

# Mesoporous silica-supported zirconocene catalysts for highly isotactic polypropylene†

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A new bis(indenyl)zirconocene bearing a pendant Si–Cl anchor has been grafted onto MCM-41, SBA-15, MCM-48 and a disordered mesoporous silica for the polymerisation of ethylene and propylene, producing polymers with very high molecular weights, low polydispersities and, in the case of polypropylene, higher levels of isotacticity than obtainable with analogous homogeneous systems.

Considerable research has been concentrated on the preparation of supported metallocene catalysts for olefin polymerisation. These offer several advantages over solution phase metallocenes, namely control of polymer properties, such as molecular weight, polydispersity, as well as the prospect of utilisation in existing industrial systems (so called 'drop-in technology').

A variety of approaches to silica-supported metallocenes have been reported, ranging from direct combination of the metallocene with the host to the preparation of MAO-treated silicas for the incorporation of metallocene. More recently, strategies have been devised to synthesise zirconocenes with tailor-made anchoring groups, with a view to immobilisation on silica surfaces so as to leave the metal centre unaffected by incorporation.<sup>1–3</sup> This offers the prospect of new single-site heterogeneous catalysts for the polymerisation of olefins. However, no attempts have yet been reported concerning the immobilisation of such functionalised metallocenes onto mesoporous or other ordered hosts. Mesoporous silicas offer attractive properties for polymerisation catalysis, namely extremely high surface areas and ordered, uniform pore structures. These may be expected to facilitate the introduction of a high loading of organometallic moieties onto the material, and to confer a uniformity of catalytic sites on the material. In addition, their well-ordered three-dimensional structures may be expected to influence the structure and properties of the polymers produced. So far, the only metallocene-mesoporous silica polymerisation catalysts have been produced by direct combination of the metallocene with the silica.<sup>4–8</sup>

Here we report the synthesis of a new zirconocene bearing a chlorosilyl anchoring group, and its incorporation onto four different mesoporous hosts: MCM-41,<sup>9,10</sup> SBA-15,<sup>11,12</sup> MCM-48<sup>10,13</sup> and a disordered mesoporous phase, herein denoted as DMS.<sup>13</sup> An amorphous silica host was also used for comparison.

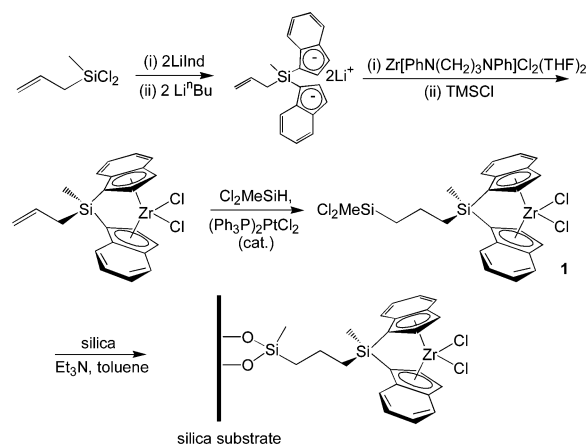
It has been the target of this work to immobilise a *C*<sub>2</sub>-symmetric zirconocene, analogous to *rac*-dimethylsilylbis(indenyl)zirconocene dichloride (*rac*-SBIZrCl<sub>2</sub>). These systems have been developed in the interests of producing isotactic polypropylene.<sup>14–16</sup> The synthetic route used here to generate a chlorosilane-functionalised zirconocene is depicted in Scheme 1. The *C*<sub>2</sub>-stereochemistry at zirconium was enforced using a chelating amide salt, Zr[PhN(CH<sub>2</sub>)<sub>3</sub>NPh]Cl<sub>2</sub>(THF)<sub>2</sub>, developed by Jordan *et al.*<sup>17</sup> The allyl group pendant to the *ansa* Si atom can be hydrosilylated with MeCl<sub>2</sub>SiH, using (Ph<sub>3</sub>P)<sub>2</sub>PtCl<sub>2</sub> to give the target molecule, **1** as a mixture of diastereomers.

The five zirconocene-mesoporous silica composites were prepared by treatment of the dehydrated silica host (heated to 100 °C under vacuum for 10 h) with a toluene solution of *rac*-**1**, in the

presence of triethylamine, to remove the HCl produced as a by-product of the reaction. The new supported zirconocenes were designated as follows: **2** – MCM-41, **3** – SBA-15, **4** – MCM-48, **5** – DMS, **6** – SiO<sub>2</sub> (amorphous). These were characterised using powder XRD, TEM, N<sub>2</sub> adsorption, elemental analysis (ICP), energy-dispersive X-ray analysis (EDX), <sup>13</sup>C and <sup>29</sup>Si CP MAS NMR spectroscopy.† The results of these experiments were consistent with the presence of a surface grafted zirconocene species of the type depicted in Scheme 1.

The loadings of Zr obtained using this approach (*ca.* 3.5–4.6%) are much higher than those of other silica-supported zirconocenes in the literature.<sup>1,2,5,7</sup> We ascribe this to the nature of the anchoring group and the reactivity of the dichloromethylsilyl functionality. The susceptibility of the composites towards leaching of Zr was investigated by treating them with MAO (10% in toluene) followed by copious washing. No trace of zirconocene could be detected by <sup>1</sup>H NMR spectroscopy in the washings, indicating that the zirconocene remained firmly grafted onto the surface of the silica.

<sup>29</sup>Si CP MAS NMR spectra of the supported zirconocenes all showed peaks at δ 4–8 and –7 ppm, which were assigned to the ≡Si–O environment (M) and the *ansa*-bridging Si respectively. (A typical spectrum is shown in Fig. 1.) This indicates that the anchoring group has reacted as expected with the silica surfaces.



Scheme 1 Synthesis of **1** and incorporation onto silica surface.

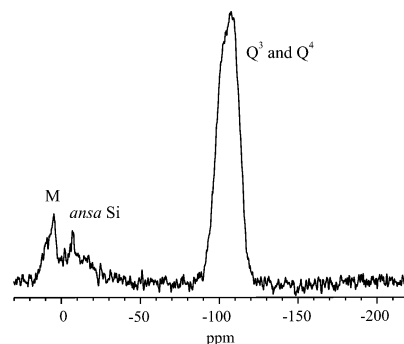


Fig. 1 Typical <sup>29</sup>Si CP MAS NMR spectrum of supported zirconocene.

† Electronic supplementary information (ESI) available: N<sub>2</sub> absorption data, solid state NMR (<sup>13</sup>C, <sup>29</sup>Si) and SEM micrographs of polymer samples. See <http://www.rsc.org/suppdata/cc/b4/b403043e/>

**Table 1** Details of some structural properties and ethylene and propylene polymerisation characteristics of zirconocene-mesoporous silica composites

Compound/ composite	Silica host	% Zr	BET surface area (composite)/m <sup>2</sup> g <sup>-1</sup>	Pore size/Å <sup>a</sup>	Ethylene polymerisation			Propylene polymerisation		
					Activity <sup>b</sup>	M <sub>w</sub> <sup>c</sup>	Pd <sup>d</sup>	Activity <sup>b</sup>	M <sub>w</sub> <sup>c</sup>	Pd <sup>d</sup>
<b>2</b>	MCM-41	3.5	558.9	<20 <sup>e</sup>	29.96	8.745	21.46	4.93	1.070	2.55
<b>3</b>	SBA-15	3.5	558.6	42.37	25.19	7.585	20.87	2.56	1.010	3.40
<b>4</b>	MCM-48	4.4	597.2	<20 <sup>e</sup>	234.00	5.390	7.00	0.32	0.887	2.25
<b>5</b>	DMS	3.7	367.9	133.58	99.50	5.100	4.20	9.15	0.673	2.60
<b>6</b>	SiO <sub>2</sub>	4.6	244.8	—	316.80	3.775	10.71	8.92	0.713	3.45
<i>rac</i> -SBIZrCl <sub>2</sub>	—	—	—	—	532.80	1.115	8.23	505.70	0.163	8.35
<b>7</b>	—	—	—	—	603.72	1.040	11.69	567.30	0.157	11.00

<sup>a</sup> Calculated using Dollimore–Heal method. <sup>b</sup> Activity in kg polymer mol Zr<sup>-1</sup> h<sup>-1</sup> bar<sup>-1</sup>. <sup>c</sup> 10<sup>5</sup> g mol<sup>-1</sup>. <sup>d</sup> Polydispersity. <sup>e</sup> Pore size outside the range of calculation.

<sup>13</sup>C CP MAS NMR spectra of the five composite materials featured peaks assignable to the indenyl and aliphatic carbon sites in the zirconocene, by analogy with **1**.

The supported zirconocenes **2–6** were tested in the polymerisation of both ethylene and propylene, both at 5 bar pressure, using 20 μmol Zr in *ca.* 250 cm<sup>3</sup> toluene and 1000 equivalents of MAO (10% by weight in toluene). The results of these experiments are shown in Table 1. For comparison, two solution phase analogues of the supported zirconocenes were also tested: *rac*-SBIZrCl<sub>2</sub>, and a model compound [Me<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>SiMe(C<sub>9</sub>H<sub>6</sub>)<sub>2</sub>]ZrMe<sub>2</sub>, **7**, formed by reaction of **1** with AlMe<sub>3</sub>.

In ethylene and propylene polymerisation experiments, the activities of the supported zirconocenes are found to be lower than those of the solution phase analogues. This is generally observed for heterogeneous catalysts, and can be attributed to deactivation of some of the metal sites on reaction with the silica, or alternatively by pore-blocking in these materials. The variation in catalytic activity between the different supports may also arise due to pore-blocking.

Although the activity of the SBIZrCl<sub>2</sub> system is rendered lower by immobilisation, the properties of the polymers produced using these new heterogeneous systems are found to differ significantly from those produced by the homogeneous systems. The molecular weights of the polymers are far higher, with **2** (MCM-41 support) giving polymers with 7–8 times higher molecular weight than *rac*-SBIZrCl<sub>2</sub>. The mesoporous silica-zirconocene systems generally produce higher molecular weight polymers than **6**, the amorphous silica-supported zirconocene. It appears to be possible to vary the precise molecular weight of the polymers produced by varying the support material, which is a promising development.

As regards the polydispersities of the polymers, the polypropylenes produced by the silica-supported zirconocenes all have lower polydispersities than those produced by the homogeneous systems. In the case of polyethylene, the MCM-48 and DMS-supported catalyst systems give the lowest polydispersities (lower than the homogeneous systems). This could be due to local hot spots occurring on the catalyst particles.

Solution <sup>13</sup>C NMR spectroscopy of the polypropylenes produced using the different homo- and heterogeneous zirconocene systems was used to investigate the stereocontrol obtained over the polymer. The only methyl signals observable in the <sup>13</sup>C NMR spectra of the polypropylenes produced by **2–6** were those arising due to isotactic polypropylene. No peaks were observed which could be assigned to atactic polypropylene. Although the signal : noise ratio varied between the samples, on account of their different molecular weights and hence solubilities, the presence of purely isotactic polypropylene in these samples can only be established with 82–94% certainty. By contrast, the pentad ratio, [mmmm], obtainable with *rac*-SBIZrCl<sub>2</sub> in solution does not exceed 0.9 (in

this investigation, the [mmmm] pentad ratio of the polypropylenes produced by *rac*-SBIZrCl<sub>2</sub> and **7** were found to be *ca.* 0.5).

The morphology of the polymer particles was studied using SEM, which revealed the polymers produced by the heterogeneous systems to have far larger particle size (*ca.* 10 times larger) than those produced by the homogeneous catalysts. This is important in the context of drop-in technology, where reactor fouling caused by small particle size inhibits the use of homogeneous catalysts.

In conclusion, this method of grafting a zirconocene onto a silica surface has been used to prepare five new heterogeneous zirconocene systems, based on different mesoporous hosts. These have been found to influence the polymers produced by these systems, namely molecular weight, polydispersity and tacticity.

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