ChemComm
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# MCM-41 immobilised borate co-catalyst for metallocene catalyzed propene oligomerisation

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***Received (in Cambridge, UK) 12th March 2003, Accepted 29th April 2003***
***First published as an Advance Article on the web 21st May 2003***

**Reaction of tris(pentafluorophenyl)boron with the silanol groups of MCM-41 resulted in the heterogeneous tris(pentafluorophenyl)borate anion. This immobilised weakly-coordinating anion retains metallocenes, thus yielding a heterogeneous propene oligomerisation catalyst. Activity comparable to the corresponding homogeneous catalyst can be obtained. The products typically consist of over 90% 1-alkenes with Flory–Schulz carbon number distribution.**

Since their discovery, metallocenes are known as very active polymerisation catalysts producing polymers with a narrow molecular weight distribution, also allowing controlled copolymerisation.[1–3] For the synthesis of oligomers, their use remains rather limited, although a large number of potential products are possible such as long chain 1-alkenes for surfactants, diesel alkanes, octane boosters and new monomers.[1] Most of the research has been performed to obtain a better insight into the reaction mechanism for the polymerisation reactions.[4] Metallocene catalysts have to be activated with a large excess of expensive methylalumoxane (MAO). Reduction of the amount of co-catalyst or its replacement by another weakly coordinating anion still remains a challenge.

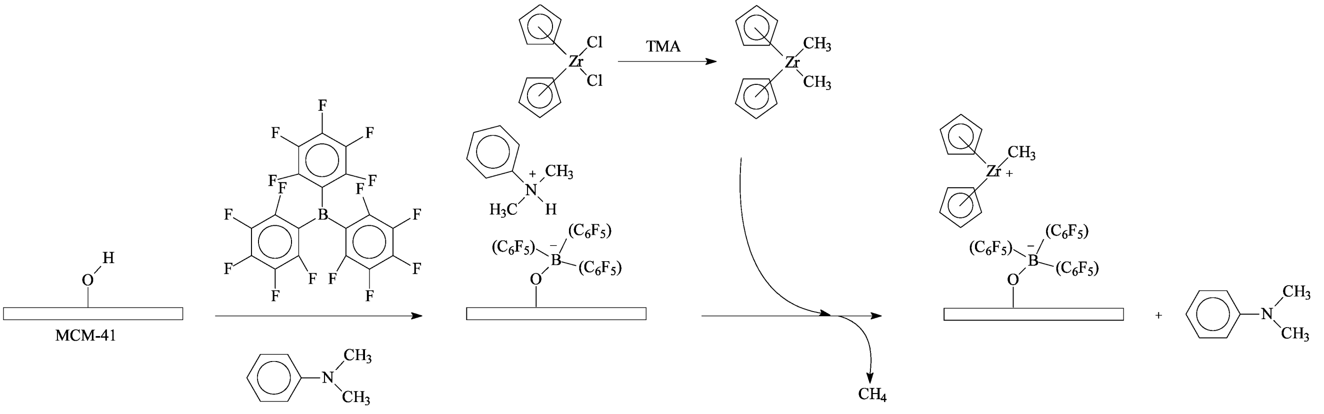
Boranes and borates, like tris(pentafluorophenyl)boron ($B(C_6F_5)_3$) and tetra(pentafluorophenyl)borate ($(C_6F_5)_4B^-$), respectively, can be used as efficient co-catalysts for metallocenes.[5] This communication reports on the design of a heterogeneous oligomerisation metallocene catalyst produced by linking the borane co-catalyst chemically to a MCM-41-type support. Its reactivity/selectivity in the oligomerisation of propene is illustrated and compared to the behaviour of the corresponding homogeneous catalyst.

The high surface area and hexagonally ordered tubular pores make MCM-41 a suitable host for anchoring the borane complex. The borane co-catalyst attached to the pore walls, remains accessible for the metallocene catalyst and retains it *via* a weakly coordinative bond (Scheme 1).

MCM-41 or its Al-substituted homolog (Al–MCM-41)[6,7] as well as the heterogeneous metallocene catalyst[8,9] were synthesised according to modified literature procedures. All manipulations were carried out in an inert nitrogen atmosphere. Prior to use, (Al–)MCM-41 with worm-like morphology (8 × 0.75 μm) was dehydroxylated at 540 °C under a helium flow for a period of 8 h to remove the majority of the hydroxyl groups. The IR spectrum shows only isolated silanol groups at 3745 $cm^{-1}$. Typically, 3 g of pretreated MCM-41 was then suspended in 30 ml of dry toluene. To this suspension a pink 0.2 M solution containing an equimolar mixture of *N*,*N*-dimethylaniline and tris(pentafluorophenyl)boron in 10 ml toluene was added dropwise under stirring. Addition was continued until fast decoloration of the solution ceased, corresponding to consumption of the surface hydroxyl groups. Filtering yielded a white solid and a pink filtrate. The supported co-catalyst was washed 3 times with 50 ml toluene and dried overnight *in vacuo*. The amount of the covalently linked borane co-catalyst, by using thermoanalysis, was calculated to be 0.18 mmol per g for MCM-41 support. Typical IR stretches pointing to the chemical link of the borane co-catalyst to the MCM-41 support appeared. Bands at 1644, 1518, 1468 $cm^{-1}$correspond to the $\nu_{C=C}$ in perfluorobenzene, while a peak at 976 $cm^{-1}$ can be attributed to $\nu_{B-O}$. $^{11}B$ MAS NMR on the heterogeneous catalyst showed a small resonance shift at −6.5 ppm compared to $Et_2O{\cdot}BF_3$ as reference. This resonance line is indicative of the presence of B(IV).[10] Sorption measurements on the support and co-catalyst on the support showed a reduction of the pore size from 3.0 to 2.4 nm, respectively, pointing to intrapore fixation of the borate compound.

Homogeneous as well as heterogeneous catalytic oligomerisation reactions were performed in a fed-batch stainless steel reactor.†

Initially, the reaction conditions were optimised for homogeneous oligomerisation reactions with *N*,*N*-dimethylanilinium tetra(pentafluorophenyl)borate as a co-catalyst (entry 4, Table 1). Because of the high reactivity of propylene as monomer, reactions have to be performed at elevated temperatures (≥70 °C) to prevent polymerisation. At these temperatures, supplementary addition of hydrogen as a chain terminating agent is no longer required. As a consequence the amount of saturated product oligomers can be kept very low. Addition of small



**Scheme 1** Heterogenisation of the borane co-catalyst on the MCM-41 support.

DOI: 10.1039/b302813e

**Table 1** Homogeneous propylene oligomerisation reactions with $Cp_2ZrCl_2$[a]

| Entry | Co-catalyst | Al : Zr | Activity/$10^5$ g (mol Zr)$^{-1}$h$^{-1}$ | $\alpha$ |
|---|---|---|---|---|
| 1 | TMA | 100 | 0.85 | — |
| 2 | MAO | 100 | 2.90 | 0.65 |
| 3 | $B(C_6F_5)_4^-$ | 100 | 3.62 | 0.77 |
| 4[b] | $B(C_6F_5)_4^-$ | 100 | 2.43 | 0.70 |
| 5 | $B(C_6F_5)_3$ | 100 | 2.08 | 0.39 |

[a] Reaction conditions: $t$ = 75 min; $T$ = 90 °C; $C_3H_6$: 1400 ml min$^{-1}$; $H_2$: 50 ml min$^{-1}$; 90 µmol $Cp_2ZrCl_2$, [b] 0 ml min$^{-1}$ $H_2$.

amounts of hydrogen however, enhances the activity significantly (entry 3, Table 1) probably due to reactivation of dormant sites. Of the formed products 70% are alkene isomers (Table 3). By altering reaction temperature, catalyst concentration, monomer feed and hydrogen supply, the oligomer distribution can be varied within a whole range of $\alpha$ values, varying from 0.8 for 11-mers to approximately 0.3 for pentamers.

In all reactions, trimethylaluminum (TMA) is added to the catalytic mixture to alkylate the metallocene catalyst and to scavenge impurities present in solvent and gases using a Al : Zr ratio of 100 (entry 1, Table 1). With the borate catalytic system under current oligomerisation conditions, higher activities are obtained than with MAO as a weakly coordinating anion (compare entries 2 and 3, Table 1). Homogeneous reactions with $B(C_6F_5)_3$ as co-catalyst lead to a drop in activity and $\alpha$-factor (entry 5, Table 1), due to stronger coordination with the metallocene.

The activities obtained with the heterogeneous catalyst are lower than those of the homogeneous catalysts under the same reaction conditions (compare entry 3, Table 1 with entry 1, Table 2). Whereas in the homogeneous system, each B atom is surrounded by 4 pentafluorinated phenyls, in the heterogeneous system each has 3 such substituents. Furthermore, its linkage *via* the surface oxygen influences the electron structure of the co-catalyst and decreases its weakly coordinating properties compared to the homogeneous case. The different chemical environment is also reflected in the difference in $\alpha$-factor between the homogeneous and heterogeneous system (0.77 (Table 1, entry 3) against 0.41 (Table 2, entry 1)). Also in Table 2 a clear effect of the kind of support is seen on $\alpha$ (compare entries 1, 3 and 4).

During MCM-41 synthesis, an Al source was added to the synthetic mixture, yielding a support with (Lewis) acid properties (after calcination at 540 °C). Enhanced catalytic activity comparable to the homogeneous reaction with $B(C_6F_5)_3$ as co-catalyst was obtained, without influencing the oligomer distribution (entry 2, Table 2). Thus it seems possible to create the heterogeneous borane co-catalyst without losing significant activity, by using an appropriately modified support. It is clear that a support with Lewis acidic properties such as dehydroxylated Al-MCM-41, enhances the non-coordinating properties of immobilized tris(pentafluorophenyl)borate. After reaction, the filtrate of the anchored weakly coordinating anion did not reveal any activity higher than that of the blank test (entry 1, Table 1) upon metallocene addition, indicating the true heterogeneous nature of the co-catalyst. Hot filtration (at a reaction temperature of 90 °C) of the heterogeneous catalyst shows a degree of Zr leaching of 25%; filtration at room temperature shows a clear solution devoid of Zr.

**Table 2** Heterogeneous propylene oligomerisation reactions with $Cp_2ZrCl_2$[a]

| Entry | Support | Activity/$10^5$ g (mol Zr)$^{-1}$h$^{-1}$ | $\alpha$ |
|---|---|---|---|
| 1 | MCM-41[b] | 1.45 | 0.41 |
| 2 | Al-MCM-41[b,c] | 2.06 | 0.41 |
| 3 | MCM-41[d] | 1.77 | 0.52 |
| 4 | Silica[b] | 1.47 | 0.32 |

[a] *Reaction conditions*: $t$ = 75 min; $T$ = 90 °C; $C_3H_6$: 1400 ml min$^{-1}$; $H_2$: 50 ml min$^{-1}$; 90 µmol $Cp_2ZrCl_2$. [b] Dried at 540 °C. [c] Prepared in the same conditions as MCM-41 with a Si : Al ratio of 8. [d] Dried at 170 °C.

**Table 3** Distribution of the propylene oligomers and dimer selectivity

| Composition (wt%) | entry 3[a] | entry 5[a] | entry 2[b] | entry 4[b] |
|---|---|---|---|---|
| Dimer | 10.1 | 56.9 | 53.2 | 62.5 |
| *2M-1-$C_5$=* | *59.91* | *88.81* | *86.39* | *85.21* |
| *2M-$C_5$* | *29.76* | *6.07* | *6.93* | *6.85* |
| *2,3diM-1-$C_4$ =* | *3.10* | *3.42* | *4.90* | *6.12* |
| *2M-2-$C_5$ =* | *5.94* | *0.82* | *0.85* | *0.79* |
| *n$C_6$* | *0.92* | *0.23* | *0.23* | *0.31* |
| *2-$C_6$ =* | *0* | *0.46* | *0.45* | *0.40* |
| *4M-1-$C_5$ =* | *0.38* | *0.19* | *0.25* | *0.32* |
| Trimer | 13.5 | 23.4 | 24.2 | 22.8 |
| Tetramer | 13.7 | 10.0 | 10.9 | 8.4 |
| Pentamer | 13.1 | 4.9 | 5.6 | 3.6 |
| Hexamer | 12.8 | 2.5 | 3.1 | 1.4 |

[a] Table 1. [b] Table 2.

An IAP-PAI grant on Supramolecular Catalysis as well as a FWO grant (G.0279.00) is acknowledged. M.K. and P.J.G. acknowledge a fellowship from IWT and a position as research director from FWO, respectively.

## Notes and references

† The homogenous or heterogenous borate co-catalyst (0.09 mmol) was dissolved/suspended in 20 ml toluene and transferred under an inert atmosphere to a 600 ml stainless steel Parr reactor filled with 260 ml of dry toluene. Next, the metallocene $Cp_2ZrCl_2$ (0.09 mmol), alkylated with TMA (Al : Zr = 100), was dissolved in 20 ml toluene and added to the reaction mixture.

Prior to use, all solvents were carefully dried over 3 Å molecular sieves. All gases were first deoxygenated over an oxy-trap and dried over molecular sieves. The catalyst and solvent were added batchwise, while the gases were continuously flowing through the reactor, entering at the bottom: propylene (1400 ml min$^{-1}$), methane (491 ml min$^{-1}$) as internal standard, hydrogen (50 ml min$^{-1}$) as chain transfer and nitrogen (40 ml min$^{-1}$). Reactions were performed at an overall pressure of 0.7 MPa. The unreacted gases were analysed on-line allowing the calculation of conversion and activity in time. After the reaction, residual TMA is decomposed with a 1 M HCl acid solution prior to analysis of the reaction mixture. Reaction selectivity of the propene oligomerisation is determined by the growth factor $\alpha$ according to Flory–Schulz kinetics:

$$\log(W_m/m) = (m - 1)\log\alpha + 2\log(1 - \alpha)$$

in which $W_m$ is the oligomer weight fraction with oligomerization degree $m$.

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