural model parameters resulting from multiple scattering treatments are shown in Table 1. Initially, a broad range of model structures was examined, however, when varying atom types and refining structural parameters using single scattering techniques a clear trend became apparent, pointing towards retention of both indenyl ligands and an

absence of the chloride ligands. The single scattering calculations, although providing sensible model parameters, were unable to account for some contributions in the Fourier transform at  $R > 2.5$  Å (not phase shift corrected). These might be due to multiple scattering effects. Multiple scattering paths involving the C<sub>5</sub> 'cyclopentadienyl' fragment of the indenyl rings correspond to a distance comparable to that of the outer ligand framework, and when this is incorporated into the refinement the second envelope might be modelled more fully. Hence, by using a three-dimensional model based on the simplified crystal structure of the starting material it was possible to obtain very good agreement between theory and experiment.

The first shell of the final model corresponds to radius of 2.12 Å which is a short distance for a Zr–CH<sub>3</sub> bond. There are crystal structures for a cationic zirconocene derivative based upon the EBI ligand, in which the Zr–C bond length was found to be 2.18

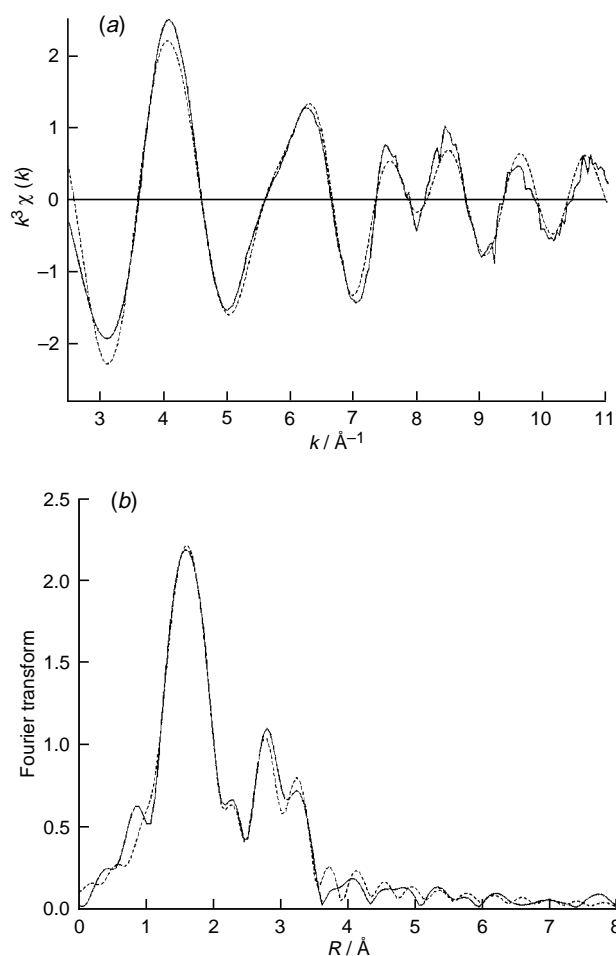


Fig. 1 (a) Zr K-edge  $k^3$  weighted EXAFS and (b) Fourier transform data for the (EBI)ZrCl<sub>2</sub>/MAO/MCM-41 material [(—) experimental and (---) theoretical]

**Table 1** Structural parameters of multiple scattering model for Zr K-edge EXAFS of (EBI)ZrCl<sub>2</sub>/MAO/MCM41<sup>a</sup>

Shell	Scattering atom	<i>N</i>	<i>r</i> /Å	$\sigma^2/\text{Å}^2$	Assignment
1	C	1.3	2.12	0.008	methyl C
2	C	5.1 <sup>b</sup>	2.60	0.008	C <sub>5</sub> indenyl C
3	C	5.1 <sup>b</sup>	2.78	0.007	C <sub>5</sub> indenyl C
4	C	1.8	3.32	0.010	methylene bridge
5	C	3.6	3.47	0.011	C <sub>6</sub> indenyl C
6	C	2.5	4.24	0.012	C <sub>6</sub> indenyl C

*N* = coordination number, *r* = interatomic distance,  $\sigma^2$  = root mean-square deviation of the interatomic distance about *r*. <sup>b</sup> Restrained to keep rings co-planar and equal number of atoms.

Å.<sup>6</sup> The EXAFS data does not show any evidence for a Zr–Cl bond, or the presence of a Cl scatterer beyond normal bond lengths. The chloride anion need not necessarily reside in close proximity to the central Zr atom; if the Zr species becomes highly polarised or cationic in nature, then the associated chloride anion can be dissipated in the MAO oligomeric cage away from the metal centre. The second and third shells have been assigned to the carbon atoms of the two C<sub>5</sub> rings of the bridging indenyl ligand, and correspond to average bond lengths for similar Zr–C bonds in *rac*-(EBI)ZrCl<sub>2</sub>. It should be noted that the two C<sub>5</sub> rings were modelled with two slightly different distances (*i.e.* 2.60 and 2.78 Å), indicating that the rings may be tilted. The fourth shell at 3.32 Å contains contributions from C atoms from both the C<sub>6</sub> rings of the indenyl system and the ethylene bridge. The fifth (3.47 Å) and sixth (4.24 Å) shells are due to the remaining C atoms on the C<sub>6</sub> rings of the indenyl system.

Our assignments for each shell are based upon the known crystallographic information for *rac*-(EBI)ZrCl<sub>2</sub>,<sup>7</sup> and are consistent with the previously proposed general mechanism for the interaction of MAO with group 4 metallocene dichlorides, which assumes the metal chloride bonds are first methylated, and a cationic monoalkylated species is formed as the active catalyst.<sup>8,9</sup> The preservation of the ligand framework is also supported in the literature.<sup>10</sup> Based upon this model of a highly electropositive zirconium centre, one could anticipate a shorter Zr–CH<sub>3</sub> distance for the species bound to the mesopore.

In conclusion, X-ray absorption spectroscopy has proved to be a powerful technique in the structural characterisation of *rac*-

(EBI)ZrCl<sub>2</sub> bound to the surface of MAO modified MCM-41. The ability to use three-dimensional models as inputs for the multiple scattering calculations in XFIT(WIN95) has been essential in deriving a good fit between theory and experiment. EXAFS data analysis of the hybrid organometallic–inorganic material indicates that the carbon framework has remained essentially intact around the central Zr. The Fourier transform also reveals a short Zr–C bond, indicative of the increased charge at the metal centre as a result of the interaction between the metal chloride and the MAO-MCM-41 support.

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## Footnotes and References

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‡ K-edge transmission EXAFS of the Zr compound were performed at room temp. on Station 9.2 at the CLRC Radiation Source, Daresbury, operating in multi-bunch mode, 2 GeV, with typical currents of 180–250 mA. A double crystal monochromator in non-dispersive configuration equipped with flat (220) Si crystals was used. Calibration was done on Zr foil of 50 μm thickness. Samples of *rac*-(EBI)ZrCl<sub>2</sub>/MAO/MCM-41 were diluted in dry MgO (5:1), compressed into a pellet of minimal thickness (*ca.* 1 mm) and then sealed in an inert polyimide wallet under N<sub>2</sub>.

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