Stereospecific propene polymerisation catalysis using an organometallic modified mesoporous silicate

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The mesoporous silicate, MCM-41 is modified by grafting the chiral alkene polymerisation catalyst *rac*-ethenebis(indenyl)zirconium dichloride onto the surfaces of the mesopore and used to produce highly isotactic polypropene with a unique spherulite morphology.

Since homogeneous catalysts for alkene polymerisation were first reported in 1957,[1] there has been much interest both in academic and industrial circles in the application and evolution of new catalytic systems. Polypropene is probably the most marketable and versatile of the polyalkenes produced industrially and is found in many industries from the automotive trade to the leisure industry. Of the three forms of polypropene, the highly ordered, high molecular mass isotactic form is the most important. Under homogeneous conditions isotactic polypropene can be produced by chiral *ansa*-metallocenes such as *rac*-EBI–zirconium dichloride {EBI = 1,2-bis(inden-1-yl)-ethane} in combination with a co-catalyst, methylaluminoxane (MAO). Compared to polypropenes produced by classical heterogeneous Ziegler–Natta catalysts, molecular masses and melting points are low, making their products of little commercial worth for most technical applications. Kaminsky reported a silica-supported metallocene catalyst which yielded isotactic polypropene with high molecular masses and high melting points.[2] This is in contrast to previous studies of metallocenes supported on silica, where high activities for polymerisation were reported, but with low molecular masses and low melting points.

We have recently reported that the cationic zirconocenium alkene polymerisation catalyst, $[Zr(\eta\text{-}C_5H_5)_2Me(thf)]BPh_4$ can be readily ion-exchanged into modified charged 2 : 1 layered silicates.[3] With propene, the catalyst system produces atactic polymer with molecular masses some 25% greater than the homogeneous analogues, but with significantly lower activities. In an effort to produce new propene polymerisation catalyst systems which yield high molecular mass polypropylene with even greater specific isotacticities we have investigated the catalytic activity of mesoporous silicates with included chiral *ansa*-metallocenes.

As an alternative host support material we have investigated the use of the siliceous mesoporous material MCM-41.[4] The internal walls of MCM-41 are lined with silanol groups, the chemistry of which the chemist can exploit to develop modified materials; there has already been reports in the literature of the encapsulation of organometallic species inside the host channels.[5–7]

Incorporation of *rac*-$[ZrCl_2(EBI)]$ into MCM-41 was achieved by heating a saturated solution of *rac*-$[ZrCl_2(EBI)]$ with a suspension of a pre-treated MCM-41 suspension. The pre-treatment involves initial dehydration of the as-prepared materials and then subsequent treatment of the anhydrous material with an excess of a toluene solution of MAO at 50 °C for 24 h, followed by filtration, washing with toluene and drying under vacuum to give a white, air sensitive mesoporous material. The Al content as determined by elemental microanalysis, gave a loading of 6.1 mmol (Al) g^{-1} of silicate, the C : H : Al ratio being 2.50 : 2.95 : 1. The final organometallic–silicate complex has a Zr loading of 0.35 mmol g^{-1}[‡] as evidenced by elemental microanalysis. Inspection of the powder X-ray diffraction pattern after modification of the MCM-41 with MAO and then with *rac*-$[ZrCl_2(EBI)]$ reveals that the reactions do not destroy the hexagonal framework of the mesoporous material; although the peak width at half maximum suggests a slight loss in crystallinity.

The material has been successfully used in the polymerisation of propene to yield highly isotactic polypropene. The results of polymerisation runs are outlined in Table 1; to serve as a comparison, polymerisation tests were also undertaken on the homogeneous system, *rac*-$[ZrCl_2(EBI)]$ and *rac*-$[ZrCl_2(EBI)]$ supported on a MAO modified clay.[§] From the data it appears that the polymer properties are little affected by grafting the metallocene to the mesopore. This implies that during the course of the reaction between metallocene and the MCM-41 support, the metallocene has remained essentially structurally intact on the mesoporous material. However, due to the nature of the support, the possibility of there being active sites on the external surfaces of the mesopore which could be responsible for the polymerisation cannot be ignored.

Inspection of Table 1 reveals several interesting properties of the isotactic polypropene produced by the three different forms of *rac*-$[ZrCl_2(EBI)]$. With respect to activity, the homogeneous system proves to be the most active. Out of the two supported catalysts, the clay support proves to be more active than the mesoporous support by about threefold. A diffusion limiting effect could be partly responsible for the lower activity; whereby active metal centres located toward the centre of the mesoporous channels are effectively screened from approaching monomer units by active centres closer to the channel ends, which harbour growing polymer chains. The number average molecular masses (M_n) also vary for each sample. The clay-supported catalyst produced the highest M_n value, with the values for the MCM-41 support slightly lower, but both of these showed an approximate fourfold increase in the number average molecular mass of the polypropene relative to the homogeneous system. The isotacticity of the three polymer samples has been investigated using ^{13}C solution NMR spectroscopy. The homogeneously produced polymer is the least isotactic, the two supported samples producing similar spectra indicative of highly isotactic polypropene. Differential scanning calorimetry of the polymer samples reveals that the MCM-41 produced material has the highest melting point of the three polymers at 141 °C, compared to melting points of 128 °C for polymer

Table 1 Propene polymerisation activities and polymer properties

Material[a]	Loading mmol (Zr) g^{-1}	Activity Kg mol (Zr h)$^{-1}$	$\bar{M}_n{}^b$/(GPC)	Polydispersity
1	0.35	1163	11849	1.95
2	2.39	4941	3110	1.91
3	0.14	3033	14038	1.92

[a] 1 = MCM-41–MAO–*rac*-$[ZrCl_2(EBI)]$, 2 = *rac*-$[ZrCl_2(EBI)]$, 3 = clay–*rac*-$[ZrCl_2(EBI)]$. [b] GPC *vs.* polystyrene, 140 °C in 1,2-dichlorobenzene, ratio of Zr : MAO was 1 : 1000 in each case.

produced homogeneously and 135 °C for the polymer produced by *rac*-[ZrCl$_2$(EBI)] supported on a layered silicate clay.

To assess morphological differences between the three isotactic polymer samples, scanning electron microscopy (SEM) was used. Figs. 1 and 2 show micrographs of homogeneously and MCM41 produced polymer samples, respectively. Inspection of the micrographs reveals striking differences between the two samples. The polymer produced by the homogeneous system (Fig. 1) consists of particles with a very porous open structure and appears to be composed entirely of sub-particles around 1 μm. A similar structure is observed for polymer produced by the clay support, except that the average particle size is much larger at *ca.* 10 μm. The micrograph also reveals the plate-like morphology of the clay material has been replicated in the polymer. The SEM micrograph for the MCM-41 produced IPP (Fig. 2) exhibits some quite remarkable features. The catalyst produces spherulite particles of approximate diameter 10 μm. The internal structure of the polymer grains can also be probed by crushing it at −120 °C and then re-examining the sintered particles with SEM. The micrograph of such a broken particle is shown in Fig. 2. This clearly shows that the very fine scale of the internal structure of the polymer is substantially different from the external structure; suggesting that the polymer consists of a distinct core and shell arrangement, a feature which is atypical for most homogeneously produced polymers. Similar freezing and sheering of the homogeneous and clay samples shows no difference between their internal and external morphology. The MCM-41 produced polymer was also studied under crossed polarising microscope. From the optical micrograph the sphericular nature of the polymer becomes clear from the large birefringent regions of the central particle. Spherulites are a morphological feature of bulk crystallised polymers with a large number of lamellar crystallites radiating in all directions from one central nucleus with well defined boundaries. The observation of birefringence in the optical measurement indicates a general tangential arrangement of the chains within the spherulites.

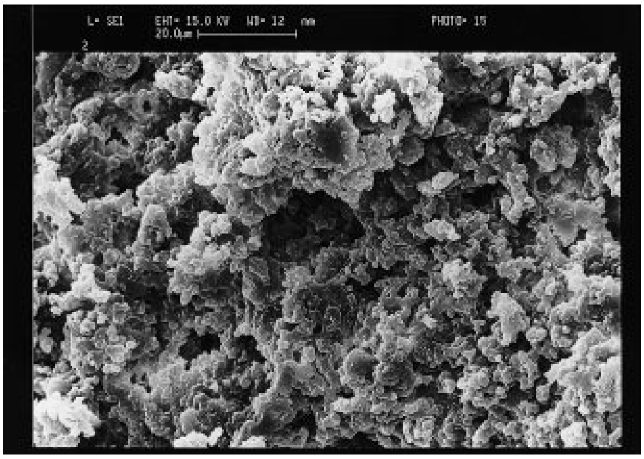

Fig. 1 SEM micrograph of isotactic polypropene produced by a homogeneous solution of [ZrCl$_2$(EBI)]

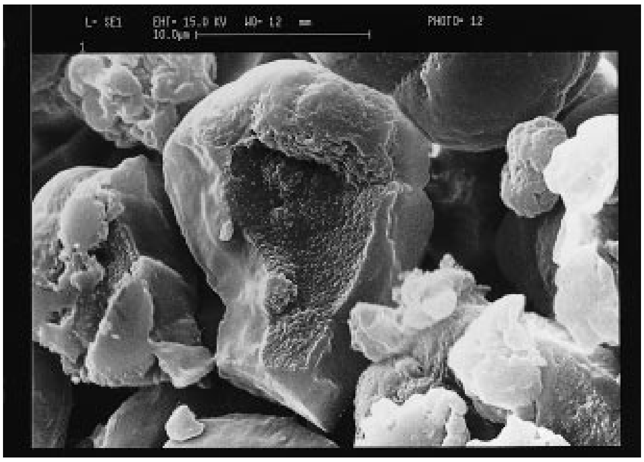

Fig. 2 SEM micrograph of isotactic polypropene produced by MCM-41 supported [ZrCl$_2$(EBI)] showing the spherulite structure. The internal structure of the spherulites can be seen by examining a crushed particle.

In conclusion, we have demonstrated the effectiveness of MCM-41 in providing a solid support for the homogeneous chiral catalyst *rac*-[ZrCl$_2$(EBI)] and its application toward controlling polymer morphology. Hence, polypropene produced by the MCM-41 derived catalyst consists of entirely of spherulite particles, with a distinct shell and core morphology. The polymer is highly isotactic and exhibits higher melting points than the corresponding homogeneous and clay supported system.

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Footnotes

† D. O'Hare is the Royal Society of Chemistry Sir Edward Frankland Fellow.

‡ Exact Al and Zr loadings vary with MCM-41 batch, the values given reflect a typical value.

§ The clay used was the synthetic smectite, LaponiteRD, $Na_{0.46}Mg_{5.42}Si_8O_{20}(OH)_4$.

Note added in proof: Following submission of this article, a related study on *rac*-EBI-ZrCl$_2$/MCM-41 has been published. Y. S. Ko, T. K. Han, J. W. Park and S. I. Woo, *Macromol. Rapid Commun.*, 1996, **17**, 749.

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